



# Copper electrowinning: theoretical and practical design

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## Synopsis

An engineering house's perspective of required inputs in designing a copper electrowinning tank house and ancillary equipment calls for both understanding of the key fundamental controlling mechanisms and the practical requirements to optimize cost, schedule and product quality. For direct or post solvent extraction copper electrowinning design, key theoretical considerations include current density and efficiency, electrolyte ion concentrations, cell voltages and electrode overpotentials, physical cell dimensions, cell flow rates and electrode face velocities, and electrolyte temperature. Practical considerations for optimal project goals are location of plant, layout of tank house and ancillary equipment, elevations, type of cell furniture, required cathode quality, number and type of cells, material of construction of cells, structure and interconnecting equipment, production cycles, anode and cathode material of construction and dimensions, cathode stripping philosophy, plating aids, acid mist management, piping layouts, standard electrical equipment sizes, electrolyte filtration, impurity concentrations, bus bar and rectifier/transformer design, electrical isolation protection, crane management, sampling and quality control management, staffing skills and client expectations. All of the above are required to produce an engineered product that can be designed easily, constructed quickly and operated with flexibility.

## Introduction

The electrowinning of copper ions derived from leaching, or solvent extraction, is a significant contributor to the global copper commodity supply. The process of electrolysis for copper was first developed in the late 19th century and despite numerous advancements in technology, the principles and basic equipment remain the same. The first part of this paper deals with the theoretical requirements and fundamental equations and principles that govern copper electrowinning. The second part discusses the practical requirements for designing a copper electrowinning plant.

The hardware used is simple in nature: for electrowinning an acid resistant bath with anodes and cathodes submersed in solution with current passing through the electrodes is the fundamental process unit. The fundamental concepts lie in reaction kinetics, mass transfer phenomenon, thermodynamics and other electrochemical specific models, the application of which leads us to a deeper and

more appreciative knowledge of the 'simple' electrowinning reactor.

The first part of the paper goes through the fundamentals and culminates in an example reactor being developed. Note that not all design procedures are named as this would compromise TMP's intellectual property. However, the reader will be able to get a very good understanding of what is required to design and build a copper electrowinning plant.

## Part 1: Copper electrolysis theoretical considerations

### Faraday's law

For the winning of copper by the addition of electrons



Cations go towards the cathode, and anions go to the anode. The working electrode is where reduction takes place and the counter electrode is where oxidation occurs. The working electrode is the cathode and the counter electrode the anode. For the general oxidation/reduction reaction:



Faraday's law gives the total amount of charge spent to reduce  $M$  mols of Ox ( $Q$ ) as:

$$Q = n.F.M \quad [3]$$

The charge spent per unit time is defined as the current ( $I$ ):

$$\frac{dQ}{dt} = I = n.F. \frac{dM}{dt} \quad [4]$$

Normalizing with unit area gives Faraday's law expressed in current density ( $i$ ):

$$i = \frac{I}{A} = n.F. \frac{1}{A} \cdot \frac{dM}{dt} \quad [5]$$

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Faraday's law then is: the current flowing in an external circuit is proportional to the rate of the reaction at the electrode.

## Nernst equation

The standard electrode potential is the potential difference between energy states of product and reactant and is a manipulation of the Gibbs free energy reaction ( $G$ ).

Reaction thermodynamics gives the following relationship for Gibbs free energy:

$$\Delta G = \Delta G^\circ + R.T. \ln \prod \frac{aP^n}{aR^m} \quad [6]$$

For a single electrode

$$G = G^\circ + R.T. \ln \frac{a_{\text{Red}}^n}{a_{\text{Ox}}^m} \quad [7]$$

Since the electrode potential regulates the energy of electron exchange, it also controls the current and thus the rate of exchange. Current and potential ( $E$ ) are dependant variables of one another. Where the work done ( $W$ ) is related to the potential difference by:

$$E = \frac{W}{Q} \quad [8]$$

Substituting for ( $Q$ ) and work ( $W$ ) for ( $G$ ), where ( $W$ ) and ( $G$ ) are in joules then Gibbs Free Energy can be re-written as:

$$G = -n.F.E \quad [9]$$

Substituting [7] and [8] with [9] gives the Nernst Equation for an electrode (or half cell):

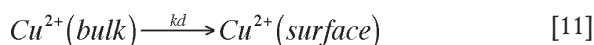
$$E = E^\circ + \frac{R.T}{n.F} \ln \frac{a_{\text{Ox}}^m}{a_{\text{Red}}^n} \quad [10]$$

## Mechanism of electron transfer

For elementary reactions at an electrode the following two mechanisms are primarily responsible for electron transfer.

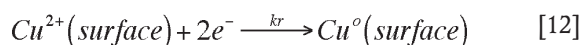
### Mass transfer controlled

(1) Diffusion of copper cations from the bulk phase to where the reaction occurs at the surface.



### Reaction kinetics controlled

(2) Heterogeneous transfer of electrons from the solid electrode to the copper cation at the surface of the electrode.



Further phenomena, coupled chemical reactions, adsorption and formation of phases are reported also to have a role in the electron transfer mechanism. The formation of phases is relevant to the plating of copper on the cathode and involves nucleation and crystal growth steps. Copper atoms diffuse through the solid phase to a location in an appropriate site of the crystal lattice. Adsorption and nucleation steps are considered to be included in the heterogeneous electron transfer reaction rate mechanism.

The overall rate is controlled by the slowest step, which can be either mass transfer or reaction kinetics. For the purposes of copper electrowinning reactor design it is

necessary to determine the rate limiting step to optimize conditions so that capital costs and operating ability are optimized.

## Heterogeneous electron transfer

By analogy with chemical kinetics for a simple first order reaction:



$$\frac{d\text{Mox}}{dt} = kf.Cox \quad [14]$$

Using [5] the current for the forward reaction is given by:

$$ic = n.F. \frac{1}{A} . kf . Cox_{(\text{surface})} \quad [15]$$

And for the reverse reaction:

$$ia = n.F. \frac{1}{A} . krev . Cred_{(\text{surface})} \quad [16]$$

The total current density for the electrode is:

$$i = ic - ia \quad [17]$$

Using Arrhenius and the Activated Complex Theory it can be shown that rate of reaction  $kf$  and  $krev$  takes the forms:

$$kf = ko. \exp\left(\frac{-\alpha.n.F.(E - E^\circ)}{R.T}\right) \quad [18a]$$

and

$$krev = ko. \exp\left(\frac{(1 - \alpha).n.F.(E - E^\circ)}{R.T}\right) \quad [18b]$$

$E$  is the applied potential to the electrode and  $E^\circ$  the formal electrode potential that differs from the standard electrode potential by the activity coefficients. Recalling the Nernst equation:

$$E = E^\circ + \frac{R.T}{n.F} \ln \frac{a_{\text{Ox}}^m}{a_{\text{Red}}^n} \quad [10]$$

The activity is equal to the activity coefficient multiplied by the concentration in the bulk phase. Therefore:

$$E = E^\circ + \frac{R.T}{n.F} \ln \frac{\gamma_{\text{Ox}}^m}{\gamma_{\text{Red}}^n} + \frac{R.T}{n.F} \ln \frac{C_{\text{Ox}}^m(\text{bulk})}{C_{\text{Red}}^n(\text{bulk})} \quad [19]$$

It then follows that:

$$E^\circ = E^\circ + \frac{R.T}{n.F} \ln \frac{\gamma_{\text{Ox}}^m}{\gamma_{\text{Red}}^n} \quad [20]$$

Equation [17] can be written as:

$$i = ic - ia = n.F. \frac{1}{A} . \left( kf . Cox_{(\text{surface})} - krev . Cred_{(\text{surface})} \right) \quad [21]$$

Substituting for  $kf$  and  $krev$  from equation [18] gives the Butler-Volmer equation (B-V):

$$i = n.F. \frac{1}{A} . ko. \left( Cox_{(\text{surface})} . \exp\left[\frac{-\alpha.n.F.(E - E^\circ)}{R.T}\right] - Cred_{(\text{surface})} . \exp\left[\frac{(1 - \alpha).n.F.(E - E^\circ)}{R.T}\right] \right) \quad [22]$$

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This current-potential relationship governs all fast and single step heterogeneous electron transfer reactions.

