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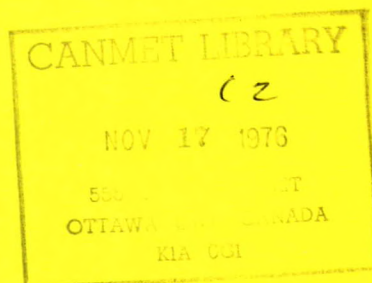and Energy   des minéraux
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RECENT ADVANCES IN COPPER ELECTROWINNING

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D.J. MacKinnon* and V.I. Lakshmanan**

ABSTRACT

The application of solvent extraction techniques to copper leach liquors has resulted in a great deal of basic research designed to improve the copper electrowinning stage. The main objective of this research is to increase the current density, and therefore the rate, at which copper is deposited in both refining and winning cells. This review details the methods currently being practised to achieve high current density in copper winning cells and the consequent effects on various aspects of the electrowinning process. New cells designed for electrowinning copper from dilute solutions are also discussed. The effect of impurities and addition agents on the growth and morphology of copper is reviewed in detail.

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LABORATOIRES DES SCIENCES MINERALES

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DE NOUVEAUX DEVELOPPEMENTS EN EXTRACTION PAR ELECTROLYSE
DU CUIVRE

par

D.J. MacKinnon* et V.I. Lakshmanan**

RESUME

L'application de techniques d'extraction au solvant à des
liqueurs de lixiviation de cuivre a résulté en une abondante recher-
che pour améliorer l'étape cuivrique de l'extraction par électro-
lyse. Le principal objectif de cette recherche est d'améliorer
la densité du courant et par conséquent la vitesse à laquelle le
cuivre est déposé dans les cellules de raffinage et d'extraction.
Cette étude explicite les méthodes employées actuellement afin
d'obtenir des opérations de densité à courant élevé dans des cel-
lules d'extraction au cuivre et les effets ultérieurs sur les dif-
férents aspects du procédé de l'extraction par électrolyse. De
nouvelles cellules conçues pour extraire le cuivre par électrolyse
à partir de solutions dissoutes sont aussi discutées. L'effet des
impuretés et des agents d'addition sur la croissance et la mor-
phologie du cuivre est revu dans les détails.

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1. Introduction

Hydrometallurgical routes for winning copper are gaining in popularity at the expense of conventional smelting operations, partly due to environmental considerations. As a result of the increasing demand for copper, coupled with the rapid depletion of the copper sulphide ores, other sources such as oxide ores, mixed sulphide ores, low-grade copper deposits and tailings dumps are becoming more important.

The advent of copper-selective solvent extractants such as the LIX and Kelex reagents can be regarded as a significant breakthrough in copper processing via hydro-metallurgy[1-10], and the new sources of ore referred to above are of interest in this regard.

The conventional cementation process is losing ground for several reasons, e.g. the poorer quality of metal produced, acid consumption, build-up of iron in the dump, and the increasing cost of scrap[1]. Hydrometallurgical processes, in contrast, require chemicals which can be produced at relatively low prices, and also offer the advantages of low-cost construction materials[2].

Therefore, interest in the hydrometallurgical processes is increasing, and it is noted that at the present time nearly 15 percent of copper production is by this route and by 1985 it is estimated this figure will increase to nearly 40 percent.

Further advantages claimed for these processes are the possibilities of selectively separating copper from heavily contaminated solutions and of concentrating solutions of low copper content. In the normal ore leaching operation, the contaminants dissolved with the copper consume acid and severely limit the electrolytic process. For example, the presence of Fe^{+3} can considerably decrease the current efficiency for copper deposition[1]. However, when a combined leaching/solvent extraction/electrowinning route is adopted, the electrowinning stage can be operated at higher current densities and at improved current efficiencies[1]. The higher purity of the electrolyte obtained through solvent extraction separation permits current densities of up to 35 ASF to be attained, even though present operations are performed at 10 - 15 ASF. When cementation is replaced by a combination of solvent extraction and electrowinning, sulphuric acid is generated and can be recycled to leaching. In the cementation process the acid is consumed in the formation of iron sulphate and hence is wasted[1].

The use of a solvent extraction/electrowinning operation creates a few problems of its own. These include organic burn (observed in a few cases at the edges of the cathode), increased acid misting in the tankhouse resulting in a more adverse working condition, and possiblities of higher equipment maintenance costs[4]. The higher sulphuric acid concentration in the tankhouse feed, compared with the feed liquors from leaching stages, sometimes causes increased corrosion of the lead-antimony anodes resulting in lead contamination of the cathode; thus anode materials capable of resisting high acid concentration are required. The solvent

extraction process for copper has been well documented in the literature during the last few years. However, as mentioned earlier, the adaptation of electrowinning to the solvent extraction process is a relatively new technique which has led to an increase in fundamental research in the field of copper electrowinning.

Although a great deal has been learned and many changes have been made during the past century, it is interesting to note that until recently the original concept of an electrolytic plant, i.e., a series of rectangular tanks built end to end with common walls, has never been fundamentally changed. In the last ten years the pace of progress, both in details and fundamental concepts, has accelerated markedly in attempts to produce high quality copper at much higher current densities (90 ASF)[11-12]. As a consequence, much of today's technical development in copper electrowinning centres around more effective electrolyte circulation, improved anode materials, and the replacement of copper starting sheets by permanent titanium or stainless steel mother blanks. The present requirement for the removal of metals down to the trace quantity level from various waste liquors has also resulted in a great deal of fundamental and developmental work to produce new types of electrochemical cells (e.g., fluidized-bed electrodes) for the efficient and economic recovery of copper from dilute solutions. The necessity to control the deposit growth and structure to maintain high current efficiencies and avoid deposit contamination has resulted

in a large number of studies on the role of additives in copper
winning and on the mechanism by which they control the morph-
ology of copper electrodeposits.

In the present review these recent developments in
copper electrowinning are discussed in detail. The first
section is concerned with the methods now being developed to
permit copper to be electrowon at high current densities. The
consequences of high current density operation for the various
components of the electrowinning operation, e.g., anode wear,
deposit contamination, acid mist, and cathode material are
presented in the following section. Subsequently, the design
and development of electrochemical cells for winning copper
from a variety of dilute liquors is considered. And finally,
the effects of impurities on copper deposition, the role of
additives in copper electrowinning and the morphology and
growth of copper deposits are discussed.

2. High Current Density Electrowinning of Copper

i. General

In recent years a major effort has been directed towards
the operation of copper electrowinning cells at increased current
densities either by optimizing cell design [13], by employing various
types of forced convection[14,15] or by applying periodic current
reversal[16,17]. In the production of electrolytic copper, many
factors, such as current efficiency, steam consumption, the number
of cells and hence the building area, metal inventory, cathode
purity, and of course power consumption are all affected by
the current density. A considerable saving of capital investment

together with a reduction in the operating cost per ton of copper produced would result if the current density was increased to twice or three times that normally practised, provided that a high current efficiency and satisfactory cathode purity were maintained. An increase in the operating current desnity for copper electrowinning results in a decrease in the number of cells, electrodes, size of buildings, etc. In fact, it has recently been reported[11] that the total capital cost of a tankhouse producing 100 tpd of copper decreases exponentially with increasing current density. Another reason for the attention currently being given to copper electrowinning at high current density is that plant construction costs are escalating at a greater rate than energy costs[11].

ii. Limitations to Achieving High Current Density

Excessive increases in current density causes cathodes to be unacceptably rough, porous and impure. The value of the current density at which this condition occurs has been termed the critical current density[11]. Increasing the current density beyond its critical value eventually leads to the limiting current density at which the deposit becomes powdery and hydrogen co-deposits with the metal. Detailed studies on metal deposition processes (including copper) at the limiting current density have been extensively reported by Ilb[18]. A transition zone, which sets the upper and lower limits for copper powder formation, has been

defined experimentally in terms of copper concentration in the spent electrolyte and current density[14].

