CHAPTER 10.16

Electrowinning

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Electrowinning is the process of electrolytically *winning* or recovering metal from a solution containing dissolved metal. The process of electrowinning is used to recover aluminum, copper, gold, magnesium, manganese, nickel, silver, zinc, and other metals from liquids on a commercial scale. For aluminum and magnesium, the process of electrowinning involves high temperatures and molten salt environments. For copper, gold, magnesium, manganese, nickel, silver, and zinc, electrowinning is performed in water-based, aqueous liquids. Electrowinning and related principles are also important to other applications such as integrated circuit fabrication and circuit board printing, electroforming of precision parts, and battery recharging. This chapter is designed to give a brief overview of the fundamentals of electrowinning of base metals in aqueous media. A more complete overview of related fundamentals is available elsewhere (Free 2013).

For electrowinning to occur, the desired metal must be dissolved in an ionic form. Common base metal ions are Cu^{2+}, Ni^{2+}, and Zn^{2+}. Each of these metal ions has a 2+ charge because of the loss of two electrons from the metal. Metal ions are usually created by breaking atomic bonds in minerals during leaching to release the metals as ions. The metal ions are often concentrated in aqueous solution and mixed with acid, most commonly sulfuric acid, to form the electrolyte. The electrolyte is the solution in which electrowinning is performed.

Water plays a key role in electrowinning of base metals. Water can be electrolytically broken into oxygen and hydrogen gas ($2H_2O \leftrightarrow 2H_2 + O_2$). The process of electrolytic water splitting or water electrolysis requires considerable energy. Water electrolysis has oxidation ($2H_2O \leftrightarrow 4H^+ + 4e^- + O_2$) and reduction ($4H^+ + 4e^- \leftrightarrow 2H_2$) components that can balance. Each of these reactions is known as a *half-cell reaction* because an opposite half-cell reaction is needed to form a complete electrochemical cell. The water oxidation reaction is the primary anode reaction for electrowinning metals from sulfate-based electrolytes. Metal reduction on the cathode is the primary cathodic reaction, an example of which is $Cu^{2+} + 2e^- \leftrightarrow Cu$. The reduction of hydrogen ions to form hydrogen gas can occur on cathodes that are at low potentials. Hydrogen ion reduction consumes electrons that would otherwise go to metal reduction in lower-potential metals such as nickel and zinc.

The polar and open structure of water molecules readily accommodates ion dissolution and mobility, making the combination of water, acid, and other dissolved ions a very useful electrolyte. The dissolved ions in the electrolyte are necessary for the conduction of current through ion movement. Although dissolved ions are necessary to conduct electrical current between the anode(s) and cathode(s), many dissolved ions do not participate in electrochemical reactions.

BACKGROUND FUNDAMENTALS

Chemical and electrochemical reaction equilibria are generally determined using thermodynamics. Chemical and electrochemical reactions can be expressed as

$$ne^- = \sum_j \nu_j X_j^{z_j} \qquad \textbf{(EQ 1)}$$

where *e* represents an electron with a superscripted minus symbol to indicate its charge; *n* is the number of electrons ($n = 0$ for nonelectrochemical reactions) in half-cell reactions; ν_j is the stoichiometric coefficient of the species (positive values represent products and negative values represent reactants, which are generally shown on the left-hand side of the equation); *X* is the chemical formula of species "*j*"; and z_j is the charge of species *j*. Half-cell reactions are written as reduction reactions to be consistent with most traditional electrochemistry. An example of the application of the general chemical/electrochemical formula equation is

$$Cu^{2+} + 2e^- = Cu \qquad \textbf{(EQ 2)}$$

in which $\nu_{Cu2+} = -1$, $z_{Cu2+} = 2$, $\nu_{Cu} = 1$, $z_{Cu} = 0$, and $n = 2$.

The free energy of a reaction, which identifies reaction direction (negative is forward) and quantifies available energy, is expressed as

$$\Delta G_r = \Delta G_r^\circ + RT\ln\prod_j a_j^{\nu_j} \qquad \textbf{(EQ 3)}$$

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in which R is the gas constant (8.314 J/mol·K), T is the absolute temperature (K), and $a_j^{\nu j}$ is the activity of species j. The standard reaction free energy, ΔG_r°, can be written as

$$\Delta G_r^\circ = \sum_j v_j \Delta G_{f_j}^\circ \quad \textbf{(EQ 4)}$$

in which the subscript f denotes the formation of the compound from the elements under standard conditions.

The standard free energy values for chemical compounds are available in data tables that are commonly based on the reaction of pure elements under standard conditions and unit activities. Pure solid substances and liquids have unit activities. Dissolved ions have unit activities under ideal conditions at a concentration of 1 molal, although in practice, a non-unity activity coefficient is used to correct for deviations from ideality. Pure gasses have unit activities at 100 kPa unless they are associated with substances that have liquid standard states.

At equilibrium, the free energy of the reaction equals zero and the equilibrium constant may be used to represent the equilibrium activity relationship between the species:

$$\Delta G_r^\circ = -RT \ln \prod_j a_{jeq}^{v_j} \quad \textbf{(EQ 5)}$$

in which each species j activity is the equilibrium activity as denoted by the *eq* subscript.

The activity of an ion in aqueous medium can be expressed as

$$a_j = \gamma_j m_j \quad \textbf{(EQ 6)}$$

in which γ_j is the activity coefficient of species j, and m_j is the molality (moles per 1,000 g of water) of species j. The activity coefficient is determined using a variety of correlations and equations and is generally significantly less than one in most common solutions. The activity coefficient is often determined using equations such as the Davies equation, which is

$$-\log \gamma_j = Az_j^2\left(\frac{\sqrt{I_{str}}}{1+\sqrt{I_{str}}} - 0.2I_{str}\right) \quad \textbf{(EQ 7)}$$

in which $A = 0.2409 + 9.01 \times 10^{-4}T$, (valid from 273 to 333 K) (equal to 0.5094 at 298 K), and ionic strength, I_{str}, is determined using the following relationship:

$$I_{str} = \frac{1}{2}\sum_j^n \frac{m_j z_j^2}{m^\circ} \quad \textbf{(EQ 8)}$$

where m_j is the molality of species j, z_i is the charge of species j, and m° is the reference molality (1 molal) for aqueous systems. Other equations are needed for solutions with I values exceeding 0.3.

Electrochemical Principles

The equilibrium electrochemical half-cell potential is determined based on free energy using the Nernst equation:

$$E_{eq} = E^\circ - \frac{RT}{nF} \ln \prod_j a_j^{v_j} \quad \textbf{(EQ 9)}$$

in which F is the Faraday constant (96,485 C/mol [coulombs per mole]) and the standard potential, E°, can be calculated from standard free energy values using the following equation:

$$E^\circ = -\frac{\Delta G_r^\circ}{nF} \quad \textbf{(EQ 10)}$$

Application of the Nernst equation to the water oxidation equation (written as a reduction reaction)

$$4H^+ + O_2 + 4e^- \leftrightarrow 2H_2O \quad \textbf{(EQ 11)}$$

is

$$\begin{aligned} E_{eq} &= E^\circ - \frac{RT}{nF} \ln \prod_j a_j^{v_j} \\ &= \frac{-\Delta G_r^\circ}{nF} - \frac{RT}{nF} \ln \frac{a_{H_2O}^2}{a_{H^+}^4 a_{O_2}} \end{aligned} \quad \textbf{(EQ 12)}$$

The standard reaction free energy is (2(–237,141) – [4(0) + (0)]) – 474,282 J/mole. After conversion to a base 10 logarithm (log) (2.303 log = ln), combined with the assumption of unity for the activity of water and oxygen, results in

$$\begin{aligned} E_{eq} &= \frac{-(-474,282)}{4(96,485)} \\ &\quad - \frac{2.303(8.314)(298)}{4(96,485)} \log \frac{1^2}{a_{H^+}^4(1)} \\ &= 1.229 - 0.0148 \log \frac{1}{a_{H^+}^4} \end{aligned} \quad \textbf{(EQ 13)}$$

Substitution of the relationship for pH [pH = $-\log(a_{H^+})$] and rearrangement leads to

$$E_{eq(H_2O/O_2)} = 1.229 - 0.0591\,\text{pH} \quad \textbf{(EQ 14)}$$

When the potential of an aqueous process, such as occurs on typical anodes, is higher than this equilibrium potential for water at the pH of the environment, the resulting oxidizing environment will cause water electrolysis or electrochemical splitting into hydrogen ions and oxygen gas. Consequently, this relationship between potential and pH is a practical upper limit for water stability. It is also a minimum potential necessary for typical anodic oxidation of water. This upper potential limit for aqueous systems indicates water will begin to decompose above it.

Water also decomposes into hydrogen gas and hydroxide ions as previously indicated. The corresponding equilibrium potential equation for this reaction ($4e^- + 4H_2O \leftrightarrow 2H_2 + 4OH^-$ or $4H^+ + 4e^- \leftrightarrow 2H_2$) as a function of pH is

$$E_{eq(H_2O/H_2)} = 0 - 0.0591\,\text{pH} \quad \textbf{(EQ 15)}$$

These relationships can be used with relationships for other species, such as metal ions, metallic metals, metal sulfides, and metal oxides to produce phase stability or Pourbaix diagrams. These diagrams are commonly used to identify potential and pH conditions needed for metal extraction and electrowinning.

An example of a stability diagram for nickel is shown in Figure 1. The phase stability diagram for nickel shows that a high potential is needed to stabilize dissolved nickel ions as Ni^{2+} ions in an electrolyte. It also shows that the electrolyte has reasonable stability in the acidic range. Furthermore, if the pH approaches the neutral range near pH 7, the nickel will precipitate out of the electrolyte. The diagram also indicates that the potential must be below –0.25 V when the pH is 0 to allow the metal to be electrowon from solution.

Note that the production of nickel occurs below the water stability line associated with hydrogen gas production when the pH is below about 4. Correspondingly, some hydrogen gas is produced at the cathode during nickel production.

It is possible to significantly reduce the electrochemical potential of an electrochemical reaction through complexation. A good example of this is gold complexation with thiosulfate. Under standard conditions, the electrodeposition of gold from its single ion valence ($Au^{3+} + 3e^- \leftrightarrow Au$) requires a potential of 1.498 V. However, if the gold is complexed with chloride ($AuCl_4^- + 3e^- \leftrightarrow Au + 4\ Cl^-$) under standard conditions, the standard potential for the reaction drops to 1.002 V.

A list of standard electrochemical potentials is given in Table 1. The actual potentials in applications can be calculated using the Nernst equation, which uses the standard potential and adjusts the potential based on actual species activities, instead of assuming all activities are one. The data in Table 1 provide a relative electromotive force (*emf* or *E*) or potential scale for standard atmospheric conditions to compare metal and other elements and compounds tendencies to acquire electrons. The higher the potential, the easier it is to cause the reaction to proceed as a reduction reaction. Thus, metals with high standard potentials, such as gold, are easily electrowon. Metals such as zinc are more difficult to electrowin than metals such as iron. Consequently, in zinc electrowinning plants, iron and other metals with higher potentials than zinc must be removed from the electrolyte prior to zinc electrowinning to prevent the undesired metals from codepositing with the zinc.

Table 1 also lists reactions such as the ferric reduction reaction ($Fe^{3+} + e^- \leftrightarrow Fe^{2+}$), which can occur as an undesired electron consuming reduction reaction on cathodes as well as in the reverse direction as an undesired oxidation reaction on anodes that resupplies the ferric ions for continued reduction on the cathode.

