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Ralph White, James A. Trainham, John Newman, and Thomas W. Chapman

August 1976

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Potential-Selective Deposition of Copper from Solutions Containing Iron and Complexed with Chloride

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August, 1976

Abstract

The hydrometallurgy of copper may involve leaching of the metal from its ore with an aqueous solution containing cupric and ferric chloride. The subsequent deposition of copper from such a process stream is modeled here in an idealized electrochemical cell with a rotating-disk electrode. The potential distribution and concentration profiles within the diffusion layer are predicted for given potential differences between the electrode and the solution.

The cuprous ion, which is formed by the reduction of the complexed cupric ion at the electrode, is stabilized in the chloride solution and can react either at the electrode or with ferric species within the diffusion layer. The assumptions that this homogeneous reaction is fast and irreversible generates a reaction plane, whose position is shown in the concentration and potential profiles. In addition, the position of the reaction plane is plotted as a function of the potential difference between the electrode and the adjacent solution.

Predicted current-potential and current efficiency-potential curves
are also reported. Finally, the iron contamination of the deposited copper is estimated to be less than $10^{-5}$ atom percent for some cases.

Key words: hydrometallurgy, current efficiency, homogeneous reaction, simultaneous electrode reactions, migration effect, reaction plane, rotating-disk electrode.
Introduction

Among the numerous hydrometallurgical schemes for extraction and recovery of copper currently under consideration there are several which employ an aqueous chloride solution as a lixiviant. The tendency of chloride to form metal complexes provides high metal solubilities; and, in conjunction with a suitable oxidizing agent such as chlorine, oxygen, ferric ions or cupric ions, excess chloride facilitates rapid leaching of not only scrap metal but also sulfide ores such as chalcopyrite, CuFeS₂.

The possibility of regenerating a leaching agent such as ferric ions at an anode while depositing copper cathodically makes the prospect of direct electrolysis of copper chloride leach liquors attractive. There are, however, two major difficulties with this approach. First, copper deposits from chlorides in a rough, porous, or even powdery form under most operating conditions so that the copper product would probably require remelting. The second problem is that the pregnant leach liquors may contain oxidized species that could react in the electrolysis cell and cause low current efficiencies for metal deposition. For example, iron occurring in an ore, or as the leaching agent, may appear in the electrolysis cell as ferric ion and be reduced to ferrous ion at the cathode. This latter problem can be avoided by assuring reduction of the electrolyte prior to electrolysis, or by precipitating iron, to eliminate ferric ions, while using a diaphragm to prevent transport of ferric ions from the anode to the cathode. Nevertheless, it is interesting to investigate the quantitative effect of ferric ions
on the deposition of copper from chloride solutions to determine whether removal of ferric ions prior to electrolysis is necessary. In this paper we compute the cathodic current efficiency for deposition of copper from a copper chloride solution which contains high levels of ferric ions and identify some interesting phenomena that can occur in this situation. The current efficiency for a cupric chloride solution which contains no ferric ions is considered elsewhere.¹⁸

The process stream that results when copper ore containing iron is leached under mildly oxidizing conditions is presumed to contain the following ionic species in water at 25°C: CuCl⁺, FeCl²⁺, H⁺, and Cl⁻. Available stability constant data¹⁹,²⁰ indicate that these are the most stable forms of the possible cupric-chloride and ferric-chloride complex ions in chloride solutions. Subsequently, these complex ions will be referred to as the cupric and ferric species, respectively.

Deposition of copper from the process stream is assumed to involve two steps. The first step is the reduction of the cupric species:

\[
\text{CuCl}^+ + e^- + 2\text{Cl}^- \rightarrow \text{CuCl}_3^{2-} .
\] (1)

The second step is the reduction of the resulting cuprous-chloride complex ion (hereafter referred to as the cuprous species) to copper:

\[
\text{CuCl}_3^{2-} + e^- \rightarrow \text{Cu} + 3\text{Cl}^- .
\] (2)
Stability constant data$^{19,21}$ also indicate that this cuprous species is the most stable form of those possible in the solution considered here. It should be emphasized that the stability of the cuprous species enables it to exist at a much higher concentration than its counterpart could in other solutions, such as copper sulfate in aqueous sulfuric acid (see reference 22, for example).