The critical current density, which is of practical importance to the tankhouse operation, is a function of the copper concentration in the electrolyte, mass transfer conditions (concentration overpotential), the conductivity of the electrolyte, the activation overpotential (presence of levelling agents), and the presence of iron and solids in the electrolyte. Some of these factors tend to promote the growth of imperfections which decrease the value of the critical current density, whereas others promote the growth of smooth cathode deposits. These aspects will be discussed in some detail in a later section of this review.

The limiting current density is that which can be achieved when the rate of mass transport of copper is maximized. The diffusion limiting current density, i_L, is expressed by the equation:

$$i_L = k \frac{c}{d} \qquad [1]$$

where c is the concentration of copper ions, d is the thickness of the diffusion layer and k, the mass transfer coefficient, is a function of the ion valency, diffusion coefficient and transport number of the ionic species, in this case, Cu^{2+}. Equation [1] shows that the maximum rate of deposition is inversely proportional to the thickness of the diffusion layer and directly proportional to the ionic concentration gradient in the electrolyte. It also defines the maximum current density above which powder formation

rather than an adherent stable deposit can be expected. Therefore the smaller the value of d, the higher is the value of the limiting current density and, hence, the critical current density.

Convection (forced and natural) and diffusion are the transport processes that contribute to the magnitude of d, and for a given chemical composition of the electrolyte and concentration gradient forced convection has the dominant effect. In a conventional electrowinning cell the electrolyte flow relative to the cathode surface is very slow, so that a stagnant layer is formed at the electrode-electrolyte interface resulting in a high d . value. Rapid movement of the electrolyte past the electrode is, therefore, an essential condition for decreasing the thickness of the boundary layer. This can be accomplished either by moving the electrode in a stationary electrolyte, or vice-versa. Although both vibrating and rotating electrodes have been used [13,19], from the viewpoint of simplicity and practicality of design and operation, the movement of the electrolyte past a stationary electrode surface is considered to be the better choice.

A knowledge of the extent to which the diffusion or boundary layer thickness can be reduced under realistic agitation conditions is obviously desirable to assess the potential of various agitation methods or, of alternative cell designs. This knowledge may be obtained by determining the local value of the mass transfer coefficient, k, in situ in full scale electrowinning cells. The mass transfer coefficient has previously been determined by measuring the limiting current density [20-23],

by interferrometric measurements[24,25] and by Brenner's freezing method[26]. While these techniques are useful they do require complicated experimental measurements and, moreover, they cannot be readily used to determine mass transfer co-efficients in large scale cells using concentrated electrolytes.

The difficulties associated with these methods for determining k values in full-scale electrowinning cells have recently been eliminated by a new technique[27]. This method permits the measurement of local values of the cathode mass transfer coefficient in electrowinning (or refining) cells of any size and under actual deposition conditions, i.e., neither the electrolyte nor the current density have to be altered. The method is based on the mass transfer controlled co-deposition of a more noble metal added to the electrolyte in trace concentration. It has yielded values of the diffusion layer thickness as a function of the cathode height under normal electrolyte flow[27]. The results indicate that the boundary layer is much thicker near the bottom than at the top of the cathode. This is because the anodically produced oxygen gas gradually begins to reduce the thickness of the boundary layer to a value of about half its maximum thickness (0.3 mm) at the top of the cathode.

Ettel and co-workers[27] subsequently found that by agitating the electrolyte by air-sparging, rather than by conventional turbulent flow, the diffusion layer thickness was reduced to 0.03 mm and, more significantly, this thickness was uniform over the entire length of the cathode. This is important

since the critical current density is determined by the maximum

and not the average value of d.

   iii.   Methods for Attaining High Current Density

      In this section the various methods used to obtain a high

current density in copper electrowinning are described. These

include air sparging, ultrasonic agitation, periodic current

reversal (PCR) and new cell designs which generally employ some

form of forced convection of the electrolyte.

   a. Air Sparging

      Of the above mentioned techniques, air sparging is

considered probably the most practical for providing the

degree of copper cathode depolarization (reduction in boundary

layer thickness) essential to permit high current density copper

electrowinning[12,28,29]. As we mentioned earlier in our discussion

on the role of the diffusion layer thickness in copper electrowinning,

the air sparging technique employed by INCO[27] proved

much more effective than electrolyte recirculation in reducing

the value of d. For example, air sparging at a rate equivalent to

6 l/min per face of 1m x 1m cathode increased the mass transfer

coefficient (mtc) about three times over the natural convection

value. Electrolyte recirculation at a rate of 12 l/min was found

necessary to achieve the same increase in the mtc on the

lower half of the cathode, while the increase on the upper half

was much smaller[11]. In addition, the power required

for electrolyte recirculation was about ten times higher than for

air sparging. The cost of the hardware for air sparging at low pressure apparently compares favourably with that required for recirculation of highly acidic electrolytes. The pressure differential required is not much larger than the hydrostatic head of electrolyte, and the power consumed is less than 10 Whr/kg Cu even at high sparging rates[11].

In the air sparging technique, compressed air is forced through perforated tubes fixed at the bottom of the cathodes, at a rate such that the entire active surface of the cathode is subjected to vigorous electrolyte turbulence. This results in a substantial but uniform decrease in the diffusion layer thickness allowing greatly increased current densities to be employed. In addition, air sparging effects the formation of exceptionally smooth and dense deposits and prevents the attachment of suspended particles to the deposit. These smooth, even, deposits permit the anode-cathode spacings in the cell to be considerably decreased thus producing remarkebly low power consumption even at high current densities. For example, at 10 A/dm^2 (90 ASF) the power consumption was only 30% higher than in a conventional operation[11].

The air sparging technique has also been developed at Kennecott's Ledgemont Laboratories[12,28,29] where it was observed that the current density employed using this technique could be at least a factor of five greater than the copper concentration in g/l. However, although high quality copper could be produced at current densities up to 30 A/dm^2 (270 ASF), it is suggested[11] that operation at about 10 A/dm^2 (90 ASF) is preferred in practice

since operating at current densities beyond this level would be accompanied by a considerable increase in power consumption and diminishing capital savings.

Kennecott workers[29] suggest that in the preferred design the air sparger consists of perforated bubble tubes having very small diameter and relatively closely spaced orifices and also that the incoming air be presaturated with water vapour at approximately the cell temperature. It is interesting to note that in recent tests at NIM[30] in which both the INCO and Kennecott air sparging techniques were compared, the best results were obtained using the INCO technique. Apparently the larger holes in the INCO system were not only easier to manufacture but appeared to give better mass transport for the same flow rate of air. It was felt that the oscillations caused by the larger bubbles resulted in a better penetration of the boundary layer. Also, in the INCO system the back pressure is independent of the air flow rate and is a function only of the hydrostatic head.