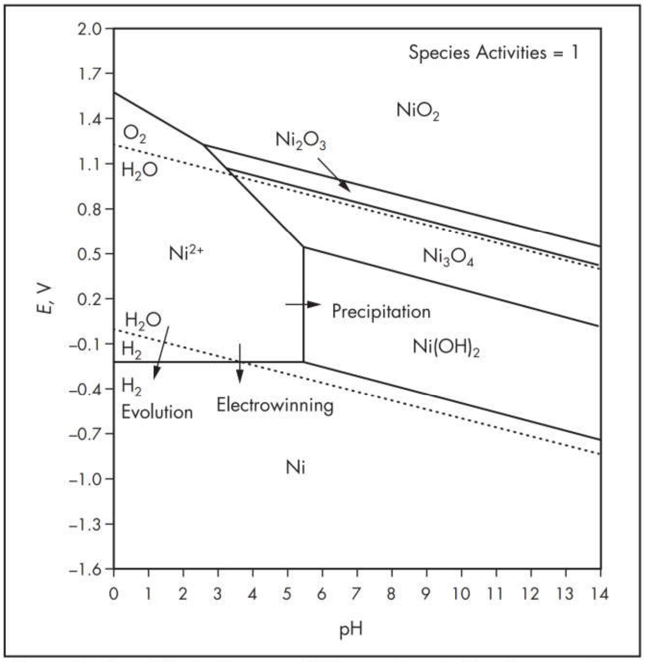


Figure 1 Simplified phase stability or Pourbaix diagram for nickel in water

Table 1 Selected standard half-cell reactions and standard potentials ($E°$)*

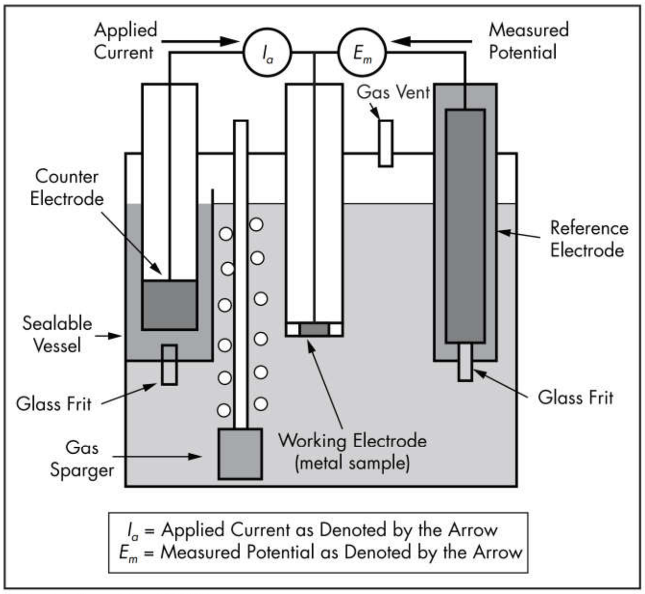
Reaction	$E°$, V
$Au^+ + e^- \leftrightarrow Au$	+1.692
$Au^{3+} + 3e^- \leftrightarrow Au$	+1.498
$Cl_2 + 2e^- \leftrightarrow 2Cl^-$	+1.358
$Pt^{3+} + 3e^- \leftrightarrow Pt$	+1.358
$Ag^+ + e^- \leftrightarrow Ag$	+0.799
$Fe^{3+} + e^- \leftrightarrow Fe^{2+}$	+0.770
$O_2 + 2H^+ + 2e^- \leftrightarrow H_2O_2$	+0.680
$Cu^{2+} + 2e^- \leftrightarrow Cu$	+0.337
$2H^+ + 2e^- \leftrightarrow H_2$	0.000
$Pb^{2+} + 2e^- \leftrightarrow Pb$	−0.126
$Sn^{2+} + 2e^- \leftrightarrow Sn$	−0.136
$Ni^{2+} + 2e^- \leftrightarrow Ni$	−0.250
$Co^{2+} + 2e^- \leftrightarrow Co$	−0.277
$Cd^{2+} + 2e^- \leftrightarrow Cd$	−0.403
$Fe^{2+} + 2e^- \leftrightarrow Fe$	−0.410
$Zn^{2+} + 2e^- \leftrightarrow Zn$	−0.763
$Mn^{2+} + 2e^- \leftrightarrow Mn$	−1.180
$Al^{3+} + 3e^- \leftrightarrow Al$	−1.662
$Mg^{2+} + 2e^- \leftrightarrow Mg$	−2.363
$Na^+ + e^- \leftrightarrow Na$	−2.712
$Li^+ + e^- \leftrightarrow Li$	−3.050

*Assumes all reactions involving hydrogen are at pH = 0.

The data in Table 1 show that metals such as magnesium have standard potentials that are far below that of hydrogen ion reduction. The potentials for aluminum, magnesium, sodium, and lithium are so far below that of hydrogen that hydrogen ion reduction to hydrogen gas is generally more rapid than that of the metal, which creates a potentially dangerous environment in addition to making the metal reduction very inefficient. Thus, commercial production of very low-potential metals, including aluminum and magnesium, is performed in molten salts rather than water.

Overall cell voltage between the cathode and anode can be measured using a simple multimeter. The electrochemical potential for half-cell reactions can be measured and characterized along with associated reaction rate kinetics using a potentiostat and an electrochemical cell, such as depicted in Figure 2 with three electrodes. The electrode that is evaluated is the working electrode. The working electrode is often rotated to control mass transport conditions. The counter or auxiliary electrode is used to produce or receive electrons for the working electrode. The auxiliary electrode is often made of inert materials, and the main auxiliary reaction is commonly water electrolysis. The current supplied to the auxiliary electrode is measured by the potentiostat.

A reference electrode is used as the third electrode. The reference electrode provides a steady reference potential from a half-cell reaction system that is inside the reference electrode but in ion contact with the solution through a porous medium. A common reference electrode half-cell system consists of silver and silver chloride solids in a solution that is saturated with potassium chloride (KCl). The associated half-cell reaction ($AgCl + e^- \leftrightarrow Ag + Cl^-$) remains at a constant equilibrium potential of 0.199 V because of the unit activities of the solid silver chloride (AgCl) and Ag and the constant activity



Adapted from Free 2013

Figure 2 Schematic diagram of a typical three-electrode electrochemical testing cell

of Cl^- in a KCl-saturated solution. Calculation of the working electrode (WE) potential relative to the thermodynamic electrochemical potential or standard hydrogen electrode (SHE) is accomplished based on the measured (meas) and reference (ref) potentials using the following equation:

$$E_{\mathrm{WE(vs.\,SHE)}} = E_{\mathrm{ref}} + E_{\mathrm{meas}} \quad \textbf{(EQ 16)}$$

Solution resistance in the electrolyte is calculated as

$$R = \frac{1}{k}\frac{d}{A} \quad \textbf{(EQ 17)}$$

where R is the resistance, k is the specific conductivity of the electrolyte, d is the separation distance between electrodes, and A is the cross-sectional area of the electrodes. Solution resistance results in a voltage drop proportional to the current. Energy consumption is directly proportional to potential (or voltage), current, and time (energy = EIt).

Electrochemical Kinetics

The rate or kinetics of electrochemical reactions determines the commercial utility of electrowinning. Electrochemical kinetics is a function of species availability, potential, and electron exchange kinetics. The rate of electrochemical half-cell reactions is well-described using the Butler–Volmer equation (Bockris and Reddy 1973):

$$i = i_o[\exp\left(\frac{\alpha_a F\eta}{RT}\right) - \exp\left(\frac{-\alpha_c F\eta}{RT}\right) \quad \textbf{(EQ 18)}$$

in which i is the current density, i_o is the equilibrium exchange current density, α_a is the anodic charge transfer coefficient, η is the surface overpotential or the difference between the surface potential (E_{surf}) and the equilibrium reaction potential (E_{eq}), and α_c is the cathodic charge transfer coefficient. This form of the Butler–Volmer equation is based on bulk concentrations of reacting species, which are generally different than the concentrations at the surface where electron exchange occurs. A more useful form of the Butler–Volmer equation that is explicit in terms of surface and bulk solution concentrations that contribute to the exchange current density can be expressed as (Newman and Thomas-Alyea 2004)

$$\begin{aligned} i = k'[C_{ba}&\left(\frac{C_{sa}}{C_{ba}}\right)^{\lambda_a}\exp\left(\frac{\alpha_a F\eta}{RT}\right) \\ &-C_{bc}\left(\frac{C_{sc}}{C_{bc}}\right)^{\lambda_c}\exp\left(\frac{-\alpha_c F\eta}{RT}\right) \end{aligned} \quad \textbf{(EQ 19)}$$

where k' is a constant that is directly related to the equilibrium exchange current density, C_b is the bulk concentration, C_s is the surface concentration, and λ is a factor that depends on reaction mechanisms and related factors and is usually between 0.25 and 1. (The additional subscript a denotes anodic, and c denotes cathodic.) Only the first term is generally needed for reactions occurring anodically and the second term for reactions occurring cathodically provided that the reactions are not near (generally within approximately 0.15 V) their equilibrium potentials.

The system of Butler–Volmer equations that applies to a given reaction scenario is subject to the constraint that

$$\sum I = 0 \quad \textbf{(EQ 20)}$$

When all currents are associated with the same homogeneous surface,

$$\sum i = 0 \quad \textbf{(EQ 21)}$$

The mass (m) changes in processes such as electrodeposition or corrosion are based on Faraday's law, which can be mathematically expressed as

$$m = \frac{ItA_w}{nF} = \frac{iAtA_w}{nF} \quad \textbf{(EQ 22)}$$

in which I is the current, t is time, A_w is the molecular or atomic weight of the species that is depositing or dissolving, A is the electrode area, and the other terms as defined previously.

Ion Mass Transport

All electrochemical reactions require mass transport of associated ions to supply the electrode reactions as well as to conduct current. The conduction of current is caused by the migration of ions in response to an electrochemical potential gradient between the positive and negative electrodes. Because some ions are more mobile than others, they are capable of carrying more current. As an example, hydrogen ions are approximately four times more mobile than chloride ions. Consequently, a solution of hydrochloric acid will have approximately four times more current carried by hydrogen ion migration than by chloride ion migration.

Ions that migrate to an electrode must be eventually consumed by the reaction or be transported away from the electrode by a combination of diffusion and/or convection. Ions that migrate from an electrode need to be eventually replenished by diffusion and/or convection.

The combination of the ion transport processes on current flow can be expressed by the following equation (Newman and Thomas-Alyea 2004):

$$\begin{aligned} i &= F\sum_j z_j N_j \\ &= -F^2 \nabla E \sum_j z_j^2 u_j c_j \\ &\quad + FV \sum_j z_j c_j \\ &\quad - F \sum_j z_j D_j \nabla c_j \end{aligned} \tag{EQ 23}$$

where N_j is the flux density of species j, c_j is the concentration of species j, u_j is the ion mobility of species j, V is velocity, D is diffusivity, and all other variables as previously defined. The ion transport current density of a reacting species at an electrode surface must balance the electrochemical reaction current density for the same species under steady-state conditions.

In most electrowinning scenarios, the background electrolyte ions, such as hydrogen ions and sulfate ions, carry most of the electrolyte current flow by ion migration. Correspondingly, the first term of the ion transport current density equation can usually be neglected for the depositing metal. The second term of the mass transport current density equation can also be neglected if the convective flux of ions is small. These are oversimplifications for accurate modeling, but they, along with a simplified concentration gradient, result in a simplified equation that is very useful in electrowinning:

$$i = -nFD\frac{(C_b - C_s)}{\delta} \tag{EQ 24}$$

in which δ is the boundary layer thickness, which is related to the fluid flow and geometry of the electrodes and the cell. If the electrochemical reaction is fast compared to diffusion, the surface concentration of reacting species will be small, and the current density will approach its limiting current density. The limiting current density, i_l, can be estimated as

$$i_l = \frac{-nFDC_b}{\delta} \tag{EQ 25}$$

The limiting current density of the metal that is being electrodeposited is important to product quality. Generally, if the metal is deposited at a rate that is higher than about 40% of the limiting current density, it is difficult to maintain smooth surfaces—even with smoothing additives. This is because the mass transport is significantly restricted by the limitations of diffusion, which forces undesired surface protrusions, such as nodules, to acquire significantly more depositing metal than flat areas, because of better access to incoming diffusing ions, thereby accelerating the growth of protrusions and increasing roughness.