At equilibrium the exchange current density is:

$$i = i_c = i_a = i_o \quad [23]$$

The overvoltage ( $\eta$ ) can be defined as:

$$\eta = E - E_{eq} \quad [24]$$

where  $E_{eq}$  is the equilibrium voltage,  $E_{eq} = E_o'$  when  $C_{ox(bulk)} = C_{red(bulk)}$  and  $E_o' = E_o$  when activity coefficients are equal to one, see Equation [20]. An expression for the equilibrium potential is derived and shows  $E_{eq}$  to be close to the standard electrode potential and to vary according to changes in temperature and bulk concentrations.

$$E_{eq} = E_o' + \frac{R.T}{n.F} \ln \frac{C_{ox(bulk)}}{R_{red(bulk)}} \quad [25]$$

The Butler-Volmer equation can then be written as follows:

$$i = i_o \cdot \left( \frac{C_{ox(surface)}}{C_{ox(bulk)}} \cdot \exp \left[ \frac{-\alpha.n.F.\eta}{R.T} \right] - \frac{C_{red(surface)}}{C_{red(bulk)}} \cdot \exp \left[ \frac{(1-\alpha).n.F.\eta}{R.T} \right] \right) \quad [26]$$

This relationship shows that exponential changes to the current can result from changes to the potential. Furthermore, current is constrained by the surface to bulk concentration ratios of oxidant and reductant species. The reaction rates do not grow indefinitely as potential is increased and are thus limited by the transport of species to the electrode. A system that is moved from equilibrium for Ox species to be reduced and Red species to be oxidized is described by the B-V equation. This is achieved by setting the potential different from the equilibrium potential; increasing the voltage thus increases the equilibrium difference which increases the current, hence speeding up the Faradaic process.

The maximum current that can be applied to maintain a reaction is known as the diffusion limited current. No matter what the standard rate constant is, if the applied potential is sufficiently large the maximum current will be reached. Assuming an adequate supply of reactants to the reaction surface (the electrode), the rate of reaction is described by the Butler-Volmer Equation. If the applied potential is adequate to maximize the heterogeneous electron transfer reactions, the rate of reaction is then limited by the supply of reactants to the electrode surface and is said to be mass transfer limiting (or controlled).

Assuming that the surface and bulk concentrations are equal (condition of non mass transfer limited), for only large negative or positive overpotentials (only forward or reverse reaction dominant), the B-V equation can be manipulated by taking a Log of both sides of the equation; then resolving for overvoltage gives:

$$\eta = \frac{R.T}{\alpha.n.F} \ln i_o - \frac{R.T}{\alpha.n.F} \ln i \quad [27]$$

And has the general form:

$$\eta = a - b \log i \quad [28]$$

This is recognized as the well-known Tafel equation and is derived from the B-V equation for the specific condition of non mass transfer limiting, equal surface to bulk concen-

trations and dominant forward or reverse reactions. The procedure provides a means of linearizing the relationship between overpotential and current or rate of reaction.

### Mass transport

The movement of species from the bulk solution to the electrode surface occurs via three possible mechanisms:

- Convection (or conveyance), forced or natural described by hydrodynamics or density/temperature differences
- Diffusion described by a gradient in concentrations
- Migration described by a gradient in electrical potential.

Experimental conditions of the electrode reactions are generally chosen to minimize the effects of migration. This is done by providing a large quantity of inert electrolyte that does not interfere with the electrode reaction, leaving only diffusion and convection mechanisms for consideration.

Fick's First Law for one-dimensional diffusion

$$Nox''_{(x,t)} = -D \cdot \frac{dC_{x,t}}{dt} \quad [29]$$

Expanded to include convection (conveyance) and migration is the Nernst-Planck Equation<sup>8</sup>:

$$Nox''_{(x,t)} = -D \cdot \frac{\partial C_{(x,t)}}{\partial t} - \frac{n.F.D.C}{R.T} \cdot \frac{\partial C_{(x,t)}}{\partial x} + C_{(x,t)} \cdot v_{(x,t)} \quad [30]$$

Minimizing the potential gradient using an inert electrolyte reduces the equation to:

$$Nox''_{(x,t)} = -D \cdot \frac{\partial C_{(x,t)}}{\partial t} + C_{(x,t)} \cdot v_{(x,t)} \quad [31]$$

This equation describes the one-dimensional flux of species across the bulk solution to the electrode interface due to the mechanism of conveyance and diffusion.

For a three-dimensional volume it can be extended to:

$$\frac{\partial C_{ox}}{\partial t} = D \cdot \nabla^2 C_{ox} + \dot{r} a_{(reactor volume)} - v_a \cdot \nabla C_{ox} \quad [32]$$

Assuming that at steady state there is no change in concentration with time and that the conveyance inside the diffusion layer is significantly smaller than the diffusion component, Equation [32] becomes:

$$\dot{r} a_{(reactor volume)} = -D \cdot \nabla^2 C_{ox} \quad [33]$$

and by definition of rate of consumption

$$\dot{r}_{ox(reactor volume)} \cdot dV = \frac{dMox}{dt} \quad [34]$$

$$\dot{r}_{ox(reactor volume)} = \frac{dMox}{dt} \cdot \frac{1}{dz \cdot dy} = \frac{dNox''}{dx} \quad [35]$$

The rate of consumption (or generation) is equal to the rate change of concentration difference across the diffusion layer. Using a circulation tank to minimize the change in concentration over two of the three spatial axes we find that:

$$\frac{\partial C_{ox}}{\partial z} \approx 0 \quad [36]$$

and

$$\frac{\partial C_{ox}}{\partial y} \approx 0 \quad [37]$$

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The use of the circulation tank to minimize the change in concentration over the two axes parallel to the electrode surface significantly simplifies the mathematical mass transfer relationship. Also sufficient concentration of ions across the face of the electrode is provided to ensure that the mass transfer and supply of species to the surface of the electrode remains sufficient. If the concentration gradients across the two parallel axes were not minimized, a varying current over the electrode surface would be required to maintain the rate of reaction. The mathematical and practical difficulties of this are self-evident. The resulting mass transfer relationships are the following, and are relevant to one-dimension normal to the electrode surface.

$$\dot{r}_{ox(reactor\ volume)} = \frac{d}{dx} \cdot (Nox'') = -D \cdot \frac{d}{dx} \left( \frac{dCox}{dx} \right) = -D \cdot \frac{d^2 Cox}{dx^2} \quad [38]$$

and:

$$Nox'' = -D \frac{dCox}{dx} \quad [39]$$

Faraday's law:

$$i = \frac{I}{A} = n.F. \cdot \frac{1}{A} \cdot \frac{dM}{dt} \quad [5]$$

where:

$$Nox'' = \frac{1}{A} \cdot \frac{dM}{dt} \quad [40]$$

gives:

$$i = \frac{I}{A} = n.F.Nox'' \quad [41]$$

Substituting Equation [39] into Equation [41] gives:

$$i = n.F. \cdot D \cdot \frac{dCox}{dx} = n.F. \cdot \frac{D}{\delta} \cdot (Cox_{(bulk)} - Cox_{(surface)}) \quad [42]$$

Defining the mass transfer coefficient ( $kd$ ) as:

$$kd = \frac{-D}{(Cox_{(bulk)} - Cox_{(surface)})} \frac{dCox}{dx_{x=0}} \quad [43]$$

then

$$i = n.F.kd.(Cox_{(bulk)} - Cox_{(surface)}) \quad [44]$$

Equation [44] is different from Equation [42] in that using the mass transfer coefficient forces an adequate hydrodynamic treatment of the flow reactor. Equation [42] is widely regarded in the technical literature as the only mass-transfer equation for electrochemical systems. While the difference may be trivial to the diffusion layer mechanism advocate, it is not so from the perspective of good chemical engineering practice; the universal application of heat and mass transfer coefficients provides a more rigorous means of solving a hydrodynamic problem.

### Mass transfer coefficients and diffusion limited current

Two equations that represent the same thing, namely the reaction rate, have been derived. The B-V equation, which describes heterogeneous electron transfer, and Ficks law substituted into Farady's law that describes mass transfer.

Increasing the overpotential up to a point increases the reaction rate. When all species that reach the electrode are oxidized or reduced, the rate of mass transfer of the species to the electrode surface is the rate limiting step for the production of copper. The diffusion limited current is the current above which an increase in potential will not increase the rate of reaction. For that reason the diffusion limited current (DLC) should be determined to optimize the reactor design. In the field, operating reactors are normally run at levels well below the DLC to achieve a good adherent product. This should be considered when determining the actual applied current to the cell.