Thus an air sparged cell can be used to electrowin very high quality copper at a high current density. Smooth and compact deposits can be obtained at reduced anode-cathode spacings with no apparent operating difficulties. Simple perforated tube sparger designs have given trouble-free operation in scale-up laboratory cells during extended testing[11,27]. At the Ledgemont Laboratory the air sparging/close spacing methods have now been adapted and applied to the major electrolyte streams of interest to the copper industry; these include: waste dump leach solutions[31], vat leach electrolyte, liquid ion exchange strip concentrate,

electrorefining bleed-off and, of course, electrorefining electrolyte.

b. Ultrasonic Agitation

The application of ultrasonic agitation to electro-
deposition is considerably more effective than conventional agita-
tion techniques since, unlike bulk mixing, ultrasonic agitation
concentrates intense mixing effects and energy dissipation at
either the solid/liquid interface or at a boundary layer.

When ultrasonic waves travel through a liquid and strike
a surface or a boundary layer small eddies which move with high
velocity are induced close to the discontinuity. This is termed
the "acoustic microstreaming effect" and its action can be quite
dramatic at the solid/liquid interface, particularly in breaking
up boundary layers and assisting the diffusion process. At higher
vibrational frequencies liquids gradually become incapable of
stable transmission of sound energy and cavitation occurs. Cavi-
tation can be likened to a mild but penetrating scrubbing action
and is more effective than microstreaming in breaking down barrier
layers. It is more intense at lower frequencies since particle
displacement is greater and the cavities larger. As a consequence,
low frequency agitation is more effective in enhancing the
electrodeposition rate of copper from solution[32,33]. At high
frequencies the pressure waves are more directional and produce
rippled cathodes having areas of alternate bright and spongy
deposits[34]. If acoustical intensities are greater than 1 watt/cm^2
much of the metal is found suspended in the solution[35].

It has been observed[35] that ultrasonic waves completely remove the concentration gradients at "reasonable" current densities, particularly when gaseous cavitation bubbles are present. The polarization effects are considerably reduced[36-38] and, in addition, the activity over the surface of the cathode is equalized producing a more even deposit[35,39-45]. The physicochemical properties of the deposit are also improved, the hardness, and elasticity being increased and the porosity diminished.

While electrochemical applications of ultrasonics have been mainly confined to the plating industry[46], the possibility of using ultrasonic agitation as a means of achieving higher operating current densities in metal winning has also received some attention[47]. A recent comprehensive review[48] concluded that the electrodeposition of metals could be considerably accelerated in an ultrasonic field by allowing the use of high current densities. Adherent, well-consolidated copper deposits were electrowon from acid sulphate solution at 50°C at current densities of 300 ASF[34], and current densities as high as 1000 ASF have also been reported[46].

Although the application of ultrasonics to copper electro-winning has been dismissed as being too expensive, and because it produces localized effects if applied to the electrolyte and is cumbersome if applied to the cathode[12], Davy Powergas in England has done considerable work on its application to full size copper electrowinning cells[47]. Their decision to undertake this study was probably influenced by the availability of completely immersible ultrasonic units which can be inserted directly into the bottom of existing cells.

Ultrasonic agitation allows good quality copper to be electrowon at high current densities. Slight reductions in cell voltage were observed, and although an overall increase in total power requirements occurred, a significant saving in the total capital cost for a 100 TPD tankhouse can be achieved by using ultrasonic agetation for the same reasons already mentioned in the case of the air-sparging technique.

c. Periodic Current Reversal

The concept of periodic current reversal (PCR) is not new having been used in the electroplating industry since 1948 for the production of bright coherent deposits. The copper refining industry has also used this technique to nullify the inhibiting effects of the barrier layers at the electrodes. This technique as applied to copper electrorefining was pioneered in Bulgaria[49] and has been used in Africa and Japan. It is currently in use in a British plant to achieve normal operating current densities in the order of 40 ASF[50]. In addition to allowing cells to be operated at increased current densities, PCR also enables smooth deposits to be made at conventional current densities without the use of additives. Similar effects are obtained with current interruption or A.C. superimposition techniques.

During conventional electrolysis, steady-state conditions are only reached after a period of time, generally 30-60 seconds. At the beginning of electrolysis the diffusion layer is very thin but grows progressively as the electrolysis is continued to reach a constant value when the system is in the steady state condition.

Thus at the beginning of electrolysis the limiting current density is higher than in the steady state because d is smaller. In an electrolysis process employing a periodically intermittent current, it is possible to maintain pre-steady state conditions, i.e., d remains small. If, during the current interruption, a reverse current (PCR) is applied, the diffusion layer is completely destroyed. For example, the reverse current produces copper dissolution from the cathode which suddenly changes the equilibrium in the diffusion layer and enriches it in Cu^{++}.

A major problem in the application of PCR to copper electrowinning is that the cell configuration produces a substantial back EMF to the rectifier upon switching. However, a recent paper[51] suggests that this obstacle can be overcome by using the cell effect resulting from the difference in composition of the insoluble lead anodes and the cathodes (copper starter sheets). After interruption of the direct current the cells are short-circuited to produce an intense current flowing in a direction opposite to the original current. This operation apparently produces a two-fold increase in the limiting current density.

Pilot plant testing of this technique produced the best results both in terms of the deposit quality and current efficiency for a direct current period of 10 seconds and a short-circuited time of 0.5 second[51]. Industrial scale trials produced excellent metallic cathodes, very compact and slightly nodulated at 43 ASF. These cathodes were comparable to those produced at 20 ASF using continuous direct current electrolysis[51].

d. Cell Design

Another approach to achieving high current density electrowinning is to design cells capable of delivering the electrolyte to the surface of the electrodes at rates much greater than those possible using conventional cells. It has been suggested that electrolyte velocities at the cathode face of 60 ft/min are necessary before any significant thinning of the boundary layer occurs[52]. It is virtually impossible to achieve such velocities in conventional cells owing to the amount of by-passing that occurs. Attempts to overcome this problem resulted in the design of the Boliden "channel electrolyser"[14] and the Continental Copper and Steel (CCS) directed circulation system[15,53].

The Boliden "channel electrolyser", which has never been used commercially, incorporates in its design an injected and directed flow of fresh and recirculated electrolyte to each electrode surface[14]. The best circulating system was that based on the injection of the electrolyte through a series of 1/4 inch orifices drilled along a pipe at 2 inch intervals. These inlet orifices were placed so as to minimize the upward sweep of the electrolyte near the cathode because an excessive amount of this action was detrimental to the deposit. The outlet pipes are parallel to the inlet pipe and are also 2 inches in diameter. The 3/8 inch diameter outlet openings are spaced 2 inches from the centre of each cathode. The outlet and inlet pipes are connected in closed circuit to a pump and a closed solution storage tank to which fresh electrolyte is added at a rate determined by the production capacity. This technique

allows each cathode to be covered by a uniform flow of electro-
lyte sweeping down the cathode. The flow velocities at each
cathode are similar and thus concentration differences throughout
the cell are eliminated. As a result of these favourable
conditions for mass transport, a high current density is attained.
The magnitude of the flow is one of the most critical parameters
for efficient operation at high current density. At 35-40 ASF,
circulation rates of 0.1-0.2 gal/min/ft^2 of cathode area resulted
in excellent deposits[14].