Fluid Flow

The effects of fluid flow, which influence ion transport to electrodeposition surfaces, can be characterized by the Navier–Stokes equation (Potter and Foss 1982):

$$\rho\left[\frac{\partial V}{\partial t} + (V \cdot \nabla)V\right] = -\nabla p - \rho g \nabla h + \mu \nabla^2 \tag{EQ 26}$$

in which ρ is the density of the fluid, V is the velocity, p is the pressure, g is the gravitational acceleration, h is height, and μ is viscosity.

Conservation of mass leads to the equation of continuity (Potter and Foss 1982):

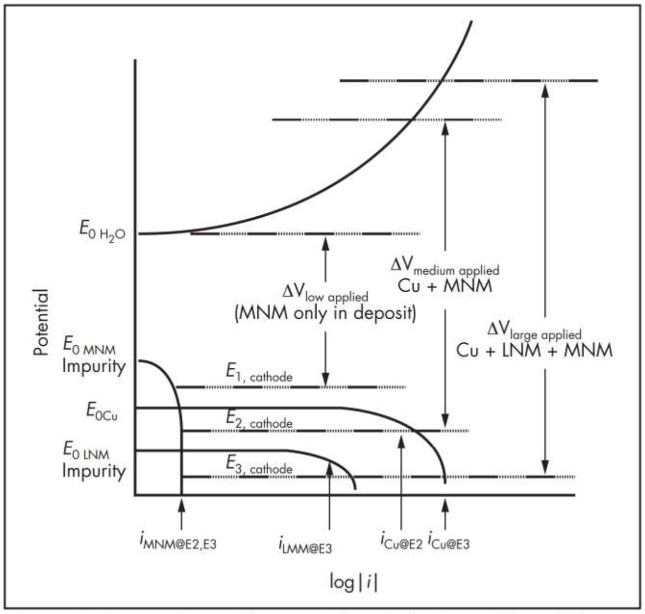


Figure 3 Comparison of potential and the logarithm of the absolute value of current density for a scenario involving copper, less noble metal (LNM), and more noble metal (MNM)

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho V) = 0 \tag{EQ 27}$$

The Navier–Stokes equation and the equation of continuity are generally simplified to facilitate practical fluid flow calculations. They can be used to determine local velocities that control convective ion transport and influence the diffusion boundary layer thickness.

Applied Fundamentals

Real-world applications such as electrowinning involve a combination of the fundamental equations that have been described. The rate of electrodeposition is related to the applied voltage, which is the driving force for the resulting current. The flow of electrolyte influences the voltage requirement as well as the quality of the resulting deposit. A comparison of voltage and rate for electrochemical reactions for a typical electrowinning scenario is shown in Figure 3.

Electrowinning operations are generally controlled on a current basis, but it is the voltage of the half-cell reactions that drives the current. The applied voltage is closely related to the current that is applied. If the applied voltage results in a cathode potential that is below the electrochemical potential of any metal, that metal will deposit at a rate given by the Butler–Volmer equation.

The rates of deposition for each of these metals depend on the dissolved metal ion concentration and associated half-cell potential for metal deposition. At $E_{1,\text{cathode}}$, the cathode potential is below that of the more noble metal (MNM) and above copper. Correspondingly, only MNM will deposit. The applied potential at $E_{1,\text{cathode}}$ is relatively low but significant, primarily caused by the difference in the potentials of the water oxidation reaction at the anode and the reduction of MNM on the cathode. At $E_{1,\text{cathode}}$, no copper will deposit because the cathode potential is above that the copper deposition half-cell reaction. Note that the rate of MNM deposition is very low because of the low dissolved concentration of MNM impurity. Generally, electrolytes are purified to eliminate nearly all MNM impurities to reduce codeposition of the MNM on the cathode.

At $E_{2,\text{cathode}}$, the rate of deposition of MNM is relatively small compared to that of copper because it is in low concentration in solution. An example of this is silver deposition with copper, which generally occurs at a very low rate, which is equal to its diffusion-based limiting current density, because of its very low concentration in copper electrowinning tankhouses. Thus, the limiting current density is important in impurity control.

At $E_{3,\text{cathode}}$, MNM, copper, and the less noble metal deposit. An example of this could be silver, copper, and nickel. However, if the nickel concentration is not high and the cathode potential is not unusually low, its potential is far enough below that of copper to prevent it from depositing in most industrial electrowinning scenarios.

The effect of MNM impurity on cathode purity can be calculated based on the MNM limiting current density and the overall current density on the cathode, provided that some basic information is available. The following equation is for lead in zinc, which can also be applied to other metals (Free 2013):

$$C_{\text{MNM, in dep.metal}} = \frac{i_{l,\text{MNM}}\, n_{\text{dep.metal}} A_{w,\text{MNM}}}{i_{\text{total}} \frac{\beta}{100} n_{\text{MNM}} A_{w,\text{dep.metal}}} \qquad \textbf{(EQ 28)}$$

where A_w is the atomic weight, β is the current efficiency in percent, and dep. is deposited.

Correspondingly, the boundary layer thickness, which can be used to calculate the limiting current density of the desired metal, can be calculated as

$$\delta = \frac{n_{\text{dep. metal}} F D_{\text{MNM}} C_{b,\text{MNM}} A_{w,\text{MNM}}}{C_{\text{MNM,in dep. metal}}\, i_{\text{total}} \frac{\beta}{100} A_{w,\text{dep. metal}}} \qquad \textbf{(EQ 29)}$$

As an example, if the concentration of lead in a zinc cathode is 10 ppm in a cell operating at 395 A/m^2 and 89% efficiency, the associated diffusivity of Pb^{2+} ions is 1×10^{-5} cm^2/s, and the concentration of Pb^{2+} ions in solution is 0.133 mg/L or 6.4×10^{-7} mol/L, then the boundary layer thickness is (Free 2013) as follows:

$$\delta = \frac{(2)\frac{9{,}6485\,\text{coul}}{\text{mol}}\left(\frac{1\times10^{-5}\,\text{cm}^2}{\text{s}}\right)\frac{6.4\times10^{-7}\,\text{mol}}{1{,}000\,\text{cm}^3}\left(\frac{207.2\,\text{g}}{\text{mol}}\right)}{(10\times10^{-6})395\frac{A}{\text{m}^2}\frac{\frac{\text{coul}}{\text{s}}}{A}\frac{1\,\text{m}^2}{10{,}000\,\text{cm}^2}\frac{89}{100}\left(\frac{65.4\,\text{g}}{\text{mol}}\right)} = 0.011\,\text{cm}$$

Figure 3 shows the applied voltage. The applied voltage is a key variable that determines the energy consumption. The applied potential (V_{applied}) can be expressed mathematically as

$$\begin{aligned} V_{\text{applied}} &= E_{\text{anodic}} - E_{\text{cathodic}} + \eta_{\text{anodic}} \\ &\quad + \eta_{\text{cathodic}} + IR_{\text{solution}} + IR_{\text{other}} \end{aligned} \qquad \textbf{(EQ 30)}$$

A simplified version of the Butler–Volmer equation that can be applied to find the charge transfer–based portion of the overvoltage when there is more than 150 mV from the half-cell potential for a given reaction is known as the Tafel equation, and it is expressed as

$$\eta = \beta \log \frac{i_M}{i_{0M}} \qquad \textbf{(EQ 31)}$$

in which η is the charge transfer overpotential; β is the Tafel slope, which is usually between 0.04 and 0.2 V per decade; i_M is the current density of the metal reduction for metal M; and i_{0M} is the equilibrium exchange current density for metal M. The anodic Tafel slope can be calculated from the following equation:

$$\beta = \frac{2.303RT}{\alpha F} \qquad \textbf{(EQ 32)}$$

in which α is the charge transfer coefficient (usually between 0.25 and 0.75). The cathodic Tafel slope is calculated using the same equation with a negative sign. In some cases, a concentration overvoltage is needed, but that is beyond the scope of this chapter, so the reader is invited to use other sources for more details.

The energy consumption (in kilowatt-hour per metric ton [kW·h/t]) needed to electrowin the metal is expressed as

$$\text{Energy}(\text{kW}\cdot\text{h/t}) = \frac{E(n)26{,}800}{A_w\left(\frac{\beta(\%)}{100}\right)} \qquad \textbf{(EQ 33)}$$

As an example, the energy consumption per metric ton of zinc in an electrowinning operation with 92% efficiency, $n = 2$, and a voltage drop of 3.5 V across the cell can be calculated as follows:

$$\begin{aligned} E(\text{kW}\cdot\text{h/t}) &= \frac{E(n)26{,}800}{A_w\left(\frac{\beta}{100}\right)} \\ &= \frac{3.5(2)26{,}800}{(65.38)\left(\frac{92}{100}\right)} = 3{,}120\,\text{kW}\cdot\text{h/kg} \end{aligned}$$

The current efficiency is calculated based on a comparison of the metal weight deposited divided by the weight that should have theoretically deposited based on Faraday's law, as shown in the following equation:

$$\beta = \frac{m_{\text{dep}} nF}{ItA_w} \qquad \textbf{(EQ 34)}$$

As an example, the current efficiency in an operation that deposits 500 t of nickel per day using a current of 21,000,000 A (current supply by rectifier multiplied by the number of cells) is calculated as shown:

$$\beta = \frac{\begin{array}{c}(100\%)(500\,\text{t})(2)(96{,}485\,\text{C/mole})\\(1{,}000\,\text{g/kg})(1{,}000\,\text{kg/t})\end{array}}{\begin{array}{c}(21{,}000{,}000\,\text{C/s})(1\,\text{day})(24\,\text{h/d})\\(3{,}600\,\text{s/h})(58.7\,\text{g/mole})\end{array}} = 90.6$$

Another factor that is worth considering is the solution resistance. The significance of resistance is often in relation to the associated voltage drop, which requires combining the equation with Ohm's law ($E = IR$). As an example, the solution resistance (in ohms) and voltage drop associated with 1-m^2 electrodes, spaced 3 cm apart that operate at 300 A/m^2 in a solution that has a specific conductivity of 1 Ω^{-1}cm^{-1} are calculated as follows:

$$R = \frac{d}{kA} = \frac{(3\,\text{cm})}{(1\,\Omega^{-1}\,\text{cm}^{-1})(1\,\text{m}^2)(10{,}000\,\text{cm}^2/\text{m}^2)} = 0.0003\,\Omega$$

$$E = IR = (300\ \text{A/m}^2)(1\ \text{m}^2)(0.0003\ \Omega)(\text{V/A}\ \Omega) = 0.09\ \text{V}$$

Although that voltage drop is relatively small, it has a significant impact on the overall power consumption.

COMMERCIAL ELECTROWINNING

The purpose of commercial electrowinning is to produce high-quality metal cathodes with utmost safety and low cost. Modern electrowinning facilities are designed to operate with high efficiency in terms of energy consumption, labor productivity, and online availability.

To produce metal, electrolyte, which is a high-conductivity solution rich in metal ions, enters from prior processing steps. Direct electrical current is applied, and metal is won from solution. Figure 4 shows a typical flow diagram where electrowinning is interrogated into a hydrometallurgical flow sheet. Electrowinning requires electrolyte of suitable purity to produce high-quality cathode. This purity is commonly achieved through the application of solvent extraction (SX) (typical for copper) and/or precipitation and cementation (typical for zinc). Producing high-quality cathode with low costs from low-quality electrolyte is difficult. Therefore, adequate solution purification prior to electrowinning is absolutely necessary to achieve the goals of high purity and low cost.