At the diffusion limited current the surface concentration of species is zero meaning that all surface species are consumed as quickly as they are supplied to the electrode. The DLC equation then becomes:

$$iL = n.F.kd.(Cox_{(bulk)}) \quad [45]$$

Two important observations can be made at this point:

- Increasing the concentration of the bulk reactant increases the DLC. This is a function of the extraction process that was used to remove the copper from the host body and other upgrade processes used before the electrowinning of the copper
- Increasing the mass transfer coefficient increases the DLC. This is a function of the hydrodynamics of the reactor cell and physical properties of the solution in which the electrolyte is present such as temperature, viscosity and other competing ions. The most efficient supply of fresh solution is provided by enhancing the bulk motion. This is easily achieved by stirring or by flowing the solution past the electrode or using other methods to enhance the mass transfer coefficient.

Mass transfer coefficients are usually determined using empirical correlations that are based on test work and made up of dimensionless parameters such as:

Reynolds number:

$$Re = \frac{\nu.L.\rho}{\mu} \quad [46]$$

Schmidt number:

$$Sc = \frac{\mu}{\rho.D} \quad [47]$$

Sherwood number:

$$Sh = \frac{kd.de}{D} \quad [48]$$

Grashof number:

$$Gr = \frac{g.\beta.(Ts - T\infty).L^3}{\nu^2} \quad [49]$$

Prandtl number:

$$Pr = \frac{c_p.\mu}{k} \quad [50]$$

Rayleigh number:

$$Ra = Gr.Pr \quad [51]$$

A number of correlations appear in the literature and for convective mass transfer have the general form:



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$$Sh = C.Re^n.Sc^m.\left(\frac{de}{L}\right)^p \quad [52]$$

For parallel plate electrodes of finite width and fully developed laminar flow (only applicable if the maximum electrode length is less than 35 times the equivalent diameter.  $Re < 2000$ )<sup>3</sup>:

$$Sh = 2.54.Re^{0.3}.Sc^{0.3}.\left(\frac{de}{L}\right)^{0.3} \quad [53]$$

For parallel plate electrodes of infinite width and fully developed laminar flow (only applicable if the maximum electrode length is less than 35 times the equivalent diameter.  $Re < 2000$ )<sup>3,15</sup>:

$$Sh = 1.85.Re^{0.33}.Sc^{0.33}.\left(\frac{de}{L}\right)^{0.33} \quad [54]$$

Natural convection nearly always occurs at an electrode even when forced convection takes place. Natural convection dominates forced convection at very low flow cell flow rates. The upward flow component of natural convection may oppose forced convection and results in very low mass transfer coefficients. The following correlations are concerned with comparing natural convection to forced convection. In stationary solutions the effects of natural convection will be the dominant mode of mass transport.

By analogy with heat transfer<sup>4</sup>:

$$Nu = 0.046.Ra^{0.333} \quad [55]$$

$$\frac{Nu}{Pr^n} = \frac{Sh}{Sc^n} \quad [56]$$

$$Le = \frac{Sc}{Pr} \quad [57]$$

$$\frac{k}{kd} = \rho.c_p.Le^{(1-n)} \quad [58]$$

For mass transfer by natural convection<sup>1</sup>:

$$Sh = 0.902.\left(\frac{Gr.Sc}{4.(0.861 + Sc)}\right)^{0.25} \quad [59]$$

Equations [53], [54], [55] and [59] are solved for the mass transfer coefficient ( $kd$ ). Using data from the world EW copper survey<sup>16</sup> values for  $kd$  and the DLC were calculated for 22 operating plants. The plants chosen represent a wide variety of plant operating conditions. Table I compares the four different correlations' mass transfer coefficients for copper electrowinning plants.

An unveiled warning to all chemical engineers is that any mass transfer coefficient correlation must be used with caution as the accuracies could easily be 50% off, as practical as possible mass transfer coefficients should try to be determined by test work.

The mass transfer coefficients compare well with each other for the different calculation methods over a wide variety of plant operating conditions.

Table II compares the DLCs calculated using the four different methods to each other and to the Faradaic current requirement.

The table shows that the DLCs calculated by the four different methods compare well with the Faradaic current density. The Faradaic current density includes the current efficiencies reported for the process plants.

The DLC should always be greater than the Faradaic current for a plant to ensure that a good adherent copper cathode is produced and that the hydrodynamics of the system are sufficient to ensure production is not limited by inadequate flow conditions.

It is important to note that the DLCs reported here are based entirely on the correlations used and not on any test work done by the authors. This method is used to demonstrate the phenomenon of determining the DLC with common literature information, as well as the reasonably comparative results obtained from the different correlations. It can be seen that some Faradaic currents are greater than

Table I

## Calculated $kd$ (m/s) for 22 operating Cu EW plants

		$kd^3$ m/s	$kd^{15,3}$ m/s	$kd^4$ m/s	$kd^1$ m/s
1	Nullabar M	2.09E-06	2.04E-06	1.76E-06	2.18E-06
2	Pasimco M	1.73E-06	1.68E-06	1.76E-06	2.11E-06
3	Girilambone Cu	2.08E-06	2.04E-06	1.76E-06	2.19E-06
4	CM Cerro Colorado	2.31E-06	2.28E-06	1.76E-06	2.18E-06
5	CM Quetrada Blanca	2.03E-06	1.98E-06	1.76E-06	2.27E-06
6	Minera El Abra	2.20E-06	2.16E-06	1.76E-06	2.20E-06
7	Codelco Chile Div	2.12E-06	2.09E-06	1.76E-06	2.18E-06
8	Empresa Minera	2.05E-06	2.02E-06	1.76E-06	2.18E-06
9	CM Zaldivar	2.18E-06	2.17E-06	1.76E-06	2.20E-06
10	Mantos Blancos	2.36E-06	2.36E-06	1.76E-06	2.11E-06
11	CM Carmen Andacolla	2.24E-06	2.21E-06	1.76E-06	2.21E-06
12	Hellenic Copper Mines	2.13E-06	2.11E-06	1.76E-06	2.18E-06
13	Nicico sarchesh	2.02E-06	1.98E-06	1.76E-06	2.12E-06
14	Mexicana de corbe	2.10E-06	2.07E-06	1.76E-06	2.05E-06
15	Miccl main plant	2.05E-06	2.01E-06	1.76E-06	2.17E-06
16	Southern Peru limited	2.22E-06	2.19E-06	1.76E-06	2.16E-06
17	Silver Bell Mining LLC	2.12E-06	2.08E-06	1.76E-06	2.22E-06
18	BHPB Copper San Manuel	1.95E-06	1.90E-06	1.76E-06	2.26E-06
19	Phelps Dodge Morenci S-side	1.79E-06	1.74E-06	1.75E-06	2.14E-06
20	Phelps Dodge Morenci Central	1.67E-06	1.61E-06	1.75E-06	2.16E-06
21	Phelps Dodge Morenci Stargo	1.85E-06	1.80E-06	1.75E-06	2.14E-06
22	First Quantum Bwana Mkubwa	1.94E-06	1.88E-06	1.75E-06	2.13E-06

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Table II

Calculated DLC (A/m<sup>2</sup>) for 22 operating Cu EW plants

		$i^3$ A/m <sup>2</sup>	$i^{15,3}$ A/m <sup>2</sup>	$i^4$ A/m <sup>2</sup>	$i^1$ A/m <sup>2</sup>	$i$ Faradaic A/m <sup>2</sup>
1	Nullabar M	240	235	203	250	226
2	Pasimco M	193	188	197	236	239
3	Girilambone Cu	246	241	209	260	321
4	CM Cerro Colorado	266	263	203	251	256
5	CM Quetrada Blanca	278	271	241	312	246
6	Minera El Abra	263	259	211	264	233
7	Codelco Chile Div	260	257	216	267	234
8	Empresa Minera	246	242	211	261	236
9	CM Zaldivar	285	283	230	287	244
10	Mantos Blancos	254	253	189	227	262
11	CM Carmen Andacolla	275	271	215	271	286
12	Hellenic Copper Mines	260	256	214	265	272
13	Nicico Sarchesh	213	209	185	224	231
14	Mexicana de corbe	207	204	173	202	246
15	Miccl main plant	236	232	202	249	240
16	Southern Peru limited	253	250	201	247	266
17	Silver Bell Mining LLC	268	264	223	281	316
18	BHPB Copper San Manuel	258	251	233	299	231
19	Phelps Dodge Morenci S-side	205	199	201	245	234
20	Phelps Dodge Morenci Central	197	190	208	255	251
21	Phelps Dodge Morenci Stargo	210	205	200	243	239
22	First Quantum Bwana Mkubwa	205	199	186	226	196

the DLCs calculated this does not mean that the plant is incapable of adequate production but only means that the correlation may not be representative of the exact conditions in that plant.