The CCS system[15] was successfully installed at SEC
Corporation in El Paso, Texas[53]. The design is based on a
directed flow of electrolyte across the anode and cathode faces.
This type of flow distribution allows the direct electrowinning
of nickel with boric acid buffers (no diaphragms)[53] and the
electrowinning of copper[15] at increased current densities.
However, studies conducted at Davy Powergas[47] suggest that the
high circulation rates and pressure drops in the CCS system incur
such high pumping costs that benefits from its use in copper
electrowinning are only marginal.

    e. Rotating Electrodes
        The use of a rotating cylinder cathode has provided
valuable information on the parameters affecting the high rates
of copper deposition in copper sulphate electrolytes[19].
However this technique is limited by the eventual rotation of
the catholyte with the boundary layer as the speed increases, thus
decreasing the relative motion between the electrolyte and the
boundary layer.

3. Consequences of High Current Density Operation

    i. General

        The beneficial effects of operating copper electro-
winning cells at high current densities such as reduced capital
cost, smaller plants, smooth, compact deposits in the absence of
additives, and so on, have been mentioned in the previous section.
However, before advantage can be taken of these beneficial effects,
some serious problems associated with high current densities must
be solved. These problems, including increased anode wear
(especially with conventional Pb anodes), acid mist control,
increased corrosion of cathode suspension bars, etc., vary
according to the technique used to obtain the high current density.
For example, PCR and ultrasonic agitation have a more serious
effect on anode life than does air sparging.

        In addition to the above-mentioned advantages and dis-
advantages of high current density operation, the possibility of
replacing the copper starter sheets with permanent cathode blanks
(either titanium or stainless steel) has also been introduced
into copper electrowinning as a direct consequence of the high
current density operation. In this section, the effects of high
current density copper electrowinning on the anodes, cathodes, acid
mist, etc. is discussed together with the methods currently
being tested to eliminate the problems associated with these effects.

    ii. Anodes

        Although many types of "insoluble anodes" have been
investigated for copper electrowinning, lead alloys and especially
lead-antimony alloys remain the predominant choice for anodes.

However, such lead based alloys can be a source of lead con-
tamination in the deposited copper. Electrolytic copper containing
>10ppm Pb (5ppm in some cases) is not suitable for wire drawing,
and when the cathode copper cannot be blended with refined copper
(low Pb content) then the Pb content of the electrowon copper
must be carefully controlled. It is possible to achieve such a
control in conventional copper electrowinning (10-20 ASF, low
acid electrolyte) through the use of suitable additives which
produce a smooth, compact deposit and thus prevent the occlusion of
Pb. However, the advent of electrolytes produced via solvent
extraction (SX) for copper electrowinning increased the problem
of Pb contamination because of the high acid content
($\geq$ 150 g/1 H_2SO_4)[54]. Increasing the operating current density
also increases the rate of anode corrosion and, when used in com-
bination with the SX-produced electrolytes, the corrosion is even more
severe. A recent study[55] has confirmed that the corrosion rate
of 0.4% As - 10% Sb-Pb anodes increased markedly with increasing
acid strength and current density.

Many of the methods applied to reducing anode corrosion
in SX-produced electrolytes are also being tested for high
current density operations. Such methods include modification
of the conventional Pb anodes either by alloying to produce a
more resistant material[56], bagging[54], coating with a resistant
or inert material (e.g., MnO_2)[57], or by the addition of cobalt
to the electrolyte[54,55,58-60]. The alternative is to replace
the Pb-based anodes by inert non-lead materials, e.g., precious
metal oxide-coated titanium, niobium or tantalum anodes.

The addition of small amounts of cobalt (~50ppm) to copper electrowinning cells has been observed to reduce the Pb contamination of the cathode copper[58], reduce the polarization at the lead anode[60] and decrease the weight loss of a Pb-Sb-As anode in sulphuric acid[55]. These beneficial effects result from the fact that the anodic scale which forms in the presence of cobalt does not flake off the anode surface. X-ray analysis of the anode scales revealed the absence of any significant amount of cobalt[58] thus disproving the hypothesis that the inhibiting effects of cobalt are due to the presence of cobalt oxides in the pores of the lead oxide layer[55]. However, little is known about the operating flexibility and long-term effects of cobalt addition to copper electrolytes. Problems associated with monitoring cobalt levels, cobalt losses in bleed streams, and the possibl contamination of SX reagents (when SX-produced electrolytes are used) suggest that this method of anode corrosion control may not be universally applicable in the long term.

Long-term laboratory tests employing Pb anodes enclosed in porous PVC bags have produced copper deposits containing <1 ppm Pb[54]. The material which flaked off the anodes remained in the bags thus eliminating the problems of slime control. Because the oxygen generated at the anodes was confined to the bags, a reduction in the acid mist over the cells was observed. In addition, the current efficiency increased because diffusion to the cathode of the Fe^{+3} produced at the anodes was inhibited.

An alternative to bagging is to protect the anode surface by applying an inert conductive coating such as MnO_2[57].

Although this technique would be cheaper than bagging, the other beneficial effects of bagging mentioned above would not result. Although the operating voltage for MnO_2-coated anodes is significantly less than that for conventional Pb anodes, the MnO_2 is soluble in the electrolyte when the anode is not polarized.

Lead-calcium and lead-calcium-tin alloys have been closely studied for use in acid batteries [61] and the technical problems associated with these alloys have now been overcome. Anodes fabricated from these alloys are presently available to the copper industry for use in electrowinning and several have been tested for this purpose on a laboratory scale [54]. The results indicate that these alloys showed superior corrosion resistance compared with the lead-antimony alloys. The oxide layers formed on the alloys were relatively thin and uniform, but were more protective than the equally thin but porous layers formed on the Pb-Sb alloys [54]. It has been suggested [54] that these low cost lead alloys will be widely used in copper electrowinning in a conventional tankhouse especially in view of the increasing cost of antimony.

The replacement of conventional Pb anodes by inert non-Pb materials would, of course, completely eliminate the problem of Pb migration to the cathode. Ideally, the material should be of low cost, be dimensionally stable as thin sheets, have good conductivity, be mechanically strong and have long life in the tankhouse. Titanium, niobium and tantalum possess the required mechanical properties but have low conductivity so that it is necessary to coat them with inert conducting material. Precious metals are often chosen as coating material but similar

anodes having noble metal oxide coatings have been used satis-
factorily in the caustic chlorine industry for a number of
years[62]. The anodes now offered to the copper industry
thus require a higher capital expenditure than conventional
anodes. However, anode manufacturers claim that the advantages
of low operating voltage and long life and the ability to
operate at high current density, decrease tankhouse size and
thus decrease the unit capital cost, which more than compensates
for the initial high capital cost of the anodes. Although some
of these claims appear to be fulfilled[54], the ability of such
anodes to stand up to ultrasonic agitation or PCR effects has
not been confirmed. At the present time it may be said that
the use of these high cost inert anodes appears attractive
when a copper producer must have high purity copper and is
willing to risk using a relatively new product.

iii. Acid Mist

Acid mist results from the emergence of tiny bubbles
of anodically generated oxygen enveloped in a film of electrolyte
into the atmosphere over the cell. Acid mist, already a problem
at 15-20 ASF, would be severe at 90 ASF and is probably the most
difficult problem to overcome at high current densities. In
conventional copper electrowinning (15-20 ASF), acid mist
generation from leach/electrowin units is satisfactorily suppressed
by foam generating agents, such as Dowfax 21A, which provide a
blanket of foam on the surface of the electrolyte. These agents
are also effective to some extent in reducing acid mist at
high current densities.