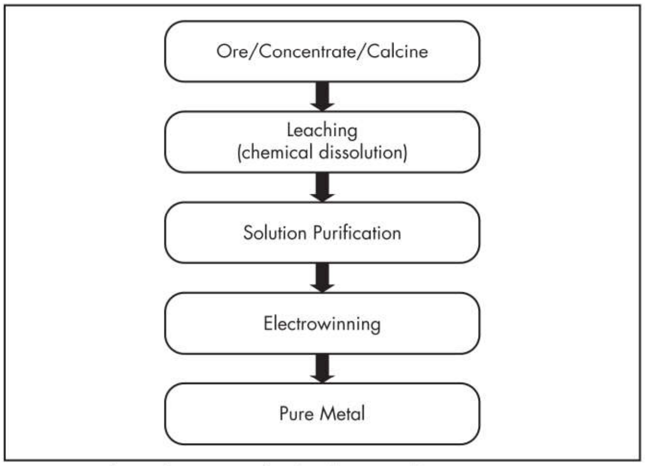


Figure 4 Flow diagram of a hydrometallurgy process to recover pure metal by electrowinning

CELLHOUSE DESIGN

Cellhouse design involves the trade-off between producing large quantities of commercial quality cathode with minimal energy input, high productivity, and safe working conditions and the need to minimize capital expenditures (Anderson et al. 2009; Honey and Watson 1985).

Cells

The largest area of any electrowinning facility is used for the electrowinning cells. Cells are where the metal is electrodeposited from electrolyte that flows through them onto cathodes that hang in them. A tankhouse (copper) or cellhouse (zinc) contains many cells. Modern cells are made from monolithic cast polymer concrete, as shown in Figure 5 (Robinson et al. 2012).

Most modern electrowinning facilities use the Walker system; that is, cells are connected electrically in series (Figure 6) while the electrolyte passes through the cells in parallel (Figure 7). Each cell has multiple anodes and cathodes. Incoming and outgoing electrolyte pipes enter the tankhouse near the electrical null point to minimize stray currents. Images of a commercial copper tankhouse and zinc cellhouse are shown in Figures 8 and 9, respectively.

The number of cells needed can be calculated using Faraday's law, a reasonable current efficiency, the projected rectifier output, and the desired design capacity of the facility. For example, a copper electrowinning facility with a design capacity of 50,000 t/a (metric tons per year) using a 40,000-A rectifier would need 138 cells. This is calculated first by using Faraday's law where I = 40,000 A; t = 1 year converted to seconds; A_w = 63.546 g/mol for copper; n = 2, because copper in a sulfate solution is divalent; F = 96485 C/mol e; and grams is converted into metric tons.

$$m = \frac{ItA_w}{nF} = \frac{40{,}000 \times 365 \times 24 \times 3{,}600 \times 63.546}{2 \times 96{,}485 \times 1 \times 10^{-6}}$$

$$= 415.4 \frac{t}{\text{cell} \times y}$$

Faraday's law calculates the theoretical maximum. To calculate a more practical output, current efficiency and time efficiency need to be incorporated. In this calculation, a current efficiency of 92% and time efficiency of 95% are used for demonstration purposes. Thus, each cell is expected to produce approximately 363 t/a. The number of cells needed is then calculated by dividing the design capacity by the production rate of each cell. The final number of cells is the next nearest even number greater than the calculated value because electrowinning facilities are almost always designed with cell lines of equal length. Hence, the calculated number of cells needed is 138 for this example.

$$415.4 \frac{t}{\text{cell} \times y} \times 0.92 \times 0.95 = 363.1 \frac{t}{\text{cell} \times y}$$

$$50{,}000 \frac{t}{\text{cell} \times y} / 363.1 \frac{t}{\text{cell} \times y} = 137.7\ \text{cells}$$

Most of the detailed information for designing electrowinning tankhouses is held by companies that perform the design and construction of these facilities, and it is not available in the open literature. However, most commercial electrowinning cells are clearly designed to conform to general industry practices as described in each of the commercial practice sections of this chapter. In the case of copper electrowinning, the following are some general design criteria that are discussed in the open literature (Beukes and Badenhorst 2009; Wells and Snelgrove 1990):

- Cathode-to-cathode center spacing is 0.1 m.
- Cell width is 1.3 m.
- Cell height is 1.5 m.
- Cell length is 5.5 m.
- Cathode face solution flow is 0.05–0.1 $\text{m}^3/\text{h}/\text{m}^2$.
- Individual cell spacing is 0.045 m.
- Distance between cell banks is 2–3 m.
- Cell walkway construction materials are nonconductive.
- Cell construction material is polymer concrete.

Source: Robinson et al. 2012

Figure 5 Large polymer concrete cell

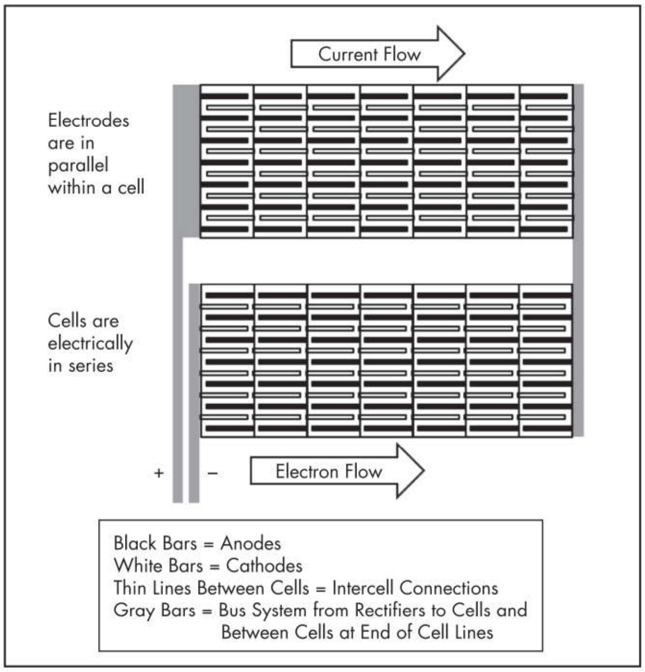


Figure 6 Schematic diagram illustrating current flow through cells in an electrowinning facility

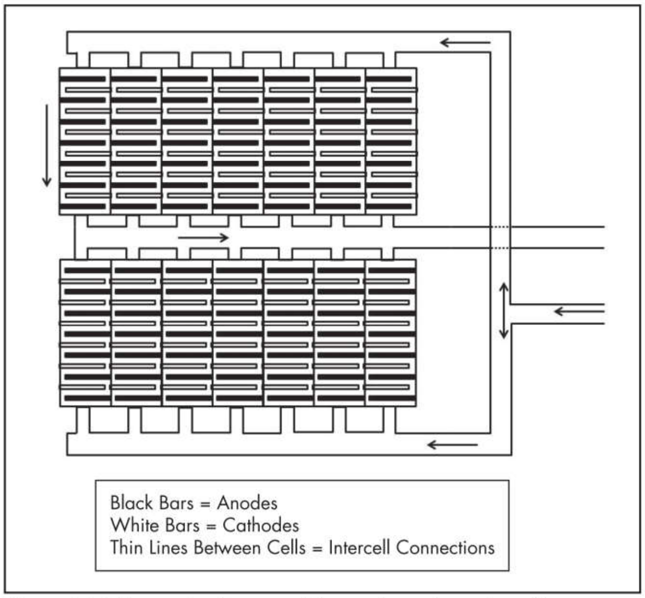


Figure 7 Schematic diagram illustrating electrolyte flow through cells in an electrowinning facility

Similar general practices are often used for zinc and nickel electrowinning. One notable difference from cells used for copper is the increased height of the cells used for zinc electrowinning. For nickel, the infrastructure is designed to accommodate cathode and anode bags, which are not present in cells for copper.

Electrical

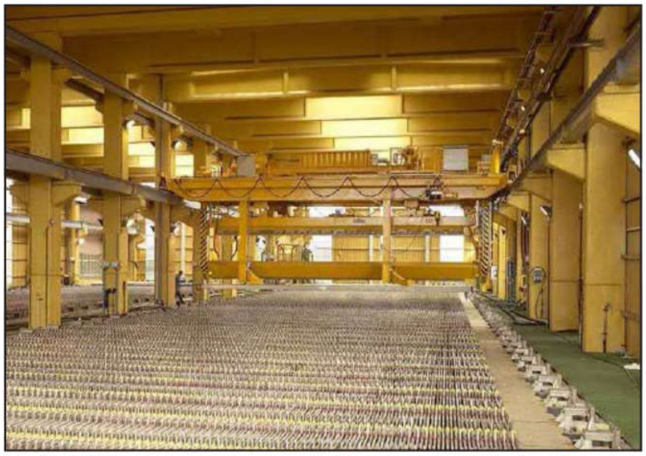
Electrowinning facilities use large oil-filled or dry-type rectifier transformers or air- and/or water-cooled thyristor-controlled rectifiers. These rectifiers are housed in prefabricated buildings with associated equipment such as switchgear, HVAC equipment, cooling water equipment, DC disconnect switches, heat exchangers, control equipment, alarms, and so forth (Brown 1990). The transformers convert high-voltage alternating current into lower-voltage direct current, and electrical power is provided to the electrowinning cells by a rectifier or rectifiers. Many older facilities use two rectifiers because of concerns about rectifier downtime (Brown 1990; Robinson et al. 2013a). Modern rectifiers are now reliable enough to allow designs with only one rectifier (Wiechmann et al. 2000).

Direct current is fed from the rectifier(s) to the cells using copper bus systems (Brown 1990). The bus system is fabricated out of rectangular bars of copper. The copper is typically 1.27-cm-thick copper bar with a height that is dependent on the current carrying capacity needed (15–35.6 cm). For copper electrowinning, six 1.27-cm by 35.6-cm copper bars with 1.27-mm spacing between each bar for ventilation and heat dissipation are used in an open-air configuration. The bars are plated with approximately 40 µm of silver at all copper contacting surfaces to reduce electrical resistance and oxidation.

This design gives a cross-sectional area of 271.3 cm^2 (e.g., 1.27 × 35.6 × 6). Using a current density design value of between 116.3 and 131.8 A/cm^2 of cross-sectional area gives a total current capacity of 31,500–35,700 A DC. The lower current density figure is used for initial design to allow for a maximum heat increase limit of 40°C over ambient conditions and to allow for future increases of the current carrying capacity of the system without major DC bus system design changes. To carry additional current (e.g., 40,000 A used in previous cell number calculations), either more bars or bars with a greater cross-sectional area would be needed. A final decision will be based on economics and after review by an electrical engineer.

Current passes from the bus system into the cells through the use of copper contact bars. These are bars of various designs, depending on the current being used in the system. In zinc electrowinning, the copper bars are often water cooled to reduce the weight of copper needed for the large currents employed. Other metal systems use lower currents

Figure 8 Commercial copper tankhouse with acid mist capture hoods



Source: Horsehead Holding 2012
Figure 9 Commercial zinc cellhouse

and thus use solid copper contact bars. Intercell contact bars were reviewed by Boon et al. (2013). A close-up image of an Outotec double-contact system is shown in Figure 10.

Cells contain many anodes and cathodes. The anodes in the cell are all at one electrical potential (hence, in parallel electrically). The cathodes are all at another (lower) potential. There is always one more anode than cathode in an electrowinning cell. Because current flows through the path of least resistance, even spacing of electrodes is essential.

Uniform electrode spacing is achieved through the use of cell top furniture. Cell furniture is typically made of fiber-reinforced plastic. Notches are molded so electrodes fit securely in the furniture. Spacing is also accomplished through the use of in-cell spacers typically attached to each anode. These spacers are made of various plastics and produced in many styles, including hairpins, buttons, A-shape, and delta blades. More sophisticated in-cell spacing systems are available.

Piping

The electrolyte used in electrowinning is, by design, highly conductive. To reduce the likelihood of stray currents and to protect personnel, nonconductive piping is used throughout and around the electrowinning facility. These pipes are typically high-density polyethylene. Metallic valves and flanges should be avoided because of corrosion and electrical safety issues.