The correlations do not take into account gas evolving electrodes of which all copper electrowinning anodes are. this omission in the correlations may underestimate the DLC significantly. This gas evolution can have a strong influence on the mass transfer of ions due to the forced convection effects inside the parallel plate arrangement.

## Overall electrode process

The earlier sections dealt with the two mechanisms of electron transfer for an electrode. This section deals with an overall process of both heterogeneous electron transfer and mass transfer that is relevant to copper electrowinning in practice.

The B-V equation that describes the heterogeneous electron transfer in terms of current and overpotential is:

$$i = i_o \left( \frac{C_{ox(surface)}}{C_{ox(bulk)}} \cdot \exp \left[ \frac{-\alpha \cdot n \cdot F \cdot \eta}{RT} \right] - \frac{C_{red(surface)}}{C_{red(bulk)}} \cdot \exp \left[ \frac{(1-\alpha) \cdot n \cdot F \cdot \eta}{RT} \right] \right) \quad [26]$$

The current density described by Fick's and Faraday's law for mass transfer is:

$$i = n \cdot F \cdot kd \cdot (C_{ox(bulk)} - C_{ox(surface)}) \quad [44]$$

and

$$iL = n \cdot F \cdot kd \cdot (C_{ox(bulk)}) \quad [45]$$

Substituting and resolving for concentrations gives:

$$\frac{C_{ox(bulk)}}{C_{ox(surface)}} = \frac{iL}{iL - i} \quad [60]$$

For copper reduction on an electrode the last term of the B-V equation can be neglected to give:

$$i = i_o \cdot \left( \frac{C_{ox(surface)}}{C_{ox(bulk)}} \cdot \exp \left[ \frac{-\alpha \cdot n \cdot F \cdot \eta}{RT} \right] \right) \quad [61]$$

Taking the log of both sides of the equation and separating for overpotential gives:

$$\eta = \frac{RT}{\alpha \cdot n \cdot F} \cdot \ln i_o - \frac{RT}{\alpha \cdot n \cdot F} \cdot \ln i + \frac{RT}{\alpha \cdot n \cdot F} \cdot \ln \left( \frac{C_{ox(surface)}}{C_{ox(bulk)}} \right) \quad [62]$$

Substituting for the concentration ratio gives:

$$\eta = \frac{RT}{\alpha \cdot n \cdot F} \cdot \ln i_o - \frac{RT}{\alpha \cdot n \cdot F} \cdot \ln i - \frac{RT}{\alpha \cdot n \cdot F} \cdot \ln \left( \frac{iL}{iL - i} \right) \quad [63]$$

This equation describes overpotential, applied current and DLC in a single equation.

## Example of a fictional cell reactor

A fictional cell reactor is developed to show the relationship of overpotential to current for varying conditions of concentration and flow in the cell. High level differences between the scenarios are:

- Cell 1, low flow rate
- Cell 2, high flow rate
- Cell 3, low flow rate, high copper concentration
- Cell 4, high flow rate, high copper concentration.

Each cell has the same physical characteristics and features a cathode plating area of 1 m × 1 m. The physical properties of the electrolyte are kept constant except for the concentrations and flow rates in the cells. Table III also gives the DLC results for various correlations.

- The forced convection correlation of Equation [53] and Equation [54] described by the hydrodynamic characteristics of the cell are strongly influenced by the change in flow rate. Compared to the natural convection correlations of Equation [55] and Equation [59] that,

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Table III

Operating conditions for the four scenarios compared

		Cell 1	Cell 2	Cell 3	Cell 4
Fictional cell design	units	Lo MT	Hi MT	Lo MT Hi Cu	Hi MT Hi Cu
Number of cathodes	no off	48	48	48	48
Number of anodes	no off	49	49	49	49
Cell spacing A-C	m	0.045	0.045	0.045	0.045
Cell inlet concentration	g/l Cu <sup>2+</sup>	40.00	35.77	38.75	36.07
Cell outlet concentration	g/l Cu <sup>2+</sup>	35	35	35	35
Cell volumetric flow rate	m <sup>3</sup> /h	2.50	16.25	5.00	17.50
Copper production rate	kg/h	12.5	12.5	18.75	18.75
Temperature	°C	65	65	65	65
Density	kg/m <sup>3</sup>	1216	1216	1216	1216
Diffusion coefficient	m <sup>2</sup> /s	1.95E-09	1.95E-09	1.95E-09	1.95E-09
Current efficiency	%	85	85	85	85
iL <sup>3</sup>	A/m <sup>2</sup>	191	300	228	309
iL <sup>15,3</sup>	A/m <sup>2</sup>	182	301	221	311
iL <sup>4</sup>	A/m <sup>2</sup>	273	244	264	246
iL <sup>1</sup>	A/m <sup>2</sup>	272	237	262	239
Faradaic current density	A/m <sup>2</sup>	129	129	194	194

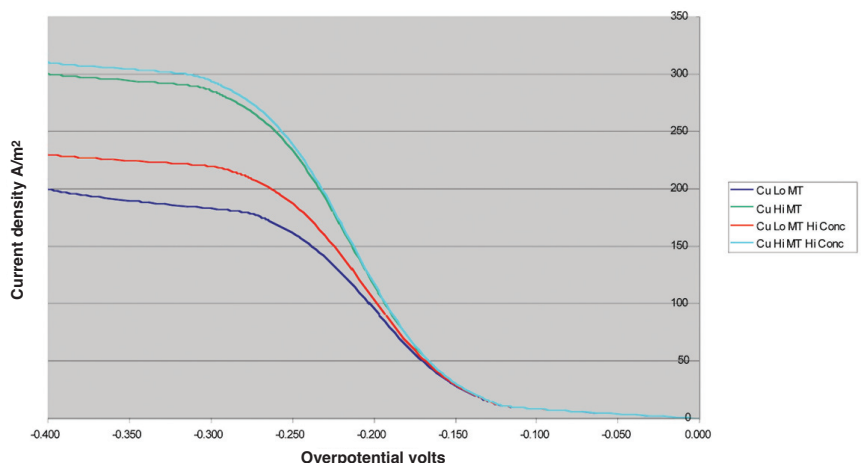


Figure 1—Voltammograms for fictional cells

as expected, are not influenced by the changing flow rate as these correlations do not take into account the flow system but only density difference along the plate surface

- The graph of overpotential versus current is called a voltammogram. For the development of the voltammogram the correlation from Equation [53] is used as this DLC changes with concentration and flow rate which is phenomenologically correct. Although it may not fully account for all mass transfer driving forces such as the gas evolution at the anode, this correlation demonstrates that reactor design is strongly influenced by flow rate and concentrations.

The DLC<sup>3</sup> for each cell is used to plot the voltammogram on overpotential versus current density graph. The exchange current density  $i_0$  is taken from<sup>17</sup> as

$$i_0 = 0.2 \frac{A}{m^2} \quad [64]$$

Figure 1 compares the voltammograms for the four fictional cells.

This graph shows the following conclusions to be drawn:

- Increasing the flow rate at the same copper production rate results in an increase of DLC from 190 A/m<sup>2</sup> to 300 A/m<sup>2</sup>, 'Cu Lo MT' to 'Cu Hi MT'
- Increasing the copper concentration and flow rate slightly results in increasing the DLC from 190 A/m<sup>2</sup> to 230 A/m<sup>2</sup>, 'Cu Lo MT' to 'Cu Lo MT Hi Conc'
- Increasing the copper concentration and flow rate significantly has the largest effect of increasing the DLC, from 190 A/m<sup>2</sup> to 310 A/m<sup>2</sup>, 'Cu Lo MT' to 'Cu Hi MT Hi Conc'.

Although the DLC equations used to determine this voltammogram are based on literature work, the functionality remains correct. In order to optimize the cell design in terms of capital cost for the same production rate, the DLC must be as high as possible so that the Faradaic current density is as high as possible (limited to producing a good product). These conditions will allow for the same transformer/rectifier arrangement to:

- Minimize installed electrowinning total plating area

# Copper electrowinning: theoretical and practical design

- Minimize installed electrowinning cell size
- Minimize installed electrowinning cell house structure and civil footprint.