It is claimed[29] that the air sparging technique used to allow high current density operation does not increase the formation of acid mist. However, this technique is not compatible with the foaming agents generally used to reduce the acid mist owing to the dispersal of the foam. Further, if one considers SX-electrowinning units, the surfactant nature of these foaming agents or their degradation products adversely affect the disengagement and kinetic properties of the organic reagents in the SX circuit. Several layers of polyolefin balls spread over the electrolyte surface seem to be a suitable alternative to these foaming agents, both for SX electrolyte and high current density operation involving electrolyte agitation by air sparging[29,30].

An alternative scheme currently being considered for high current density copper electrowinning plants is that of specialized ventilation systems such as those already installed in some zinc plants[63] and which have been effective in reducing the acid mist to the statutory requirements.

iv. Cathodes

Elimination of the starting sheet operation already practised in modern electrolytic zinc plants has long been advocated for the copper industry. The reasons for this include simplification of operation, improved cathode quality, reduction in short-clearing labour, etc. Copper mother blanks are increasingly being replaced by titanium which offers a number of technical advantages that outweigh its extra cost; it has a very long life and requires surface preparation, whereas copper blanks have to be carefully prepared after each stripping cycle. It has been

suggested[50] that the switch to permanent cathode blanks may affect the cell design in two ways: jumbo sized electrodes could come into general use and good heat insulation for cells would become much more important because even minor variations in electrolyte temperature may cause premature loss of contact between Cu cathode and Ti baseplate.

Recent developments in edge strip design and Kennecott's system for controlled area deposition[29] have now made the total production stripping concept using titanium or stainless steel blanks throughout the tankhouse more attractive. Whether or not this process is advantageous depends mainly on the relative values (per lb of Cu) of two opposing factors: increase in the capital cost of the plant and elimination of conventional starting sheet preparation. The relative values of these factors will depend at least to some extent on the scale of operation. Capital cost savings can result if the tankhouses are operated on a longer cathode life cycle. Conventional practice produces cathodes weighing 90-150 lb and the life cycle is generally 5-6 days. The final cathode size is governed by such factors as nodule formation, impurity level (itself a function of nodule formation) and loop corrosion. The various methods for increasing current density discussed in the previous section also significantly reduce nodule formation so that the major consideration for increased cathode life cycle is loop corrosion. Information on the chemical factors which produce loop corrosion, e.g., ferric ion concentration, is needed. Some of these chemical factors are discussed in a later section of this review.

4. Electrowinning Copper from Dilute Solutions

i. General

In addition to meeting the requirements of high current density operation for the purpose of reducing the copper inventory in the cells, the design of new electrochemical cells and, indeed, the improvement of existing designs has also been approached with the objective of winning copper economically from dilute (ppm range) process streams. These requirements, as mentioned previously, involve operation at rates above the limiting current density due to natural convection. The methods of attaining high current density in conventional copper electrowinning such as air sparging[11,12,28,29], and the production of turbulent flow by fast pumping[14,15] are also being applied to the electrowinning of copper from dilute solutions[31,64]. In addition, a number of cell designs suitable for the electrolytic recovery of copper from dilute solutions have recently been described[65]. Below, are brief descriptions of a number of the more significant designs and suggested applications.

ii. Particulate Electrode Cells

Particulate electrode cells can consist of either packed bed electrodes or fluidized-bed electrodes. These particulate electrodes offer a considerable increase in surface area over a conventional plate electrode occupying the same volume, and their surface area can be varied by varying the particle size. Thus they are particularly useful for processes that can only be carried

out economically at low current densities, e.g., electrowinning of copper from dilute solutions such as leach liquors and waste solutions.

The fluidized-bed electrode is a recent invention[66-70] which stemmed from the observation that when a bed of conducting particles is fluidized by an upward flow of electrolyte, the bed can function as an electrode. Several configurations have been proposed for fluidized-bed electrodes but the one considered most suitable for manufacture and operation on an industrial scale is the "side-by-side" design[71]. In this design, the anode and cathode compartments are separated by a vertical, non-porous ion-exchange membrane, and either one or both of the electrodes may be fluidized.

Several papers[72,73] have examined theoretically the mode of operation of fluidized-bed electrodes while others have considered their application to organic electrosynthesis [66], extractive metallurgy[71,74,75], metal electrowinning[76,77] and fuel cells[78].

The potential advantage of the fluidized-bed electrode system as a cathode in an electrowinning circuit lies in its ability to provide high throughput and high current operation for the direct electrowinning of metals (e.g., Cu) from dilute solutions. Many recently published papers[65,71,76,77] indicate that, compared with conventional systems, definite advantages may be gained by employing fluidized-bed cathodes for electro-winning copper from dilute solutions. These include acceptable rates of copper deposition and reasonable power efficiencies[76,77],

and the reduction of copper levels down to 0.2 ppm[77]. Based on these observations it has been suggested[50] that fluidized-bed cathodes would be most successful for purely corrective pruposes. For example, in scavenger or liberator systems fluidized bed electrodes could be used to strip down to the minimum practical copper level, preferably under conditions which yield a saleable produce or they could be used for de-ionizing cells to eliminate copper or other heavy metals from pickle liquor effluents for discharge or for thorough purification.

However, the optimistic views presented above for the application of fluidized-bed cathodes may be premature since a recent paper describing their application to low acid, low copper leach liquors presented some rather discouraging results[79]. The presence of Fe^{+3} in solution, for example, is more serious in its effect on current efficiency and power consumption than in conventional cells, and the low conductivity of the leach solutions give rise to higher cell voltages and thus higher power consumption.

The only published data for power consumption for copper electrowinning in fluidized-bed cells in which the values are similar to those obtained in conventional practice are those quoted by Flett[76] who obtained his data using iron-free solutions. In contrast, Wilkinson and Haines[77], using low acid - iron free solutions quoted values which, depending on the cell current and final copper concentration, ranged between 1.5 - 5 times higher than conventional practice,which is almost 2 kWh/kg Cu.

Thus it was concluded[79] that the direct treatment of dilute copper leach liquors using a fluidized-bed cathode,

even in the absence of iron, would be subject to rather high power costs which could prejudice their use for this application. For solutions containing iron there is an additional operating cost due to the necessity of reducing all the iron to the ferrous state. However, power costs might be acceptable if the dilute leach liquor contained appreciable quantities of other dissolved salts which would increase the conductivity sufficiently to lower the cell voltage to reasonable levels. As will be discussed in the next section, it should be noted that the presence of $Al_2(SO_4)_3$ and $MgSO_4$, for example, increase the viscosity of the solution and therefore hinder the diffusion of Fe^{+3} to the cathode[80].

It has been suggested[79] that the fluidized-bed electrode system also be considered as an alternative to the conventional electrowinning cells for the treatment of normal copper electrolytes, e.g., 20-40 g/l Cu^{++}. The fluidized-bed cells offer the possibility of automatic feeding and discharge of copper particles to and from the cells, leading to continuous operation and elimination of the expensive labor-intensive cathode handling operation involved in the conventional process. Although power consumption would be much less significant in this operation because of the high copper and acid content of the electrolyte, Fe^{+3} would continue to be a serious problem. Although conventional electrowinning systems can tolerate a few g/l Fe^{+3} without serious loss in current efficiency the intense agitation in fluidized-bed cathodes results in an increase in the limiting current for Fe^{+3} reduction by probably one order of magnitude[79].