Figure 10 Electrodes resting on a contact system in a copper electrowinning facility

Electrodes

In aqueous electrowinning, metal is deposited at the cathode while an oxidation reaction occurs at the anode. Two types of cathode systems are used: permanent blanks and starter sheets. There are two types of anodes used: Pb-alloy and mixed metal oxide (MMO)–coated titanium. Regardless of the type, each electrode consists of a sheet or mesh of material, where the electrochemical reactions occur, attached to a header bar. The header bar makes electrical contact with the surrounding system and provides mechanical support to the sheet or mesh.

In permanent cathode blank systems, the metal being produced is electrodeposited onto a substrate of a different material, such as aluminum, stainless steel, or titanium. Plastic edge strips are used to ensure that the metal deposit does not grow around the cathode blank, and the strips allow for deposit removal. The metal is typically deposited for 2–10 days and then harvested. Harvesting occurs by removing the deposited metal along with the cathode blank from the cell. The deposit metal is then removed from the blank either manually or by machine (Lenz and Ducharme 2000; Sabau and Bech 2007). The blank is then returned to the cell for reuse. Harvesting is done by a manual or computer-controlled overhead crane. The crane lifts a rack of cathodes, which can be a third, half, or all of the cathodes in the cell.

The life of a cathode blank is 1.5 to more than 10 years, depending on the electrowinning system and material of construction. Permanent blanks are used in the electrowinning of

A. Older style small aluminum cathode with zinc deposit

B. Stainless-steel blank with copper cathode

C. Copper starter sheet

Figure 11 Commercial electrowinning cathodes

copper, nickel, zinc, and other metals. Images of aluminum and stainless-steel blanks used in zinc and copper electrowinning are presented in Figures 11A and 11B, respectively. To facilitate lifting, some electrodes have hooks (Figure 11A) and some have *windows* under the header bar (Figure 11B).

Starter sheets are produced by plating (for one or two days) onto a permanent *mother* blank of stainless steel or titanium. Polymer edge and bottom strips are fitted on the blanks to permit easy stripping of the starter sheets. The stripping is done manually or by automated machinery. Trimming and support loop cutting and attaching are also done manually or with automated machinery. Starter sheets are then placed into *commercial* cells to continue plating until full thickness is achieved (Figure 11C).

Materials Handling

In the design of electrowinning facilities, materials handling and specifically crane movement must be considered. Harvesting of cathodes and replacement of anodes are time-consuming events. Therefore, significant planning occurs on the ability to move electrodes around the plant.

In the design of plants (Beukes and Badenhorst 2009), travel distance between the stripping machine and the end of the cell line is considered. This can lead to the decision to have multiple cranes and centralized stripping machines. Obviously the decision between one crane and multiple cranes is based on economics.

Cranes are also designed to carry a third to half of the electrodes of one type to the cells. To achieve this, strongbacks or other carrying devices are used. Because the weight of lead anodes and the strongback can be significant, the weight capacity of the crane should be considered during the design phase.

Cranes can be fully or partially automated (Kuusisto et al. 2005). The automation of cranes can improve the efficiency of crane movement and remove personnel from the electrowinning environment.

Capital Expenses

Very limited cost information is specific to electrowinning. The general estimate of the capital cost for a small electrowinning tankhouse facility (100 t/d) is \$550–\$900 t/a capacity (Wells and Snelgrove 1990). If this is adjusted for inflation to 2015 using the Chemical Engineering Plant Cost Index (CEPCI), the range is \$890–\$1,460 t/a capacity. Roughly 30% of the capital cost is for the cells, 15% for electrical infrastructure, 15% for building infrastructure, and the rest for remaining expenses (Wells and Snelgrove 1990). Based on information from overall operations for some of the newer combined copper mining/leaching/SX/electrowinning facilities for which overall capital cost information is available, such as those for the Safford mine (\$550 million in capital cost for 120,000 t/a capacity; International Mining 2006), adjusted to \$637 million for inflation using CEPCI data for 2015 (Cheresources 2017), the overall capital cost is anticipated to be about \$5,310 t/a capacity. Thus, using inflation-adjusted values, the fraction of an overall project's capital cost that can be attributed to electrowinning is likely to range from about 17% to 28% for a midsize plant.

Operating expenses for electrowinning for a 36,500-t/a facility were estimated to be \$0.130 per kg of copper, which when adjusted for inflation is \$0.211 in 2015 (Cheresources 2017; Wells and Snelgrove 1990). Because the power consumption for copper production in electrowinning operations is a large portion of the operating expenses and because of variations in power costs, there are notable differences in individual plant-site expenditures. Thus, in areas with high power costs, the operating costs will be substantially higher.

PROCESS CONTROL

The ability of an electrowinning facility to produce low-cost, high-quality cathode is driven by electrolyte control, operational details, current density, acid mist abatement, and impurity treatment.

Electrolyte Control

Modern electrowinning can produce higher than 99% purity for many metals. One of the keys to producing this high quality is electrolyte control. The concentration of metal to electrowin is usually maintained at a high level and only a small amount is removed during a single pass of the electrolyte through the cell. For copper and zinc, concentrations of

35–45 g/L are typical with a plating solution depletion (inlet concentration minus outlet concertation) of 5 g/L. The electrolyte conductivity is also maintained at high levels to reduce electrical consumption by the inclusion of a supporting electrolyte, such as sulfuric acid or sodium sulfate. Temperature is carefully controlled as it can affect metal deposit structure (e.g., higher temperature in nickel electrowinning produces less stressed deposits), side reactions (e.g., zinc electrowinning maintains lower electrolyte temperature to minimize hydrogen evolution), and the interaction with the electrolyte with upstream processing (e.g., electrolyte contacting the organic phase in SX).

Contamination of inorganic and organic impurities is minimized. Each metal electrowinning system has different impurity requirements. Metals with more negative standard reduction potentials have more stringent requirements. The cause for this is the increased chance for hydrogen evolution at the cathode and lower current efficiency. Because of the differences in requirements, some operations analyze electrolyte composition hourly while other may analyze once or twice per shift.

In most electrowinning systems, inorganic and/or organic additives are used to facilitate the production of dense, smooth deposits that are low in impurities. Organic smoothing agents, such as glue, gelatin, guar, or starch, are used. Inorganic ions, such as cobalt and manganese, are used to minimize lead anode corrosion in copper and zinc, respectively. Boric acid is used as a buffer in nickel electrowinning.

Operational Details

As with any large operation, attention to details is critical in metal electrowinning. Operations should strive for uniform current distribution within a cell to produce deposits of consistent thickness. This will decrease the likelihood of uneven growth and short circuiting (e.g., physical contact between anodes and cathodes). Short circuits result in current bypassing the electrochemical reactions, which decreases the productivity of the cell and increases the energy cost to produce metal.

Because cathodes or anodes are electrically in parallel within a cell to minimize the variation in current distribution, anodes and cathodes need to be straight, evenly spaced, and well aligned. This is achieved thorough the maintenance of cell top furniture, cathodes, and anodes and consistent electrode placement in the cells. Removal and correction of bent electrodes is necessary to operate low-cost electrowinning facilities.

Electrowinning is best performed under steady-state conditions. Thus, disruptions to electrical power and/or electrolyte flow, upsets in electrolyte quality, and changes to harvesting schedules will cause operational difficulties. These will likely cause increased costs and a lower-quality product.

Current Density

The final operational control for electrowinning is current density or applied current. In most facilities, the applied current may be adjusted based on external factors, such as metal availability from the mine or availability and/or cost of electrical power. Each metal electrowinning system operates best within a certain range of current densities. If the current density is too high, deposit quality usually suffers and the likelihood of short circuiting increases. If current density is too low, then capital utilization is reduced or current efficiency may suffer, as in the case with zinc electrowinning. Effort should be made to maintain current density within the normal range found in similar operations.

Acid Mist Mitigation

The anode in aqueous electrowinning operations creates oxygen bubbles that rise and collapse at the top of the highly acidic electrolyte. McGinnity and Nicol (2014) recently reviewed the fundamentals of acid mist generation and practical methods to control it in industrial practice. The bubble collapse causes the formation of tiny droplets of the acidic electrolyte that produces an acid mist in electrowinning tankhouses. Most countries regulate the acid mist that is allowable in the air in tankhouses to 1 mg/m^3 or less (OSHA 1985; Otero et al. 2003). Consequently, electrowinning operations use one or more methods of reducing acid mist in addition to using personal protection equipment to limit worker exposure to acid mist.

Many industrial sites use ventilated hoods to capture acid mist above the cells (Mella et al. 2003) or forced-air ventilation for the entire facility (Davis and De Visser 2000).

One method of reducing acid mist is the use of plastic balls or beads (Robinson et al. 2013b). The layer of balls or beads that is a few centimeters thick floats on the electrolyte. The balls or beads provide a surface on which acid droplets collect and drain back into the electrolyte. Some sites use barriers such as brushes or wipers attached to anodes, which generally require some periodic spraying of water to keep them clean, or polymeric pads or sheets to cover the cells.

Another method involves the use of chemicals to reduce surface tension and/or create a foam to suppress the formation of acid mist. In the copper industry, it is common to use a suppressant such as a fluoropolymer (e.g., 3M's FC-1100) at a dosage level of 10–20 ppm, which does not interfere with SX phase disengagement. In the zinc industry, it is common to use compounds such as licorice to create a foam to mitigate acid misting (Cheng et al. 2004).

Impurity Treatment

Electrowinning follows processing that is used to remove impurities, so key impurities that cause problems in electrowinning are removed prior to electrowinning as part of solution purification (SX, precipitation, cementation, or ion exchange). Consequently, most related impurity removal technologies are described in other chapters. If a problematic impurity does enter the electrolyte, it is usually controlled by electrolyte bleeding. Bleeding is commonly employed in copper electrowinning and is used to control the concentration of iron, manganese, and/or chloride in the electrolyte. A small, continuous flow of electrolyte is typically sent back to solution purification (often the first stage of extraction in SX) to allow for copper to return to the tankhouse while reducing the transfer of the offending element.

Only the removal of lead and/or manganese are exceptions. Most electrowinning uses lead anodes that corrode during the process and generate lead corrosion products that fall to the bottoms of cells and can become suspended. To control lead contamination, cells must be periodically cleaned to remove lead-bearing sludge. The sludge can be manually removed or eliminated through the use of diaphragm pumps. The lead-bearing sludges are decanted, drummed, and returned for recycling of the lead content. Many electrowinning facilities also filter electrolyte to reduce the concentration of suspended lead-bearing particles. In zinc electrowinning, strontium carbonate is added to the electrolyte entering each cell to precipitate soluble lead as an insoluble salt to allow for the production of special high-grade zinc.

In zinc electrowinning, manganese dioxide will also form in significant quantity on the anode, cell walls, and within pipes. This requires periodic cleaning of cells, pipes, and anodes. The resulting sludge is used as an oxidant in solution purification.

SPECIFIC METALS

The preceding sections provided general descriptions of industrial metal electrowinning for aqueous solutions; however, many specific operating details are dependent on the metal being recovered. The specific details are caused by the electrochemistry of the system, the integration of electrowinning with upstream unit operations, and/or the market for the metal. In the following sections, more details are presented regarding the electrowinning of zinc, copper, nickel, and gold. Other metals, such as manganese, cobalt, cadmium, chromium, antimony, and tellurium, are also electrowon commercially (Habashi 1998).

Zinc

Zinc is the largest tonnage metal electrowon from water-based solutions. In 2014, approximately 12 Mt (million metric tons) of electrolytic refined zinc were produced (International Lead and Zinc Study Group 2015; International Zinc Association, n.d.). The electrowinning of zinc occurs after leaching with sulfuric acid and solution purification by neutralization, and zinc dust cementation produces a high-purity electrolyte. Traditionally, sphalerite concentrates are roasted to produce a zinc oxide calcine and sulfur dioxide (which will be converted in sulfuric acid or a sulfate-bearing fertilizer). The calcine is then leached using sulfuric acid. The resulting solution is purified through a multistep process by pH control to precipitate an iron-bearing residue and zinc dust cementation to remove inorganic contaminants. Finally, the neutral leach solution is mixed with return electrolyte from the cellhouse to produce commercial electrolyte for electrowinning. This process is called roast-leach-electrowin (Habashi 1998). In the past few decades, several zinc facilities have added or replaced roasting with direct leaching of concentrates using high temperature and pressure conditions. Pressure leach produces an elemental sulfur product, which reduces the need to find local markets for sulfuric acid or fertilizer (Sutherland 1988; Masters et al. 1989).