## Methods to increase current density

Increased DLCs can be achieved by a number of different methods described in an excellent paper on the subject<sup>10</sup>. Three main ways to increase the current density are suggested:

- Optimizing the cell design
  - EMEW cell<sup>13</sup>
  - Continental copper and steel (CCS) cell<sup>11</sup>
  - Increased flow rate pattern and distribution in standard cell
- Employing various types of forced convection
  - Air sparging
  - Ultrasonic agitation
- Periodic current reversal.

The EMEW cell is a recent design used to produce copper powder and circular plate at high flow rates and high current densities. The CCS cell is a redundant design that used nozzles placed at the cathode face to improve flow patterns.

The present paper does not discuss the various types of improvements that can be made but does note that significant increases in current density can be obtained by using the methods listed above. Table III compares operating conditions that produce a stable adherent pure copper product at vastly increased current densities. The table is based on information from reference<sup>10</sup> as well as other sources.

The reported figures for the various techniques are significantly greater than standard practice and design currently allows for. There are negative effects at these current densities such as:

- Increased anode wear
- Acid mist control
- Corrosion of suspension bars.

## Cell potential

The total voltage across the cell can be divided into three components:

- The reversible decomposition potentials ( $V_{\min}$ )
- The activation and concentration overpotentials of the electrodes ( $\eta_a$ ) ( $\eta_c$ ).
- The potential drop due to ohmic resistance of the electrolyte and the electrical contacts ( $V_{ohm}$ ).

$$V = V_{\min} + |\eta_a| + |\eta_c| + V_{ohm} \quad [65]$$

Table IV

### Comparison of current density (A/m<sup>2</sup>) operating conditions of different cell types

Type	Reported current densities A/m <sup>2</sup>	
	Low	High
Traditional cell <sup>3,6,10,15,16</sup>	110	350
EMEW cell <sup>12,13</sup>	250	600
CSS cell <sup>11</sup>	430	1000
Air sparging <sup>10</sup>	1000	3000
Ultrasonic agitation <sup>10</sup>	3300	10500
Periodic current reversal <sup>10</sup>	430	---

The reversible decomposition potential is:

$$V_{\min} = V_a - (-V_c) \quad [66]$$

This is the difference between the two standard reduction potentials for the species being oxidized and reduced and is the minimum voltage required at standard conditions.

The overpotential due to potential and concentration has been discussed previously and is represented by the modified B-V equation as:

$$\eta = \frac{R.T}{\alpha.n.F} \cdot \ln i_0 - \frac{R.T}{\alpha.n.F} \cdot \ln i - \frac{R.T}{\alpha.n.F} \cdot \ln \left( \frac{iL}{iL - i} \right) \quad [63]$$

and for no concentration overpotential influences then

$$\eta = a - b \log i \quad [28]$$

The ohmic resistance due to the solution and the contacts are:

$$V_{ohm} = V_{IR} + V_{contacts} \quad [67]$$

by Ohm's law for a current flowing between the solution and an electrode. The relationship between current drop and potential drop in an electrical conductor is<sup>5</sup>:

$$i = -\kappa \cdot \left( \frac{\partial \phi_s}{\partial n} \right)_{n=0} \quad [68]$$

For current density in one direction only (parallel plates), Ohm's law reduces to:

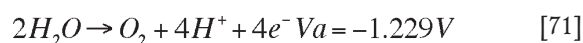
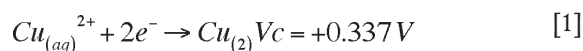
$$V_{IR} = i \cdot \frac{L}{\kappa} \quad [69]$$

where the specific conductivity is a function of concentration and ionic mobility of the form<sup>5</sup>

$$\kappa = F^2 \cdot \sum n_i^2 \cdot u_i \cdot C_i \quad [70]$$

The solution resistance and required potential difference are then a function of the interelectrode gap, the ionic mobility, the concentration of the species in solution and the current density applied to the solution.

Then for the electrowinning of copper from acid sulphate matrix:



$$V_{\min} = -1.229 + 0.337 = -0.892 V \quad [72]$$

Operated at a DLC of 300 A/m<sup>2</sup> and an applied current density of 200 A/m<sup>2</sup> (Cell 4 conditions) the cathodic overpotential is:

$$\eta_c = -0.225 V \quad [73]$$

For the production of oxygen at the anode, excluding the acid concentration overpotential, the Tafel equation is<sup>3</sup>

$$\eta_a = 0.5 + 0.12 \log i \quad [74]$$

This gives:

$$\eta_a = 0.543 V \quad [75]$$

The solution and contact resistance can be taken as <0.6 V combined<sup>6</sup>.

Then the required cell voltage to obtain a current flow to produce copper cathode from solution is

$$V = 0.892 + 0.225 + 0.543 + 0.6 = 2.26 V \quad [76]$$



## Copper electrowinning: theoretical and practical design

Copper electrowinning cell voltages are well standardized at ~2-2.3 V per cell.

### Current efficiencies

The current efficiency is the ratio of the current producing the copper to the total current applied to the cell. It is normally quoted in percentages. Practically it is determined by the amount of copper produced divided by the amount of current applied to the system for a theoretical amount of copper.

$$\varepsilon = \frac{\left( \frac{dM_{Cu}}{dt} \right)}{\left( I \cdot \frac{t}{n.F} \right)} \quad [77]$$

The efficiency is strongly dependent on additional side reactions that occur; for the electrowinning of copper the decomposition of water lowers the current efficiency. However, the single greatest effect is the presence of iron in the solution. The cyclic oxidation and reduction of dissolved iron can significantly reduce the efficiency of an operation. Iron can be removed by a number of methods that include.

- Solution precipitation
- Prior reduction of iron (III) by SO<sub>2</sub> or copper metal
- Increasing the bleed stream volume
- Use of a diaphragm cell.

Current efficiencies for direct electrowinning operations can be as low as 65% whereas efficiencies for post SX electrowinning can be as high as 95%.

### Part 2: Practical considerations

The following is based on a case study of the Ruashi BMR designed by TWP Matomo Process Plant.

#### Production rates

Production rates are usually specified by the client, depending on the mass balance and the environment for which the electrowinning is to be designed. Design conditions will normally be in the region of specified rate plus 10%; this excludes availability.

#### Availability

Mechanical availability depends on the following factors:

- Site conditions and location. The Ruashi BMR is located in Lubumbashi, DRC, and as such, consideration was given to have stand-by units for all key mechanical equipment. Operation within South Africa would not necessarily require the same design. Dual availability design was included for cellhouse circulation pumps, feed to and return from pumps servicing the cellhouse, overhead cranes, stripping machines (for which an additional allowance was made to allow manual stripping of cathodes in a specifically designated area in case of equipment breakdown). Both the loaded electrolyte pond feeding the cellhouse as well as the spent electrolyte pond returning spent electrolyte solution to the solvent extraction circuit is of split design, providing for maintenance on the pond linings without having to shut down the plant
- Maintenance programmes proposed or in place at the operation depend on site management in terms of proactive maintenance, service schedules, etc. This cannot

always be quantified, especially for new operations; however, in general, larger established companies normally have a better maintenance system in place than small companies

- Education and experience level of both maintenance and operational personnel. Consider geographic location of the area, whether there are existing operations from where personnel could be sourced, language barriers, culture of work, political stability.

### Current density

Depending on the type of operation, current densities can vary between 200 and up to about 375 A/m<sup>2</sup>. Operations where solvent extraction precedes electrowinning normally produce cathodes with a good surface quality at higher current densities than direct electrowinning operations. Furthermore, the clarity of the feed solution needs to be taken into account. The Ruashi design includes multimedia coalescing filters for the removal of both solids as well as organics from the Cu feed solution before the solution reports to the cellhouse. Process engineers are in general quite comfortable operating in the region of 250 to 300 A/m<sup>2</sup> when SX and multimedia filters are employed.

It is also advisable to consult the vendors of the rectifiers. There are standard designs for the transformer-rectifier pairs, ranging in size from small up to 30 kA. For the Ruashi design, two sets of 30 kA were purchased to satisfy the design requirement of 60 kA total DC supply to the electrowinning cells. Depending on the rectifier supply, the cell design can be modified to suit.