In spite of the abvious differences of opinion on the application of fluidized-bed electrode systems, it must be concluded that for the present at least it seems such systems will undoubtedly find a place in the copper extraction industry, but perhaps not to the extent expected from the early results.

It has also been demonstrated that it is possible to reduce the copper concentration in sulphuric acid electrolyte from 10 to 0.01 g/l using a cathode consisting of a fixed bed of graphite particles[30]. It was concluded that although the system was superficially attractive as a replacement for the last few liberator cells, the savings in power did not justify the development costs and capital required for the membranes.

iii.   Alternate Cell Designs

In addition to the particulate electrode systems described above, many alternate electrochemical cells designed to operate at low metal ion concentrations have also been described. These design concepts, including the particulate electrode systems, have recently been reviewed[81] in terms of their application to industrial or large scale operations. The various cell designs were compared on a quantitative basis in terms of the limiting current, and also in terms of some of their advantages and disadvantages. For further information on these electrochemical reactors, the reader is referred to the above excellent and comprehensive review.

5. Effect of Impurities

Impurities present in copper electrowinning solutions depend on the source of that solution, i.e., whether it comes directly from a leaching curcuit or from a solvent extraction stage. The most troublesome impurity is dissolved iron, present in both types of electrolytes but, obviously, to a much lesser degree in the electrolyte produced by solvent extraction. In the leach/electrowin system, the presence of inert salts, e.g., $Al_2(SO_4)_3$, $MgSO_4$, etc., also plays an important role, whereas in the solvent extraction - electrowin (SX/EW) system they are absent. However, the SX/EW system must contend with the effect of entrained solvent components on the copper deposition stage and also, it seems that many of the additives presently used to promote smooth copper deposits are not compatible with the solvent extraction stage. The adverse effects on the SX stage of foaming agents which suppress acid mist have already been mentioned.

Poor quality deposits combined with low current efficiencies, as well as problems associated with localized corrosion of electrode suspension loops, often occur in copper electrowinning. It has been suggested that these difficulties are related to the concentration of dissolved Fe, Al, Mg, Ca and to suspended solids or gelatinous materials[82-84]. Although a variety of operating techniques have been used in an attempt to minimize these problems, the way in which the various operating variables influence the Cu electrowinning process is complicated, and as a result the operating techniques have been an art developed through experience. Only recently has an attempt been made to understand the

relationship between solution composition, temperature, current density, agitation and the observed tankhouse phenomena[110].

Cyclic oxidation and reduction of iron consumes current and therefore decreases the current efficiency. In a recent analysis of the variables in copper electrowinning it has been shown that the electrode reaction rates at a given current are determined by the diffusion of Fe^{+2} ions to the anode and Fe^{+3} ions to the cathode[80]. A comprehensive equation relating the rate of diffusion of iron species to an electrode (i_L) and the operating parameters has been developed, viz.,

$$i_L = \frac{Fk^{2/3} \ T^{2/3} \ V_\infty^m \ C}{(6 \pi r_i)^{2/3} \ K_g \eta^{2/3} \ (\eta/\rho)^n} \qquad [2]$$

where K_g is a constant for a given electrode geometry

V_∞ is the velocity constant of the electrolyte parallel to the electrode surface at a distance greater compared to the diffusion layer thickness

η/ρ is the kinematic viscosity of the solution where η is the dynamic or absolute viscosity and ρ is the density

m,n are constants depending on whether the solution flow is turbulent or laminar. For laminar flow $m \simeq 0.5, n \simeq 0.16$; for turbulent flow $m \simeq 0.9$ and $n \simeq 0.57$[85]

r_i is the radius of the diffusing species

k is the Boltzmann constant. Note that the term $kT/6\pi r_i \eta = D$, the diffusion coefficient.

The above equation predicts that increases in temperature, solution velocity and copper ion concentration make important

increases in i_L whereas an increase in the viscosity η, decreases i_L.

The limiting current for the reduction of Fe^{+3} increases with solution agitation which, in turn, is influenced both by the circulation rate of the electrolyte through the cell and by the O_2 bubbles from the anode. Since the concentration of bubbles decreases with depth in a cell and increases with current density, solution agitation also varies with these parameters. It has been reported[80] that the diffusion rate is proportional to the height, which in turn is proportional to the concentration of O_2 bubbles. Thus the overall effect of agitation is complicated, depending on the cell design as well as the above mentioned factors. For these reasons a quantitative theory of agitation in electrowinning has not been developed.

Impurity salts in the electrolyte, e.g., $Al_2(SO_4)_3$ and $MgSO_4$, increase the viscosity, η, of the solution and therefore impede the diffusion of Fe^{+3}. The results of laboratory studies[80] indicate that the $\eta^{2/3}$ term of equation [2] makes a greater contribution than the $(\eta/\rho)^n$ term to inhibiting the diffusion.

From equation [2] it is observed that increases in temperature increases i_L, both because $T^{2/3}$ increases and η decreases with an increase in temperature. It was concluded[80] that the primary influence of temperature on i_L is on the diffusion coefficient, $D = kT/6\pi r_i \eta$, which is in agreement with the general finding that the diffusion coefficient of ions in solution usually increases by about 2 per cent per degree[86].

The dependence of the current efficiency (CE) on
the operating parameters may be expressed by the equation[80]:

$$CE = 1 - \frac{Fk^{2/3}T^{2/3}v_\infty^m C_{Fe^{+3}}}{(6\pi r)^{2/3}Kg\ \eta^{2/3}(\eta/\rho)^n i_c} \qquad [3]$$

where i_c is the applied current density. Thus both the concentration of ferric ion and the applied current density have a strong influence on the current efficiency. Increasing the current density increases the current efficiency because the rate of reduction of Fe^{+3} is diffusion controlled, so that any increase in the current density must be sustained by an increase in copper deposition. Large increases in the salt concentration $(Al_2(SO_4)_3,$ $MgSO_4)$ of the electrolyte tend to increase the viscosity of the electrolyte and hence increase the current efficiency.

The presence of Fe^{+3} and other salts $(Al_2(SO_4)_3,$ $MgSO_4)$ also affect the quality of the deposited copper. The presence of $Al_2(SO_4)_3$, etc., increases the viscosity which diminishes i_L and therefore leads to a slowing down in the diffusion of Cu^{+2} to the electrode surface. The deposits become more porous and nodular and hence contain greater sulphur and oxygen impurities[11,80].

It is technically possible to improve the current efficiency in copper electrowinning by decreasing the temperature, increasing the inert salt concentration, decreasing the Fe^{+3} concentration, increasing the current density and decreasing the electrolyte agitation. The most effective of these methods is to decrease Fe^{+3} since it is the only method which does not deteriorate the quality of the deposit. The various methods for decreasing Fe^{+3} include:

1) Solution purification by hydrolysis, precipitation, solvent extraction, etc.

2) Reduction of Fe^{+3} to Fe^{+2} by SO_2, Cu^O, etc.

3) Increase in the bleed stream volume

4) Use of a diaphragm cell.

Methods 1 and 3 have the advantages of improving the cathode quality because they decrease the inert salt concentration. Methods 2 and 4 do not affect the cathode quality but 2 would have to be applied quite often because Fe^{+3} is generated at the anode.