Electrowinning operating data from a survey of zinc smelters (Moats et al. 2010) is presented in Table 2. Each operation uses hundreds of cells. The cells are typically made of polymer concrete (Moats et al. 2008). Each cell contains 30–50 cathodes. The distance between cathodes is 64–90 mm. The size of cells and electrodes are different and reflect a drive toward higher productivity. Modern cellhouses use 3.0–3.4-m^2 plating area cathodes while older cells use 2.0- and 2.6-m^2 plating area cathodes (Martin et al. 2000).

Moats et al. (2008) surveyed 10 zinc cellhouses in more detail. From their data, cathodes are commercially pure (grade 1050 or 1070) strain-hardened aluminum alloys welded to a 6000 series (Al-Mg-Si) header bar. To facilitate zinc stripping, 60% of the cellhouses use separation aids. Cathode life varied from 10 to 33 months, and a correlation of cathode life and fluoride concentration in the electrolyte feed was found and is shown in Figure 12. Fluoride concentrate is also known to lead to pitting of the aluminum surface, which leads to stickers. *Stickers* are zinc deposits that stick to the aluminum mother blank. Stickers are minimized by routine brushing of the aluminum blanks.

Most anodes employed in zinc electrowinning are binary Pb-Ag alloys with Ag content ranging from 0.45% to 1%. Anodes are rolled or cast. Most operations precondition their anodes prior to their initial use employing either physical (sandblasting) or chemical/electrochemical means. Anode service life is impacted by anode composition, fabrication method (rolled or cast), current modulation (operation at too low or too high a current density), cell monitoring (i.e., how quickly short circuits are corrected), anode pretreatment method, anode cleaning cycles, and electrolyte composition. Anode lifetimes range from 24 to 72 months. Manganese concentration in the electrolyte is maintained at 2.5–5 g/L to facilitate the deposition of manganese dioxide (MnO_2) on the lead anodes and reduce their corrosion (Zhang and Cheng 2007).

Zinc cellhouses typically operate at cathode current densities around 500 A/m^2. To lower electricity costs, some operations will lower their current during times of high-cost, peak-power demand and increase them during the night or off-peak. Current densities can range from 240 to 690 A/m^2. Current efficiency is usually 88%–91%. Cell voltages and electrical power consumption are typically 3.2–3.5 V and 2,800–3,400 kW·h/t of zinc, respectively (Moats et al. 2008).

The electrolyte specifications for zinc production are quite stringent because of zinc's low standard reduction potential (–0.77 V vs. SHE). The concentrations of zinc and sulfuric acid are closely monitored with most plants operating with 45–65 g/L Zn and 160–200 g/L sulfuric acid (H_2SO_4). Electrolyte temperature is also controlled between 35° and 45°C with preference given to 37°–40°C. Electrolyte is heated by electrical resistance within each cell. To maintain electrolyte temperature, all cellhouses cool their electrolytes. Porter (1991) estimates that 3.5–4.0 GJ/t of zinc cathode is wasted through electrolyte heating.

The presence of too many impurities can lead to product contamination and/or low current efficiency caused by hydrogen evolution or re-solution of the zinc deposit. The effects of common impurities from Robinson and O'Keefe (1976) are listed in Table 3. An example of an electrolyte specification (Houlachi 2008) is presented in Table 4 along with reasons for the requirement. Impurities can

- Cause cathode purity issues (Pb, Cd, Cu),
- Lower current efficiency because of hydrogen evolution and re-solution of zinc (Ge, Sb, Co, Ni),
- Disrupt operations by enhancing corrosion (Cl),
- Cause zinc to stick to the aluminum mother blanks (F), and
- Lead to scaling of pipes and equipment (Ca).

Plating times are maintained between 24 and 72 hours to avoid re-solution caused by the deposition of impurities with lower hydrogen overvoltage such as nickel and cobalt.

Inorganic and organic additives are used to control and facilitate the production of special high-grade zinc. Organic compounds such as glue/gelatin, gum Arabic, and licorice are used. Glue/gelatin/gum Arabic are used to control the structure of the zinc deposit. Licorice is used to create a foam layer on top of the electrolyte and reduce the presence of

Table 2 Zinc electrowinning operating data from selected operations

Location	Hiroshima, Japan	Iijima, Japan	Kidd, Canada	Trail, Canada	Budel, Netherlands	Kokkola, Finland	Plovdiv, Bulgaria	Baiyin, China	San Luis Potosi, Mexico
Number of cells	360	680	660	548	432	840	468	416	384
Cell dimensions, m									
Depth	1.6	1.526	1.50	2.18	2.07	3.6	1.55	1.7	1.4
Width	0.9	0.89	0.99	1.22	1.47	1.97	0.94	0.95	1.2
Length	2.9	3,250/3,998	3.84	4.93	4.75	0.845	2.5	4.1	3.5
Cathodes per cell	33	48/58	40	50	44	44	27	44	44
Cathode–cathode distance, mm	75	64	75	89	90	75	75	75	73
Size of cathodes, mm									
Height	1,220	1,150	1,156	1,650	1,600	1,275	1,100	1,190	1,165
Width	800	800	660	1,025	902	698	666	800	765
Thickness	6	6	7	6.35	7	6	4	6	5
Cathode life, months	20	27	22	17	12	18	10	15	18
Number of stickers/d	126	N/D*	79	13	2	250	40	N/D	N/D
Plating area, m^2	1.67	1.67	1.35	3.07	2.6	1.55	1.28	1.16	1.8
Deposit time, h	24–48	24/48	30, max.	72	32	38	N/D	24	24
Current density, A/m^2	70–600	50–690	544.4	440	491	564	520	450	474
Cell voltage, V	2.8–3.5	2.6–3.5	3.5	3.41	3.26	3.5	3.6	3.2–3.4	3.3
Current efficiency, %	89.5	91.5	89–90	90–92	92.5	91.6	93	88–90	90.5
Power, kW·h/t	3,205	3,171	3,309	3,200	3,247	3,205	3,200	3,100–3,200	2,990
Stripping method	Automatic	N/D	Automatic	Automatic	Automatic	Automatic	Manual	Manual	Manual
Anodes per cell	34	49/59	41	51	45	45	28	45	45
Size of anodes, mm									
Height	1,164	1,070	1,053	1,570	1,605	1,245	1,055	1,170	1,122
Width	730	745	590	965	828	630	620	728	715
Thickness	10	6.5	8	10.75	14	8	8	7.3	8
Anode life, months	48	72	36	36	48	36	24	24	24
Anode material									
% Ag	0.75	0.8	0.75	0.75	0.5	0.7	1	1	0.75
Electrolyte									
Temperature, °C	40	44	37	37	45	39	34–36	35–42	42
Zn, g/L	50	53	65	55	50	53.8	50–60	45~55	65
H_2SO_4, g/L	190	160–190	203	165	180	170	160–175	160–180	185
Mg, g/L	10	15	1.6	3	10	15.7	3.3	2.5	4.5
Mn, g/L	15	5.5	3	2.4	5	5.5	2	5~10	7
Cl, mg/L	500	N/D	84	225	600	210	160	100	45
F, mg/L	10	N/D	5	30	5	31	25	20	9
Additives used									
Glue, kg/d	N/D	N/D	210–1,300	25.2	N/D	2.87	8	80	75
Gelatin, kg/d	N/D	66	22.5	N/D	30	N/D	0	N/D	N/D
Licorice, kg/d	N/D	N/D	0.19	63	7	N/D	0	N/D	N/D
Strontium carbonate, kg/d	100	531	5.6	800	350	580	150	330	6.5
K-Sb-tartrate, g/d	N/D	18	67.5	N/D	35	91	N/D	N/D	N/D

Source: Moats et al. 2010

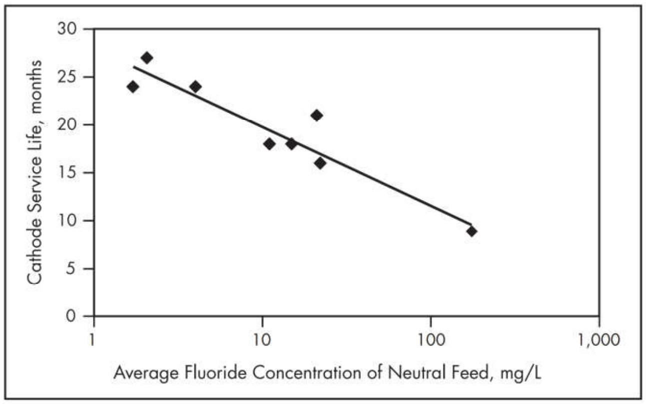
*N/D = no data provided.

acid mist within the cellhouse. Most operations add strontium carbonate to precipitate soluble lead from the electrolyte to reduce its contamination in the cathode. Some operations add soluble antimony to improve stripping and/or affect zinc electrodeposition.

Zinc cathode produced by electrowinning is rarely sold to market. Zinc refineries melt and cast their cathodes to produce ingots of various shapes, sizes, and composition. The ingots are produced to meet customer specifications.

Copper

Copper is the second largest tonnage metal electrowon from aqueous solutions. In 2016, nearly 3.9 Mt of electrowon copper were produced (International Copper Study Group 2017).



Source: Moats et al. 2008

Figure 12 Cathode service life versus fluoride concentration of the neutral feed

Copper electrowinning typically occurs after SX has concentrated copper while excluding most impurities from a leach solution. Detailed operating data from a selected number of newer copper tankhouses are presented in Table 5 (Robinson et al. 2013a). Newer tankhouses utilize polymer concrete cells, and older facilities can still use concrete lined with polyvinyl chloride (PVC) or lead. Newer cells contain 60–80 cathodes with older cells using less. The distance between cathodes is 95–105 mm. Most tankhouses use ~2.0-m^2 plating area cathodes.

Robinson et al. (2013a) surveyed 34 tankhouses. Most facilities use stainless-steel blanks while a few older plants are still using starter sheets. 316L is the most common grade of stainless steel used. 316L plates are inserted in copper hanger bars and typically welded into place. Blank life is a function of chloride concentration and less than 25 mg/L is recommended for 316L. Some facilities are using duplex stainless, which has low nickel levels, partially because of lower costs when the nickel price is high. Numerous older facilities have converted from starter sheets to stainless-steel blanks (Addison et al. 1999). As stainless-steel cathodes represent a multimillion-dollar capital investment, repairs are needed and can be done on-site (Valentine 2002).

Most copper electrowinning anodes use a rolled Pb-Ca-Sn plate soldered into a copper hanger bar that is covered in Pb. The typical Sn and Ca contents are 1.35% and 0.07%, respectively. Lead anode lifetimes are typically greater than 5 years, and some report lifetimes up to 10 years. Lead anode lifetime is affected by temperature, current density, power consistency, cobalt concentration, chloride concentration, and short circuiting (Rasmussen 1995).

Three tankhouses have converted to MMO-coated titanium anodes. MMO anodes use an iridium dioxide-tantalum oxide (IrO_2-Ta_2O_5) coating on commercial pure titanium mesh. Pieces of coated mesh are welded to titanium-clad copper conductor bars that are press fit into copper hanger bars. MMO anodes operate at lower potential than lead anodes (reported to be 13%–15%) and do not need cobalt in the electrolyte. MMO anodes, however, initially cost more and can suffer damage from short circuiting. Conversion to MMO anodes from Pb-alloy anodes will significantly depend on the electrical power costs of a facility (Moats 2008).