### Cathode centre to centre spacing

Design current density is also dependent on electrode spacing. The minimum spacing recommended for Cu electrowinning operations for cathode centre to cathode centre is 95 mm. Below this the risk of shorts due to electrode alignment and nodular growths is considered to be unacceptably high.

### Cathode quality

This is normally specified by the client. Within the cellhouse, there are very few variables that influence cathode quality; it is normally a function of the preceding purification steps.

### Sampling specification and procedure

Sampling on site is normally done on site for in-house quality control purposes only. The client usually sells his product through a third party, who will be responsible for sample analysis. Some mining houses have accredited laboratories; in this case, the laboratory analyses samples received from the plant. Two commonly used methods to obtain a sample are either to drill holes in randomly selected samples on randomly selected locations of the cathode. The drillings are then sent for analysis in the accredited laboratory. The second method follows the same procedure; however, instead of drillings, a manually operated punching machine is used. It has to be taken into consideration that normal drill bits are not used for drilling samples, since iron contamination of the samples frequently occurs. Regarding the selection of cathodes in a group to be analysed and the location on each cathode, a standard procedure was

## Copper electrowinning: theoretical and practical design

published by the ISO organization. The standard title is 'ISO 7156 – Refined Nickel – Sampling'. No procedure for copper sampling could be found; however, the same principles for Cu sampling as for Ni sampling are assumed to be applicable.

### Number of cells

This depends on a number of factors, including cell dimensions, real estate available for the cellhouse building, applied current density, production rate, DLC, and current efficiency. There is normally an equal number of cells, making the busbar arrangement practical. Cells in a leach-solvent extraction-electrowinning design should be split into scavenger and production cells to limit organic contamination of cathodes in case of organic carry-overs occurring at the solvent extraction purification plant. Scavenger cells are then designed to maintain the same cathode face velocity as for the production/commercial cells of approximately  $0.08\text{m}^3/\text{h}/\text{m}^2$  cathode surface, the difference being that there is a once-off pass of electrolyte through these cells. The scavenger cells then produce the potentially poor surface quality cathode by burning off any organic substances, before the bulk production of cathodes in the commercial cells. For Ruashi, the design accommodated 24 scavenger cells, which constituted exactly one bank of cells. This design facilitated an easy piping arrangement of feed and overflow to the cells.

### Cellhouse layout

Practical considerations to be considered include optimizing availability and maintaining flexibility inside the cellhouse. For Ruashi, the cellhouse was split into two sides, each containing two banks of 24 cells. This configuration allowed the two stripping machines to be placed in the middle of the cellhouse, minimizing travel time for the cranes harvesting the cathodes and returning blank cathodes to the cells. Furthermore, it allows one-half of the cells to be shorted out with relatively little effort, which came in handy during the commissioning of the cellhouse. The connecting busbar from the end of the cellhouse was connected to the centre of the cellhouse, allowing a ramp-up stage of electrowinning on the one side, while construction was still going on the other side of the cellhouse.

The distance between the end of the cell and the supporting structure of the cellhouse has to be taken into consideration in order to minimize the possibility of electrical

accidents. A distance of at least 2 to 3 metres is recommended. The same applies to the distance between the cells comprising one bank and the opposite bank of cells (the 'middle' of the cellhouse walkway).

Feed valves to the individual cells should be practically located in order to allow easy operation of these valves, without interfering too much with the harvesting procedure. For Ruashi, the feed valves were located on top of the cells in the middle of the cellhouse walkway.



Figure 3—Showing intercell busbar and lead anode

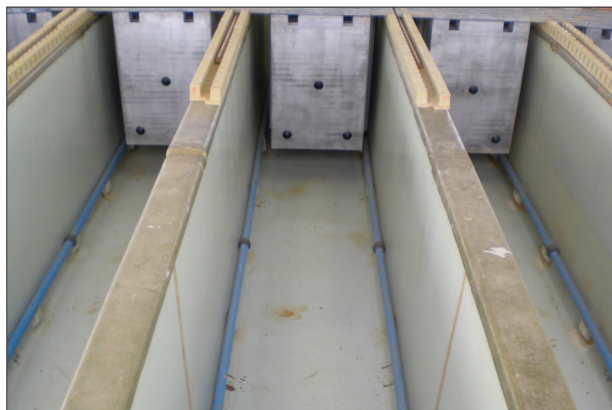


Figure 4—Showing internal feed pipe arrangement



Figure 2—Cellhouse layouts showing access platform, feed pipes



Figure 5—Showing cathode bail removing four cathodes



## Copper electrowinning: theoretical and practical design

Walkways need to be constructed from non-conductive material. Two options are available, the one being wooden walkways, of which a high grade knot-free pine is considered the most feasible option. Wood is then also treated with CCA (copper/chrome/arsenic). The second option is the use of FRP grating. This is much more expensive, but the operating cost is much lower. Certainly. For the areas close to the liquid, FRP will have to take preference, since the timber will not last in this environment. For Ruashi, the majority of the walkways consist of CCA treated timber, with some FRP inserts at the two ends of the cell to allow for visual inspection of overflows.

### Piping layout

For practicality, the cell feed inlet pipes all run along the centre of the cellhouse, allowing for only two feed manifolds to feed the entire cellhouse, that is, both the east and the west banks. The feed manifolds enter the cellhouse at the electrical neutral point in case of the production cells, and enters in the middle of the cellhouse for the scavenger cells. This was to accommodate piping where limited space was available between the two banks of cells. Ideally, the scavenger cells' feed manifold would also have entered the cellhouse at the electrical neutral point to minimize stray currents. Cell drain points were also located in the centre of the building, thus allowing the civil slope of the floor to act as a run-off trench for spillages. Spillages are thus mainly confined to only the centre of the cellhouse, minimizing acidic attack of the civil structures to only the centre of the building.

### Cell elevation

In order to facilitate the gravity overflow of cells to the circulation tank, cells need to be elevated of the ground. When elevation is already a necessity, it is then useful to elevate the cells high enough to accommodate access for personnel to inspect the civil structures from time to time, especially since the cellhouse is such a corrosive environment. Additionally, floor space underneath the cells can then also be used as storage space for cell furniture. The Ruashi Cells were lifted approximately 1.6 m of the ground. Even so, the terrace level of the tankfarm had to be lowered to allow overflow into the circulation tank. Additionally, the circulation tank was designed low with a high floor space (3.5 m high by 12.5 m diameter) to further accommodate gravity feed into the tank.

### Cell potential and current efficiency

Cell potential is a function of the respective half-reaction potentials, losses through electrolyte, busbars and competing reactions. It is normally in the range of 1.9V to 2.3V, lower for the purer Leach-SX-EW operations than for the direct electrowinning operations. Current efficiency for direct electrowinning operations can be as low as 65%, and for leach-SX-EW operations up to about 93%. It depends on the concentration of Fe in the feed solution, as well as proper housekeeping to ensure good electrical contact between electrode hanger bars and the triangular busbars.

### Cathode face velocity

A number ranging between 0.05 and 0.1 m<sup>3</sup>/h/m<sup>2</sup> of cathode surface area available for plating. It influences the surface quality of the cathode by breaking down the diffusion layer,

but too high a face velocity can cause 'flushing' of the cathode surface area, creating an area of no plating where the feed is introduced into the cells. For Cu electrowinning operations, a face velocity of 0.08 is normally employed. The cathode face velocity will then determine the flow rate per cell, and thus the internal recycle required inside the cellhouse.

### Feed and spent tenors

The leach and solvent extraction processes will determine the copper and acid tenors of the feed to the cellhouse. For leach-SX-EW operations, feed tenors of Cu can go as low as 25 g/l Cu, depending on the applied current density, which will have to be reduced as the Cu tenor is reduced. The sulphuric acid tenor of the feed solution is a function of the stripping process inside SX, and that of the spent solution is a function of the rate of copper production, where a stoichiometric balance exists of 1.98 g of acid produced for every gram of copper plated.