Solvent extraction is now accepted as a major method for recovering copper from leach liquors, and consequently its use eliminates many of the impurities encountered in the leach-electrowin system. However, although the solvent extraction stage produces high purity electrolytes, it introduces other problems in the electrowinning stage. The increase in acid mist resulting from the high acid content of these electrolytes has already been mentioned. Entrained organic matter in the copper electrolyte can result in deposits exhibiting organic burn[4], manifesting itself as a dark chocolate-coloured material (consisting of an intimate mixture of copper and organic material) deposited mainly at the air/electrolyte interface, but occasionally spreading down the cathode. It is interesting to note that workers at Kennecott[29] claim the use of air sparging to achieve high current density for copper electrowinning from a pure electrolyte saturated with 40% LIX64N produced quality copper deposits showing no adverse effects from the LIX reagent.

6. Role of Additives in Copper Electrowinning

The effect of the concentration polarization in establishing a limiting current density and its consequent role in the electrowinning of metals was described in detail in Section 2. Also of great importance is that concentration polarization tends to promote the growth of minute surface imperfections. The mass transfer to the tips of these imperfections protruding into or through the diffusion layer is greatly improved compared with the smooth parts of the cathode. The low concentration polarization at these tips compared with the rest of the cathode disturbs the uniformity of the current distribution and results in increased current density on these imperfections. This effect is more severe in operating near the limiting current density where the concentration polarization is large and contributes more to the microdistribution of current [18].

The major factor that counteracts these negative effects of concentration polarization is the activation or charge transfer polarization. This overpotential is a function of the current density only, and when it is large compared with diffusion overpotential and ohmic drop components it tends to impress about the same current density on both peaks and valleys. The activation polarization is often artificially increased by adding levelling agents to the electrolyte. Since the levelling agent is transported to the electrode surface by diffusion, the increased flux of levelling agents toward imperfections may actually suppress their growth relative to the rest of the cathode [87]. For this reason, addition agents such as glue, thiourea and chloride ion are added to

copper electrowinning solutions. Although the concentrations of these substances in the electrolyte are several orders of magnitude less than the concentration of Cu^{2+} or H_2SO_4, these addition agents have a profound effect on the deposit quality through their levelling action and grain refinement. Because the amount of an addition agent required depends on the current density and agitation within the cell, other components within the cell, and even on the other types of addition agents used, an a priori calculation of the amount needed is difficult, if not impossible, at this time.

As mentioned, these addition agents can be organic (glue, thiourea) or inorganic (Cl^-) in nature[88-103]. Their presence in the electrolyte generally has physical as well as metallurgical effects on the deposit. These can be changes in deposit properties such as brightness, hardness, grain refinement and surface smoothness. Addition agents can also increase the limiting current density for the electrodeposition process. Their action has been associated with various properties, such as their ability to form complex ions, become colloidally dispersed in the electrolyte, or adsorbed on the cathode surface[88]. The additives modifying the properties of the deposit do so by virtue of their effect on the microstructure of the deposit and on the nature and distribution of codeposited impurities[101]. Since these two factors are determined by the nucleation and growth of the deposit, it is the effect of any addition agent in these respects which is important.

Among the organic reagents used as additives, the effects of thiourea, glue, gelatin, glycine, cystine, dextrin and

sulphonated products have been studied[88-103]. Among the inorganic ions, the effects of Co^{2+}, Mn^{2+}, Mg^{2+}, Al^{3+}, Cl^-, SO_4^{2-}, ClO_4^-, fluoroborate and NO_3^- on the electrodeposition of copper have been studied[94,103,105].

The effect of thiourea on copper electrodeposition has been thoroughly investigated by many authors[89,90,93,102-119]. The mechanism of the effect of thiourea has also been studied extensively[89]. Llopis and co-workers,[109] using radioactive tracers, found sulphur and not carbon in the deposit when the tank-house liquor contained thiourea. This indicated that either the thiourea hydrolysed to urea and H_2S, or else it was reduced, forming NH_4SCN and H_2S. The latter mechanism according to Turner and Johnson[92], is thought to be the more likely. The solubility product of CuS in aqueous solution is very low, 8.5×10^{-45}, thus CuS will precipitate at the cathode surface at a relatively low sulphide concentration. It is suggested that CuS is strongly adsorbed on active sites, so that minute concentrations of thiourea (1-5 mg/l) are enough to stabilize (100) rather than (110) oriented structures. This results first in an increase in grain size, but with higher concentrations of inhibitor the grain size again decreases even with (100) orientation[110]. At concentrations greater than 25 mg/l, surface adsorption is predominant and the overvoltage increases considerably. This results in predominant (111) orientation and the surface of the deposit becomes increasingly nodular. Above 75 mg/l of thiourea in the electrolyte very poor quality deposits are obtained due to increasing amounts of CuS in the deposit. The optimum effect is observed

when a complete monolayer is formed on the surface[89]. Normally this is about 5-10 mg/l of thiourea depending, of course, on the volume of the tankhouse liquor and cell design. Cystine is shown to exhibit effects similar to thiourea in copper electrodeposition and is again related to precipitated CuS. Its effect on overpotential-log (current density) curves is shown to be similar to thiourea except that it does not shift the rest potential, and a hystersis curve loop is observed between increasing and decreasing current-potential curves.

Glycine has only a small effect on the cathode potential-current density relations. Thus while glycine has a profound effect on the distribution of copper deposition on the microscale, it does not influence the kinetics of copper deposition[93].

The effect of dextrin as an additive is not conclusive and it is reported that it enhances the effect of thiourea[90]. Glycine when present at concentrations higher than 10^{-2} M/l causes polycrystalline material to be deposited with considerable distortion in the metal lattice[88]. Haschez[111] studied the effect of gelatin, a protein polymer. The surface roughness is improved by adding gelatin to a level of 5 mg/l, but also results in disorientation of deposits. The (110), (111), and (100) oriented deposits are observed in variable and nonsystematic proportions. Gelatin has no influence on nodular growth. The effect of glue was studied by Jenning and Rizzo[100]; when present in low concentrations it depolarized the cathode at all potential values. At higher concentrations the effect was a strong polarization at low potentials. The limiting current density increased to a maximum and then decreased with increasing

concentrations of glue, but not below the limiting current density for the base solution. The decrease in limiting current density coincided with severe polarization at low potentials. This behaviour can be explained on the basis that at low concentrations glue enters the diffusion layer, disrupts it, and hence increases the current density. The polarizing effect of porteins at these lower concentrations is not concentrated enough to initiate sufficient adsorption at points on the cathode surface to demonstrate polarization. At higher glue concentrations a sharp polarization is observed, which could be the result of increased concentration of polarizing material on the cathode surface. The disruption of the diffusion layer has reached a maximum and is now not as important as the shielding phenomenon due to glue adsorption at the peaks, and polarization thus becomes severe. At higher potentials a removal of the polarizing effect of the protein is observed. This may be due to a partial reduction of protein, to a desorption of the protein, or to covering of the protein by an increased rate of copper deposition.

The theory put forward by Price and co-workers[112] suggests a mechanism by which organic addition can modify the crystal structure of electrodeposits by adsorption and by interfering with the motion of lattice steps over the surface. As the concentration of adsorbed molecules reaches the critical value (depending on the overvoltage), the step motion is completely blocked and no further growth of the crystal occurs. The adsorbed molecules on the rapidly growing surface can, on the other hand, be buried into the crystal as the lattice steps move around and move past them.