Table 3 Impurity effects on current efficiency and zinc purity

Elements	Effect	Comment
Al, Mg, Ca, Na	Little effect	Standard reduction potential more negative than zinc
Cd, Pb	Decrease cathode purity	Marginally more positive potentials than zinc; high hydrogen overpotential
Pt, Ag, Au, Fe, Co, Ni, Cu	Decrease current efficiency	More positive reduction potentials than zinc; low hydrogen overpotential
Sb, As, Ge, Se, Te	Complex, but usually a decrease in cathode efficiency	Can lead to localized corrosion cells and zinc redissolution

Source: Robinson and O'Keefe 1976

Table 4 Example of a zinc electrowinning electrolyte specification

Element	Value	Reason
Mg, g/L	<6	Higher solution viscosity and cell voltage
Mn, g/L	2.5–5.0	Protect anode coating, lower Cl_2 gas evolution
Fe, mg/L	<5	Indicator of purification problems
SiO_2, mg/L	<100	Settling and filtration problems
Ge, mg/L	<0.01	Poor current efficiency
Sb, mg/L	<0.02	Poor current efficiency
As, mg/L	<0.02	Poor current efficiency and potential arsine generation
Cu, mg/L	<0.1	Poor current efficiency and product contamination
Cd, mg/L	<0.3	Product contamination
Co, mg/L	<0.2	Poor current efficiency; re-solution after an induction period
Ni, mg/L	<0.2	Poor current efficiency; re-solution after an induction period
Tl, mg/L	<0.3	Product contamination, stripping
Ca, mg/L	<450	Gypsum buildup
F, mg/L	<30	Pitting aluminum, stickers, frequent brushing
Cl, mg/L	<250	Enhanced anode and cathode corrosion

Adapted from Houlachi 2008

Copper tankhouses typically operate at cathode current densities of 250–350 A/m^2, but some facilities can operate up to 400–450 A/m^2. Current efficiencies are usually between 88% and 92%. Cell voltages are typically 1.7–1.8 V for cells with MMO anodes and 1.9–2.1 V for cells with lead anodes, resulting in energy consumptions of 1.7–1.8 or 1.8–2.1 MW·h/t of copper, respectively (Robinson et al. 2013a).

The electrolyte specifications for copper production are less stringent than most other metals because copper's standard reduction potential (0.34 V vs. SHE) is more positive than most other metal impurities potentials as well as that of hydrogen. The concentrations of copper and sulfuric acid are monitored usually once or twice a shift with most plants operating with 35–45 g/L Cu and 160–200 g/L H_2SO_4. Electrolyte temperature will depend on whether the tankhouse is downstream from SX. If it is, then the temperature will be 35°–50°C to avoid overheating of the organic phase. If it is not, then higher temperatures are permissible with temperatures approaching 60°C at some plants. Because the current density employed at copper tankhouses is not as high as zinc electrowinning, electrolyte heating is less of an issue and no active cooling is necessary.

Common impurities that cause production issues in copper electrowinning electrolytes are iron, manganese, chloride, and SX organic. The reduction of ferric to ferrous ($E° = 0.77$ V vs. SHE) is thermodynamically preferred to copper electrodeposition. The presence of iron in the electrolyte causes a decrease in current efficiency, but not cathode contamination. The best methods to control iron concentration in the electrolyte is proper operation of the SX circuit or bleeding electrolyte back to the extraction circuit to recover copper and exclude iron.

Manganese in the electrolyte is oxidized by the anode. Oxidized manganese can cause (1) MnO_2 formation on MMO anodes, which could shorten anode lifetime if a blinding deposit occurs; (2) MnO_2 formation on lead anodes, which can disrupt the lead dioxide (PbO_2) scale, leading to cathode contamination and/or enhanced anode corrosion; or (3) permanganate formation, which can oxidize and damage the organic in SX (Cheng et al. 2000; Zhang and Cheng 2007). The best methods to mitigate manganese issues is to control manganese concentration by proper SX operation or electrolyte bleed and to maintain an Fe/Mn ratio ≥ 10 to avoid permanganate formation (Miller 2011).

Chloride in copper electrowinning electrolyte can be a problem for stainless-steel cathodes as it can cause pitting corrosion. Most cathode suppliers recommend chloride concentrations less than 25 mg/L. As with iron or manganese, chloride concentration is controlled by proper SX operation or electrolyte bleed. In operations where the chloride concentration of the pregnant leach solution is very high, SX requires a wash stage or two to mitigate chloride carryover to the tankhouse.

The last common impurity is organic from the SX circuit. Most operations have sand filters, dual-media filters, and/or Jameson cells to capture organic that leaves the SX circuit with the electrolyte. Filters should be routinely backwashed to minimize organic carryover. Organic in the cell can cause *organic burn* of the cathode (a blackish oxide near the solution line) and is a fire hazard.

Additives are used to control and facilitate the production of grade A copper cathode. Organic compounds such as guar, modified starch, or polyacrylamide are used as smoothing agents to produce dense copper cathode. A polyacrylamide has also been shown to inhibit MnO_2 formation on MMO anodes (Sandoval et al. 2013). Cobalt sulfate is added to maintain the cobalt concentration in the electrolyte near 150 mg/L to minimize lead anode corrosion and reduce cell voltage.

Acid mist generation is a concern in many copper tankhouses because a foaming agent cannot be used. A foaming agent would cause a significant phase disengagement problem in SX. Therefore, copper tankhouses use mist suppression balls, hoods, crossflow ventilation, and FC-1100 to reduce the generation of acid mist.

Electrowon copper cathode is often sold to market. Therefore, cathodes typically need to meet the London Metal Exchange or Commodity Exchange grade A specifications. These include composition and appearance criteria.

Nickel

Unlike zinc and copper, nickel electrowinning is always performed in separated cells (Crundwell et al. 2011). A diaphragm is needed to ensure that the pH near the cathode surface remains relatively high (pH >3) to avoid significant evolution of hydrogen gas. A diaphragm or bag is placed around a frame that contains either the cathode or anode. Anode bags are always used in chloride electrolyte. Cathode bags are typically used in sulfate electrolyte. To minimize migration of high-acidity electrolyte produced at the anode, higher pH catholyte is added to the top of each cathode. The solution flows through the diaphragm to the anode and is then removed as anolyte. Boric acid is added to the electrolyte as a buffer to help control the pH. Sodium lauryl sulfate is added at some locations to help release H_2 bubbles from the cathode surface, thus improving the quality of the deposit.

Nickel electrowinning is performed from chloride- or sulfate-based electrolytes. Electrowinning of nickel from chloride electrolyte is done with 0.8-m-wide, 1-m-deep anodes and cathodes interleaved in an electrolyte-filled rectangular cell. Nickel is electrowon on starter sheets or as *crowns* on masked stainless blanks. Nikkelverk's electrowinning plant produces nickel crowns as well as full cathode plates (Stensholt et al. 1988) that are used by the nickel-plating industry. They are produced by masking titanium mother blanks with polymer, except for unmasked circles where nickel electrodeposition can occur.

In nickel chloride electrowinning, coated titanium anodes are used. Lead alloy anodes are not used because they corrode quickly. Modern anodes are titanium coated with ruthenium and/or iridium oxide and other non–precious metal oxides. They are conductive but inert. Each anode is placed in a permeable polyester cloth bag topped with a solid polypropylene gas-collection *lid*. Chlorine and chlorine-saturated electrolyte (anolyte) are continuously drawn from each anode compartment by vacuum through an individual polymer tube.

Cell currents are typically 20–30 kA (~240 A/m^2 of cathode, both sides). Plating typically occurs for seven days and then the nickel cathodes are harvested. Current efficiency is 98%–99%. Each cell operates at ~3 V.

Industrial nickel from sulfate electrowinning is similar to industrial nickel from chloride electrowinning. The major difference is that chlorine is not generated at the anode. This means that lead alloy anodes can be used and anode bags do not have to be used. Anglo American Platinum commissioned a new nickel sulfate electrowinning tankhouse in 2011 using state-of-the-art equipment and technology at Rustenburg, South Africa (Hagemann et al. 2016). Permanent cathodes, mechanical stripping, anode skirts, and cell hoods are used to reduce worker exposure to aerosols and solutions that contain nickel sulfate and acid. The development and testing of the technology was performed in-house. Operational details from Rustenburg are presented in Table 6.

Gold

Gold electrowinning is usually performed in relatively small vessels or cells that are about 1 m long and contain less than 1 m^3 of solution. A schematic drawing and picture of gold electrowinning cells are provided in Figure 13. These cells often contain several cathodes and anodes, although there is one extra anode. The cathodes commonly consist of steel wool (30 kg/m^3) supported by a stainless-steel frame, and anodes are generally perforated stainless-steel plates or woven stainless-steel mesh (Wells et al. 1992). The cells generally operate between 2 and 5 V at a current density between 30 and 100 A/m^2 (Marsden and House 2006). The cells are designed to effectively recover most of the gold from solutions containing around 0.2 kg of dissolved gold per cubic meter of

Table 5 Copper electrowinning operating data from selected operations

Operation	Collahuasi	Gaby	Minera El Abra	Safford	Chino	Kansanshi
Location	Chile	Calama, Chile	Calama, Chile	Safford, AZ, USA	Santa Rita, NM, USA	Solwezi, Zambia
Date of survey	2013	2010	2013	2013	2013	2012
Date of commissioning	1997	2008	1996	2008	1986	2004
Nameplate cathode capacity, t/a	60,000	150,000	225,000	105,545	68,040	139,000
Actual cathode production, t	36,808	150,000	153,424	87,653	21,047	104,677
ANODES						
Type	Pb alloy	—*	Transitioning from Pb to Ti mixed metal oxide	Pb/Ca/Sn	Ti mixed metal oxide	Pb/Al/Ca
Lead anodes						Supplier: Castle Lead Works
Composition	98.55	98.6–98.4	98.585	Balance	—	Remainder
Pb, %	—	—	—	—	—	—
Sn, %	1.375	1.25–1.50	1.35	1.30–1.45	—	1.25–1.75
Ca, %	0.075	0.06–0.10	0.065	0.065–0.085	—	0.05–0.10
Sb, %	—	—	—	<0.0005	—	—
Other	—	0.005–0.02 Al	—	0.015 min Al	—	0.0005–0.02 Al
Rolled or cast	Rolled	Rolled	Rolled	Rolled	—	Cross rolled
Life before replacement, years	6	5	6	7–10	—	5
Blade length × width × t, mm	990 × 940 × 7.5	1,080 × 938 × 6	1,074 × 940 × 6	1,319 × 968 × 6.35	—	1193 × 922 × 6
Hanger bar material	Cu	Pb-covered Cu	Pb-covered Cu	Cu	—	Cu
Hanger bar protection	—	Soldered	—	Pb	—	6 mm Pb/6% Sb cast over bar and extending 54 mm below the bar
Bar/blade connection	Welded	—	Soldered	Welded	—	Full penetration weld
Anodes hung symmetrically or asymmetrically	Asymmetric	Symmetrically	Symmetrically	Symmetrically	—	Symmetrically
Anode/cathode spacers	—	Delta separator	Abra style	Hairpin insulator	—	3 PVC buttons per side
Titanium anodes						
Coating description	—	—	Mixed metal oxide	—	Mixed metal oxide	—
Mesh length × width × t, mm	—	—	935 × 940	—	952.5 × 889 × 3.175	—
Number of conductor bars	—	—	8	—	6	—
Header/mesh connection	—	—	Press fit	—	Press fit	—
Anodes hung symmetrically or asymmetrically	—	—	Symmetrically	—	Asymmetrically	—
Anode/cathode spacers	—	—	Abra style	—	3 PVC hairpins	—

(continues)

Table 5 Copper electrowinning operating data from selected operations (continued)