The Ruashi EW operation was started up with unpurified primary leach solution at a pH of ~1.8 and a copper tenor of 24 g/l, the resultant cathode had a very good surface quality, albeit at an applied current density of only 75 A/m<sup>2</sup>. Raising the current density to 110 A/m<sup>2</sup> resulted in the formation of nodules, but this was attributed to no control over the flow rate (cathode face velocity) to the cells. Since the flow rate



Figure 6—Overflow launders between cells



Figure 7—Copper busbars

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Figure 8—Cathode stripping machine

was increased, good surface quality cathodes are achieved at current densities of  $100 \text{ A/m}^2$  and Cu tenors of  $\sim 27 \text{ g/t}$ . Ruashi design caters for a Cu feed tenor of  $50 \text{ g/t}$  and a cellhouse bite of  $5 \text{ g/t}$  Cu, at these operating conditions; the design applied current density of  $275 \text{ A/m}^2$  is expected to deliver good surface quality cathodes. This has not yet been achieved at Ruashi, due to the SX section still being constructed and the front end of the plant still being commissioned.

### Cathode harvesting

The cathode harvesting cycle was designed so as to accommodate a deposit thickness of  $\sim 5 \text{ mm}$ . The thickness depends on the capability of the stripping machines to separate the copper from the blanks, for which the stripping machine suppliers have to be consulted. Furthermore, the longer a cathode is allowed to plate in a cell, the higher the risk of shorting becomes due to the exponential nature of nodular growths inside the cell. A harvesting cycle of more than eight days is not recommended, but this again depends on the applied current density (rate of plating).

### Busbar design

In order to minimize heat losses through the busbars, the current density through the busbars has to be limited. Conservative clients prefer not to go above  $1 \text{ A/m}^2$ , while design companies are normally quite comfortable designing busbars at  $1.2 \text{ A/m}^2$ . Of importance is to run parallel busbars with a gap between them so as to allow heat reduction through air cooling. The Ruashi busbar designs for the main busbars were 6 busbars, each of size  $450 \text{ mm} \times 20 \text{ mm}$ , separated by a  $20 \text{ mm}$  gap between each busbar. This fulfilled the  $1.2 \text{ A/mm}^2$  requirement for the total design current of  $61 \text{ kA}$ .

### Intercell busbar design

Two options are available for the design of intercell busbars. A conventional dog bone type of designs was previously employed and is still preferred by some clients. It is, however, much more expensive than triangular busbars, due to the larger amount of copper needed. Triangular busbars are a more viable option, provided that proper consideration is given to the design and layout of contact points between hanger bar (cathode and anode) and triangular busbar. It

becomes even more critical when the design has to cater for cathodes that are symmetrical to cater for the  $180^\circ$  rotation during the stripping operation. Furthermore, due consideration needs to be given to the different elevations between cathode and anode hanger bars on the cell to allow for shorting out of the cell with a shorting frame. Although this can be avoided if a bull-horn anode hanger bar design is employed, it is unnecessary, and a straight anode hanger bar design allows for the maintenance of anodes using the same bailer as is used for cathode harvesting.

Cathode design to cater for hooking by the bailer can be through either cut-outs from the cathode surface above the liquid level, or through the attachment of stainless steel fish eyes to the hanger bars. Fish eyes are economically more feasible since they require less work by the suppliers. It then implies that cut-outs are made from the anode surfaces to accommodate the use of one bailer size to both harvest cathodes as well as do anode maintenance.

### Dimension and number of electrodes per cell

Cathode size is selected to accommodate industry standards, where shipping of cathodes in containers as well as furnace openings in the production industry have to be taken into consideration. Client liaison will normally give a good guideline as to cathode sizing. Anodes are designed at least  $30 \text{ mm}$  bigger than cathodes on both the width and the height (wetted dimensions). This is to ensure that copper plating does not occur around the sides of the cathode. There will always be one more anode than cathode per cell, and depending on the harvesting design, either every second or every third cathode is harvested per pull. Using the standard design of every third cathode, cathodes per cell then have to equal multiples of three.

### Anode composition and type

New electrowinning operations at the moment almost exclusively employ cold-rolled lead anodes, since they yields better dimensional stability. Standard additions to the lead anode includes a fraction of calcium ( $0.05$  to  $0.08\%$ ) and tin ( $1.2$  to  $1.5\%$ ). Anode life expectancy is in the order of  $7$  to  $9$  years.

### Electrode furniture

Anode buttons from non-conductive PVC material are readily available on the market. Three to five anode buttons are located to the anode, in the two bottom corners of the anode, one in the centre of the anode, and an optional two at the two top corners of the anode. The anode buttons prevent shorts between cathode and anode. Edge strips are located to the edges of the stainless steel cathodes to ensure that the two sides of the cathode are not intergrown. Various types of edge strips are available. Ruashi and various EW operations in Zambia employ the Rehau 'cross-slot' configuration of edge strips. It is important to design the edge strips long enough so that they end well above the liquid level of the cell, since liquid between the edge strips and the cathode will cause metal plating and thus damage to the edge strips.

### Electrowinning cells

Continuous improvement to the polymer concrete industry has led to the almost exclusive use of polymer concrete as the material of construction for electrowinning cells. There are



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two main suppliers in Southern Africa, CSI and PCI. Product quality from both suppliers is acceptable and the copper industry in Zambia is split almost equally between the two suppliers. The polymer concrete cells contain a fiberglass lining, which is part of the moulding/casting process. This further protects the concrete from acid attack. Other operations use lead linings or normal concrete with fibreglass lining moulds to house the electrowinning process. This is not feasible for new operations.

### **Cathode stripping**

Various suppliers can custom design stripping machines for the electrowinning operation. Options include fully automatic machines, semi-automatic machines and options for water spray rinsing booths. Design considerations should include simplicity if the machine is used in remote locations, availability of spares, stripping rate and capital expenditure. Ruashi employs two semi-automatic Styria stripping machines; this gives flexibility in case of a breakdown as well as ease of maintenance.

### **Plating agents**

Various smoothing agents are commercially available, ranging from glues to guar to synthetic products. It is best to test these in research facilities such as Mintek to determine the effect of the smoothing agent on current efficiency and surface quality of the cathode. Dosage rates range from 150 to 400 g of smoothing agent per ton of Cu produced. Chloride levels inside the cellhouse should be kept below 30 ppm to ensure the stainless steel cathodes are not corroded. Additional points can be at the circulation tank for the commercial cells and inline at the Feed manifold for the scavenger cells. Care should be taken to design the scavenger system so as not to have reverse flow of electrolyte back into the smoothing agent supply tank; as such a non-return valve is recommended in line for the scavenger cells' smoothing agent supply.

### **Acid mist management**

Hollow polypropylene balls are commonly employed in cellhouses. Additionally, synthetic foaming agents are available; the effect of these on the solvent extraction should be considered. Designing a cellhouse with open sides helps with natural ventilation, and if CAPEX considerations are not of primary importance, extraction fans can be employed to minimize acid mist.

### **Temperature management**

Feed to the cellhouse could be heated using heat exchangers; the optimum temperature is considered to be in the range of 45 to 55°C for optimum electrolyte conductivity. Due to heat generation inside the cellhouse, a cooling heat exchanger is then required for both circulating electrolyte and spent electrolyte. Solvent extraction plants, which use spent electrolyte for stripping, need to be maintained below 40°C to prevent the degeneration of the organic phase.

### **Inventories**

For optimum plant availability, sufficient storage capacity is required. Ruashi employs split ponds with double liners and leak detection systems. In designing the storage pond systems, consideration need to be given to the type of pumps to be used. Options available include self-priming pumps (Sulzer) or conventional pumps with priming tanks. The self-

priming pumps employed at Ruashi have proved to be difficult to commission, and to date little support from the supplier was received. Additionally, self-priming pumps are considerably more expensive than the combination conventional pump and priming tank system.

### **Cathode washing**

Heated dip tanks are allowed for at the Ruashi BMR; however, other systems available include the use of heated water spray systems or, as previously mentioned, spray systems as part of a stripping machine.

### **Electrolyte filtration**

Scheibler filters are employed in industry to aid in the filtration of circulating electrolyte, thereby reducing the need to clean cells. Capital expenditure availability have to be considered, and if a filter is not part of the initial design, real estate allowance should be made to later locate the filter when client finances allow.

### **Conclusions**

This paper has two parts: the first part describes the theoretical requirements for copper electrowinning and the second part describes the practical requirements based on the Ruashi case study.