Hardesty[94] found that for solutions of comparable concentrations the surface morphology of copper deposits is radically affected by the anions present. Bockris and Enyo[113] suggested that the differences in observed double layer capacities in SO_4^{2-}, ClO_4^- and sulphamate electrolytes were attributable to differences in polarizability due to differences in the size of the anions.

The effect of halides on copper electrodeposition has been studied by many authors[100,103,104,114,115]. Gurevisch[104,105] has observed that Cl^- is adsorbed on the cathode forming an intermediate complex of the type Cu^{2+}— Cl^- — e^- (Cu) which is supposed to facilitate the transport of Cu^{2+} into the deposit. This results in lowering the discharge activation energy of Cu^{2+} and depolarization of the cathode. It has been reported that the crystallization overvoltage in (110) is a minimum and hence results in the increase in preferential growth of copper deposits in this orientation as Cl^- is added[116]. However, as the solubility of CuCl (4.0×10^{-4} g ion/l) is exceeded and CuCl is adsorbed on the cathodic deposit, the active cathodic surface area is reduced. Under conditions of a large diffusion over-voltage, this results in a smaller number of growing crystals per unit cathode area and can give rise to preferential (111) orientation leading to nodular growth[99]. However, Lakshmanan, MacKinnon and Brannen have also observed that the orientation of the deposited copper at various chloride ion concentrations depends on several other factors such as current density, dissolved organics, stirring rate, deposition time, etc.[99,116,125].

7.   Growth and Morphology of Deposited Copper

An excellent review on this subject has been recently written by Winand[110]. From the available literature he concludes that, for copper electrodeposited from various pure sulphate solutions at very low current densities, spiral growth plays an important role in determining the morphology of the deposit. This is particularly so for the pyramidal growth observed on the (100) substrate.

Vaughan and co-workers[117] found that the initial mode of copper deposition is strongly dependent on the purity and orientation of the cathode. They also suggest that the nucleation effects observed in polygonised copper should be related to the presence of impurities at the dislocations. Pick et al[118] suggest, that any change in variation of the deposit structures can be explained on the hypothesis that the growth proceeds by a "bunching mechanism".

Economou and Trivich [119] revealed through their microscopic and radiotracer studies that at low current densities the order of decreasing ease of growth in orientation is (110) > (100) > (111). This is in accordance with the results obtained by Wrangler [121]. At higher current densities the (100) structure appears in preference to the (111). These results can also be correlated with Postl, Eichorn and Fisher[122] who reported that crystallization overvoltage in (110) is a minimum.

Cuminsky[123] made X-ray diffraction studies of copper deposits formed on low index planes of copper single crystals. His studies revealed that there are three characteristic stages occurring during the deposition process i) epitaxial growth ii) twin development and iii) polycrystalline growth. The results obtained also show that for a given current density, the deposit thickness, Δh, is a function of crystallographic orientation of the base single crystal in the order:

$$\Delta h_{(111)} > \Delta h_{(100)} > \Delta h_{(110)}.$$

Recent research work carried out by Lakshmanan, MacKinnon and Brannen[99,116,125] on copper electrowinning reveals much useful information. Their data on changes in current density suggest preferential (220) orientation at higher current density and (111) at lower current density under the conditions studied. The decrease in overvoltage by the addition of chloride ion leads to preferential (220) orientation. This is in agreement with Barnes[124] who suggested that, in the (110) orientation, ions travel furthest and reach the sink position and grow at low overpotential values. The increase in (111) growth at higher chloride ion concentration after the limiting current density is exceeded as suggested by Gurevisch[104] is in agreement with the recent results of Lakshmanan, MacKinnon and Brannen[99]. These authors have also studied the changes in the orientation of deposited copper occurring under a wide range of conditions, including varying concentrations of chloride ion, thiourea, glue, dissolved and entrained commercial solvent extraction reagent, and alkaline earth metal salts, as well as

current density and deposition times[99,116,125]. For example, chloride ion concentrations ≤ 10 ppm promote preferred (220) orientation in copper deposits obtained at 40 ASF whereas higher concentrations of chloride ion favour (111) oriented copper deposits resulting in nodular growth[99]. The effect of dissolved LIX65N (8 ppm) improves the copper deposit by promoting a ridge type structure, (220) orientation[116]. Also, higher chloride ion concentrations (e.g., 40, 100 ppm) can be tolerated at this concentration of LIX65N. Entrained LIX65N (50 and 100 ppm) results in highly preferred (111) oriented copper deposits which are extremely powdery and nodular. However, the addition of 100 ppm of chloride ion appears to offset this effect to some extent[116]. The combined additions of glue, thiourea, LIX65N and chloride ion on copper deposits obtained at 40 ASF essentially favour (111) oriented deposits. However, the deposit grain size is considerably refined so that less nodule formation is observed under these conditions[125].

Storey and Barnes[91] have found that the topography of the deposit formed on any grain of the polycrystalline aggregate is identical to that of the deposit grown under similar conditions on a single crystal of the same orientation.

CONCLUSIONS

The solvent extraction/electrowinning process is successful as an alternative to the smelting/cementation route for the recovery of copper. The operation of electrowinning

plants has previously been critically dependent on the character-
istics of the leach liquor serving as the electrolyte. A process
such as SX, which makes possible a selective transfer of the
copper in the pregnant solution to an electrolyte of optimum
properties for electrolysis, considerably increases the profit-
ability of electrowinning and encourages the application of the
process for copper production. Impurity of product, build up of
iron in the dump, acid consumption and increased cost of scrap
iron all have led to the increasing popularity of the solvent
extraction/electrowinning route for copper recovery. However,
when solvent extraction strip liquors are accepted for electro-
winning operations the associated problems also need to be
considered in detail. These include i) organic burn of the
cathodes ii) acid misting in the tankhouse iii) alternative
anode materials capable of resisting high acid concentration and
methods to overcome the inclusion of Pb in the cathode copper.
Detailed investigations in this field should be a welcome
contribution. The interaction of the solvent extraction stage
with the electrowinning operation warrants detailed investigation.
The influence of dissolved and entrained organics in the
electrowinning stage, and the effects of organic additives
from the tankhouse when taken to the stripping operation,
require detailed investigations. The effect of flotation
agents, if used before electrowinning to remove dissolved and
entrained solvent extractant at the solvent extraction stage,
also needs careful study.

Another area which is considered important and bene-
ficial in the field of hydrometallurgy as a whole is the use of
diaphragm cells. With increasing energy costs it may prove
worthwhile to investigate in detail the feasibility of
operating anodic dissolution with a separation process such as
solvent extraction to make high purity feed liquors as catholyte.
Such a combined process can probably be developed with the aid
of properly designed diaphragm cells.

Recent studies involving the application of cyclic
voltammetry and scanning electron microscopy techniques to
characterize copper deposition from acid sulphate electrolytes
have shown that there is a correlation between the type and
concentration of addition agent and the voltammagram, and that
a relationship also exists between the morphology of the copper
and the processing conditions used during deposition. This
type of study therefore warrants further investigation as it
appears that a combination of voltammetry and scanning electron
microscopy can be potentially useful in predicting the electro-
lyzability of commercial refining or winning solutions.

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