Operation	Collahuasi	Gaby	Minera El Abra	Safford	Chino	Kansanshi
CATHODES						
Plating time, days	6	6.5	5	7	7	6–7
Stainless steel or starter sheets	Stainless steel	Stainless steel	Stainless steel	316L stainless steel	Electrorefined starter sheets	Stainless steel
Cu starter sheets						
Length × width × thickness, mm	—	N/A	—	—	952 × 946 × 1.6	—
Mass after plating, kg	—	N/A	—	—	85–100	—
Hanging method	—	—	—	—	2 hanger strap loops	—
Stainless-steel blanks						
Technology provider	Kidd process	IsaKidd process	Kidd process	ISA process	—	Cathodex
Length × width × t, mm	1,220 × 1,040 × 3	1,132 × 1,018 × 3.25	1,018 × 1,232 × 3	1,300 × 1,000 × 3.25	—	1,193 × 922 × 3
Type of stainless steel	316L	316L 2B	Duplex	316L	—	316 L
Side edging	Strip	—	Xstrata-ICL	Side edge strip	—	Yes
Bottom edging	None	—	None	None	—	Yes
Hanger bar						
Type	—	Rectangular	Rectangular	Rectangular	—	Rectangular
Material	Cu	Cu-covered stainless steel	Cu	Cu-plated 316L SS	—	Cu
Height × width × length, mm	—	—	38 × 25 × 1,430	44 × 31 × 1,294	—	50 × 50 × 6,645
Joint between bar and blade	—	—	Welded	Intermittent weld	—	None
Mass each side, kg	35–40	—	32.5–37.5	50–60	—	40
Stripping method						
Manufacturer	Kidd	—	EPCM, AISCO, and MESCO	Outokumpu	—	MESCO
Water temperature, °C	80	70	65–85	70	—	70
Blanks/hour	300	—	300	320	—	50–70
Features	—	—	No.1—No. 2—No. 3	—	—	—
Washing	Yes	Yes	Yes—Yes—Yes	Yes	—	Yes
Stripping	Yes	Yes	Yes—Yes—Yes	Yes	—	Yes
Stacking	Yes	Yes	Yes—Yes—Yes	Yes	—	Yes
Sampling	Yes	Yes	No—No—No	No	—	Yes
Weighing	Yes	Yes	Yes—Yes—No	Yes	—	Yes
Strapping	No	Yes	—	Yes	—	Yes
Blank buffing	No	—	—	—	—	Yes
Cathode Cu						
Pb, ppm	<1		<3	<1	<0.3	1–4
S, ppm	6		<8	4	<8	2–8

(continues)

Table 5 Copper electrowinning operating data from selected operations (continued)

Operation	Collahuasi	Gaby	Minera El Abra	Safford	Chino	Kansanshi
CELLS						
Number	188	504	3 banks in operation, actually 486 cells	182	210 (80 in current operation)	320
Length × width × depth, m	6.3 × 1.27 × 1.4	6.42 × 1.30 × 1.386	6.57 × 1.30 × 1.40	7.63 × 1.18 × 1.63	6.8 × 1.2 × 1.3	7.06 × 1.144 × 1.57
Height above cell floor, m	0.49	—	1–2	0.052	0.76–0.91	1.5
Construction material	Polymer concrete	Polymer concrete	Polymer concrete	Polymer concrete	160 paralined concrete, 50 polymer concrete	Precast vinyl-ester resin concrete
Lining material	19-mm polypropylene	—	None	—	—	Vinyl-ester resin concrete
Capping board material	—	Polymer concrete and fiber-reinforced polymer	Polymer concrete	Protruded vinyl-ester fiberglass	Polyester, polyvinyl	Concrete
Intercell busbar	—	Triangular	Double-double Abra style	Double-double contact	Double-double contact	Floating null point, non-grounded system
Cross-sectional area, mm^2	—	—	855	2,904	1,140	—
Current density, A/mm^2	—	276.5/333.3	—	—	—	280–320
Anodes/cathodes per cell	61/60	60/61	67/66	145	—	70/69
Cathode–cathode centerline distance, mm	100	100	95	101.6	—	95
Cell inspection system	Gaussmeter	Yes	Infrared camera	—	Infrared camera	Manual
Inspections	Once per day	—	Once per shift	3 per day	2 per day	Daily
Mist suppression system						
Hoods	No	—	—	No	—	—
Balls	Yes	Yes	Yes	Yes	Removed	Yes
Ventilation	Yes	Outokumpu	Yes	No	Yes	—
Mist suppression reagents						
FC-1100	Yes	No	Yes	Yes	Yes	Yes
Mistop	No	—	—	—	—	No
Other	No	—	—	—	—	No
Concentration, mg/L	3	—	—	—	—	10
Consumption, kg/t cathode	0.13	—	—	—	—	0.15
Cell cleaned after (days)	130	120	—	90–100	No cell cleaning	180
ELECTRICAL						
Rectifiers, kA/V	38/207	4 at 40/491–40/539	4 of 45/400	0.135	4 at 18, 2 at 20, 2 at 8	21–55/160–175
Current per cell, kA	20	33	32–40	47	40 or 44 maximum	—
Cathode current density, A/m^2	170	276.5/333.3	255–315	253	250–300, 360 maximum	280
Cathode current efficiency, %	93	90	92	89.1	93	85
Anode–cathode voltage, V	—	1.95/2.14	1.89	1.877	1.8	2
Total AC energy conserved (MW·h/t)	1.9	—	1.74	1.8	1.80	2.63

(continues)

Table 5 Copper electrowinning operating data from selected operations (continued)

Operation	Collahuasi	Gaby	Minera El Abra	Safford	Chino	Kansanshi
ELECTROLYTE						
Total volume in plant, m^3	3,000	—	1,1700	5,800	2,410	5,000
Flow per cell, m^3/min	0.3	0.29	0.32	0.6	~0.18	0.25
Flow control system	—	Own design	One flowmeter per 340 cells	—	In-line ball valves on each section of cells	Total flow control with individual cell valves
Electrolyte distribution system and hole diameters	Manifold, 3 mm	—	No	Cell manifold, 6.35–9.525 mm	50-mm PVC inlet pipe, no manifold	Ring main, 4 mm
Electrolyte entering cells						
Cu, g/L	39	50	>36	36	38	50–60
H_2SO_4, g/L	190	157	170–200	185	170–180	160–190
Temperature, °C	47	44	40–44	47	32	50–55
Temperature control method	—	—	Thermometer	Heat exchangers	Heat exchangers	Heat exchanger
Circulation pumps	—	—	Horizontal centrifugal	—	Durco centrifugal	Yes
Electrolyte leaving cells						
Cu, g/L	37	35	>34	33.8	35	32–38
H_2SO_4, g/L	195	180	195	188.6	180–190	180–200
Temperature, °C	48	45	40–43	47	33	40
Fe^{2+}, g/L	0.2	—	0.5	0.55	1.0–1.5	1–2
Fe^{3+}, g/L	0.8	—	1.2	2.09	2.0–2.5	3–4
Co^{2+}, mg/L	150	150	180	160	15	100–130
Mn, mg/L	60	—	<40	66	300–400	350
Cl^-, mg/L	25	<30	<25	16	25	20
Smoothing reagent	DXG-F7	—	HydroStar	HydroStar	Cyquest N-900	Guar/starch
Addition rate, g/t cathode	175	250	>300	347–716	650	700
Cobalt addition, g/t cathode	1,300	365	Maintain 180 ppm	113	None	400
Electrolyte bleed, m^3/d	144	—	384	98	136	5
Bled to control	Mn	—	Fe^{3+}, Mn, Cl	Mn and Cl	Fe, Mn	Fe
Destination	E1	—	Solvent extraction wash and others	Solvent extraction E1, E2, or E3	Solvent extraction E1	Leach

Adapted from Robinson et al. 2013a
*A dash indicates no data provided.

solution. Most of the applied current is used by side reactions such as hydrogen production from water. The solution from the electrowinning cell is recirculated back to the stripping process to replenish the dissolved gold content. The steel wool cathodes that contain the deposited gold are harvested for subsequent refining after the weight of deposited gold exceeds the weight of the initial cathode.

LABORATORY AND PILOT TESTING

Sizing

Laboratory-scale or pilot testing of electrowinning can be performed using electrodes of 1 cm^2 to full commercial-size electrodes in cells of widely various sizes. As electrochemical reactions are surface area dependent, they typically adjust to changes in scale (electrode size). Thus, results in small experiments can predict large-scale operations well. Other features such as hydrodynamics, fluid flow, gas bubble movement, and/or particle settling do not necessarily scale well. Therefore, the selection of electrode and cell size is dependent on the phenomenon being studied.

Electrochemical Measurements

Basic electrochemical measurements use a potentiostat/galvanostat connected to a three-electrode cell as described earlier in the "Applied Fundamentals" section. A potentiostat/galvanostat is a high-impedance power supply that is often computer controlled. Depending on the experiment, potential is controlled and current is measured or vice versa. There are numerous electrochemical experiments that can be performed to study electrowinning. For more details, readers are directed to consult a text specific to electrochemical methods such as Bard and Faulkner (1980).

Pilot Testing

Electrowinning pilot testing is typically performed if (1) longer term phenomena are being studied, such as anode corrosion or deposit stress, or (2) the integration of electrowinning with upstream processing is being evaluated. Pilot electrowinning cells can also vary in size and shape. Sizing is typically dependent on the purpose of the test and the cost of operating the pilot cell. Usually, the smallest possible cells that accomplish the purpose of the test are used to minimize costs.

For pilot testing, a cell with electrodes, an electrolyte reservoir, a heat source, pump, power supply, and data recording system are the minimum equipment needed. Control of the electrolyte needs to be evaluated prior to the experiment. A decision concerning single-pass electrolyte use versus

Table 6 Operational parameters for a modern nickel electrowinning plant from sulfate electrolyte

Location: Rustenburg, South Africa, 2009	
Cathode production, t/a	20,000
Sulfate Electrolyte	
Ni, g/L	80 in, 50 out
Addition agents	Boric acid, guar gum
Temperature, °C	60–65
pH	3.5
Anodes	
Material	Lead alloy (0.6% Sn, 0.05% Sr)
Cathodes	
Material	Nickel starter sheets
Center-to-center distance apart, m	0.16
Number per cell	41 anodes, 40 cathodes
Plating time	6 + 2 days making starter sheets on Ti mother blanks
Cathode Compartment (construction materials)	Yes
Frame	Oregon pine
Membrane	Woven terylene
Cells	
Materials	Precast concrete
Inside length × width × height, m	6.6 × 1.2 × 1.2
Electrical	
Cell potential, V	3.6–3.9
Cathode current density, A/m^2	220
Current efficiency, %	97

Source: Crundwell et al. 2011

Courtesy of FLSmidth

Figure 13 Schematic drawing and photograph of gold electrowinning cells

electrolyte recirculation with ion replenishment and acid neutralization needs to be made. The continuous addition of smoothing or polarizing compounds is highly advised if metal deposition is being studied.

In an electrowinning cell, anodes are connected to the positive terminal of the power supply. Cathodes are attached to the negative. Cells and electrodes should be electrically operated similar to industry; that is anodes and cathodes are in parallel within a cell. Cells are connected in series.

Electrolyte flow rate to each cell should be controlled. Flow rate is usually selected to be similar to commercial cells in terms of average residence time, specific flow rate (electrolyte flow rate divided by surface area of cathodes or anodes), or decrease in metal concentration being plated.

The power supply should be sized to provide enough current and voltage to operate the pilot system. As most electrowinning systems operate with constant current, the power supply should be set to maximum voltage and controlled using the current setting.

Data recording can include cell voltage, oxidation-reduction potential, pH, and temperature. Measurement frequency will depend on the phenomena being studied and the duration of the pilot testing. Measurements can occur manually or automatically with a computer-controlled system.

Safety

As with any experiment, care must be given from a safety standpoint as electricity and highly conductive electrolytes and electrodes are used in electrowinning research. Additionally, most electrowinning solutions are highly corrosive and may contain hazardous compounds. Care must be given to safe and proper handling and disposal. Depending on the size and location of a pilot system, proper ventilation or mist capture may also be needed.

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