The first part is based on the fundamental equations of reaction rate kinetics and thermodynamics as well as hydrodynamics to describe the baseline equations that can be used in designing a copper electrowinning process. The important considerations for the designer are determination of the diffusion limited current and the appropriate selection of the operating current. These numbers, which are based on numerous variables such as flow rate to cell, cell bite, plating area, copper, acid and iron concentrations, temperature of electrolyte and current efficiency, will determine the structural size and footprint of the copper electrowinning process building. They have the largest effect on overall capital cost and consequently the timeline of building the process plant. It has been discussed that the use of high current densities requires some modifications to the conventional 100-year-old electrowinning cell design. Conventional cells are operated at maximums of approximately ~350-400 A/m<sup>2</sup> but most designers will not exceed these values in conventional designs, with good reason. With adequate hydrodynamics and increase of the diffusion limited current, the capital cost of a copper electrowinning building can be reduced. There are problems associated with this, particularly acid mist generation. Adequate ventilation systems or enclosed hoods similar to those used in the nickel industry can be used. Any designer straying from the path of tried and tested technology should confirm the new design with appropriate test work before committing the client's project and their career to the annals of technical success or failure.

The second part of the paper discusses practical requirements around the electrowinning building and process areas based on the Ruashi case study. A significant number of issues need to be addressed during the design phase to ensure a successful project and an operable plant. Key aspects such as plant location and skill set are critical. Physical aspects such as electrolyte storage, operating temperatures, cell sizes, busbar design, circulation tank and piping layout are very important. Plating and levelling agents need to be considered. Cathode product handling and acid mist control are vital.

# Copper electrowinning: theoretical and practical design

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## Nonmenclature

Symbol	Definition	SI Units
$Q$	Charge	Coulombs
$I$	Current	Amps, C/s
$n$	Valance	gEq/gmol
$F$	Faraday's constant	C/gEq
$M$	Number of Mols	gmol
$i$	Current density	A/m <sup>2</sup>
$A$	Area	m <sup>2</sup>
$dQ/dt$	Charge per time	C/s
$dM/dt$	Mols per time	gmol/s
$G$	Gibbs free energy	J/gmol
$G^o$	Standard Gibbs free energy	J/gmol
$R$	Universal gas constant	J/(gmol.K)
$T$	Temperature	Kelvin
$aP^n$	Activity of products	Dimensionless
$aR^m$	Activity of reactants	Dimensionless
$aRed$	Activity of oxidized species	Dimensionless
$aOx$	Activity of reduced species	Dimensionless
$V$	Potential	Volts
$W$	Work	Joule
$E$	Potential	Volts
$kd$	Mass transfer coefficient	m/s
$kr$	Reaction rate constant	1/s
$Ox$	Oxidized species	Dimensionless
$Red$	Reduced species	Dimensionless
$e^-$	Electrons	Dimensionless
$kf$	Rate constant of forward reaction	1/s
$Cox$	Concentration of oxidized species	gmol/m <sup>3</sup>
$ic$	Current density of cathodic reaction	A/m <sup>2</sup>
$ia$	Current density of anodic reaction	A/m <sup>2</sup>
$krev$	Rate constant of reverse reaction	1/s
$Cred$	Concentration of reduced species	gmol/m <sup>3</sup>
$ko$	Rate constant at equilibrium	1/s
$\alpha$	Separation factor	Dimensionless
$E^{o'}$	Formal electrode potential	Volts
$E^o$	Standard electrode potential	Volts
$\gamma$	Activity coefficient	Dimensionless
$io$	Exchange current density	A/m <sup>2</sup>
$Eeq$	Equilibrium potential	Volts
$\eta$	Overpotential (overvoltage)	Volts
$Nox''$	Mass flux of oxidized species	gmol/(m <sup>2</sup> .s)
$D$	Diffusion coefficient of species	m <sup>2</sup> /s
$(x, t)$	Species vector at time $t$ and position $x$	-----
$v$	Velocity of species	m/s
$d\phi/dx$	Potential gradient across electrolyte	Volts/m
$\nabla$	Laplace operator	-----
$i_a$	Reaction rate for species a	gmol/(m <sup>3</sup> .s)
$i_{ox}$	Reaction rate for oxidized species	gmol/(m <sup>3</sup> .s)
$i_{red}$	Reaction rate for reduced species	gmol/(m <sup>3</sup> .s)
$dx, dy, dz$	Distance in x, y and z directions	m
$\delta$	Boundary layer thickness	m
$iL$	Diffusion limited current	A/m <sup>2</sup>
$Re$	Reynolds number	Dimensionless
$L$	Characteristic length	m
$\rho$	Density	kg/m <sup>3</sup>
$\mu$	Viscosity	kg/(m.s)
$Sc$	Schmidt number	Dimensionless
$Sh$	Sherwood number	Dimensionless

$de$	Characteristic length/hydraulic diameter	m
$Gr$	Grashof number	Dimensionless
$g$	Gravitational acceleration	m/s <sup>2</sup>
$\beta$	Thermal expansion coefficient	1/K
$T_s$	Temperature at the surface	K
$T_\infty$	Temperature at bulk	K
$Pr$	Prandtl number	Dimensionless
$C_p$	Specific heat capacity	J/(kg.K)
$k$	Thermal conductivity	W/(m.K)
$Ra$	Rayleigh number	Dimensionless
$Nu$	Nusselt number	Dimensionless
$Le$	Lewis number	Dimensionless
$V_a$	Anodic standard electrode potential	Volts
$V_c$	Cathodic standard electrode potential	Volts
$V_{min}$	Decomposition potential	Volts
$V_{ohm}$	Ohmic resistance	Volts
$V_{ir}$	Solution potential	Volts
$V_{contacts}$	Contacts potential	Volts
$\kappa$	Resistivity	S/cm
$ui$	Ionic mobility of species $i$	gmol.cm <sup>2</sup> /(J.s)
$\epsilon$	Current efficiency	percentage

## References

- HAYES, P.C. *Process Principles in Mineral and Materials Production*, Hayes Publishing Co., 1983.
- PETRUCCI, R.H. and HARWOOD, W.S. *General Chemistry Principles and Modern Applications*, Prentice Hall International, Inc., 1993.
- LORENZEN, L. *Mineral Processing Class Notes*, Electrochemical Reactor Design, University of Stellenbosch, 2000.
- INCOPERA, F.P. and DEWITT, D.P. *Fundamentals of Heat and Mass Transfer*, John Wiley and Sons, Inc., 1996, (4th Edition), Chap 6, Chap 9.
- PERRY, R.H. and GREEN, D.W. *Perry's Chemical Engineers' Handbook*, McGraw-Hill, 1997.
- JACKSON, E. *Hydrometallurgical Extraction and Reclamation*, Ellis Horwood Limited, 1986, Chap 5.
- WANG, J. *Analytical Electrochemistry*, John Wiley and Sons, Inc., 2001, (2nd Edition).
- ZANELLO, P. *Inorganic Electrochemistry: Theory, Practice and Application*, The Royal Society of Chemistry, 2003.
- BRETT, C.M.A. and BRETT, A.M.O. *Electrochemistry Principles, Methods, and Applications*, Oxford University Press, 1993.
- MACKINNON, D.J. and LAKSHMANAN, V.I. Recent Advances in Copper Electrowinning, Mineral Research Program, Mineral Research Laboratories, CANMET Report 76-10, 1976.
- ANDERSEN, A.K. and BALBERYSZKI, T. Electrowinning of Copper at High Current Densities with the CCS Cell, The Metallurgical Society of AIME, TMS Paper Selection, Paper A68-17, 1968.
- ESCOBAR, V., TREASURE, T., and DIXON, R.E. High Current Density EMEW® Copper Electrowinning, Electrometals Technologies Ltd. Official Website. <http://www.electrometals.co.au>.
- ROUX, E., GNOINSKI, J., EWART, I., and DREISINGER, D. Cu-Removal From the Skorpion Circuit Using EMEW® Technology, The South African Institute of Mining and Metallurgy, *The Fourth Southern African Conference on Base Metals*, 2007.
- Short course on Electrochemistry, Electrochemical Engineering and Electrometallurgy: Module on Thermodynamics and Kinetics, University of the Witwatersrand, Johannesburg, 2005.
- SANDENBERGH, R. University of Pretoria Electrochemistry class notes, 2007.
- HOULACHI, G.E., EDWARDS, J.D., and ROBINSON, T.G. *Cu 2007*, vol. V, Copper Electrowinning and Electrorefining, Toronto, Metsoc Publication, August 2007.
- Short course on Electrochemistry, Electrochemical Engineering and Electrometallurgy: Module on Applications of Fundamentals to Electrowinning and Electrorefining of Metals. University of the Witwatersrand, Johannesburg, 2005. ◆