Two additional electrode reactions are the cathodic deposition of iron

$$\text{FeCl}^+ + 2e^- \rightarrow \text{Fe} + \text{Cl}^- \quad (3)$$

by reduction of a ferrous-chloride complex ion, which is produced within the diffusion layer (see reaction 5), and the reduction of hydrogen ions to form dissolved hydrogen gas

$$\text{H}^+ + e^- \rightarrow \frac{1}{2} \text{H}_2 \quad (4)$$

This ferrous species, FeCl$^+$, is also considered to be the most stable form that could exist in this solution.$^{19}$

One could also conceive of the direct reduction of ferric to ferrous species on the electrode, and this would occur at quite positive electrode potentials (where copper and iron would, in fact, dissolve). However, the presence of the ferric species is incompatible with the simultaneous presence of the cuprous species, and the ferric species cannot exist in the region near the electrode in the range of potentials where reactions 1 and 2 may occur. Instead, in addition to its participation in reactions 1 and 2 at the rotating-
disk electrode, the cuprous species can diffuse away from the electrode and react with the ferric species, which is being transported toward the working electrode from the bulk solution, according to the following oxidation-reduction reaction:

\[ \text{CuCl}_2^- + \text{FeCl}_2^+ \rightarrow \text{CuCl}^+ + \text{FeCl}^+ + 2\text{Cl}^- \]  

(5)

This reaction occurs within the diffusion layer adjacent to the rotating-disk electrode. Since such ionic reactions are usually relatively rapid, reaction 5 is essentially equilibrated locally, and the treatment is similar to that for partial dissociation of bisulfate ions within a diffusion layer.23

The ferrous species produced by reaction 5 diffuses back into the bulk solution and is also transported toward the electrode (where it may react according to reaction 3).

The equilibrium constant \( K \) for reaction 5 can be estimated to be \( 1.43 \times 10^5 \) (kg/mole)\(^2\) by using standard electrode potentials as well as the stability-constant data referred to above. Because this is a large number, the analysis can be simplified by assuming that \( K \) is infinitely large. (Further work on this problem in which \( K \) is not set equal to infinity is contemplated.) As a consequence of the assumption that reaction 5 has an infinitely large equilibrium constant, a reaction plane forms within the diffusion layer and thereby separates it into two regions (see figure 1). Furthermore, because of this assumption the ferric species is absent in region 1 and the cuprous species is absent in region 2.
Figure 1. The separation into regions of a diffusion layer within which a fast oxidation-reduction reaction occurs with an infinitely large equilibrium constant.
Also of concern with this system is the possibility that the chloride complexing will stabilize the cuprous species to such an extent that iron is deposited in preference to copper. The standard electrode potentials of reactions with the chloride-complexed species were calculated from those of reactions of noncomplexed species and the stability constants from the literature. Table I shows that, at the potentials at which copper will begin to be plated, the ferrous ion is more stable than either the ferric ion or metallic iron, and this is true in both the complexed and noncomplexed systems.

The desired process in the electrochemical cell is the reduction of cupric species to deposited copper, which requires two electrons per copper atom deposited. The current efficiency will therefore be defined as the number of copper atoms deposited for each two electrons passed through the cell. The principal process which tends to reduce the current efficiency is the diffusion of cuprous species back into the solution where it can escape or lead to the indirect reduction of ferric species to ferrous according to reaction 5. Any reduction of ferrous ions to iron at the electrode will also lower the current efficiency as well as contaminate the deposit. In addition, the current efficiency is lowered by the reduction of hydrogen ions according to reaction 4.

The electrochemical cell used to model the physical phenomena discussed above consists of a rotating-disk electrode (the active portion of which is made either of copper or of an inert material such as platinum), a normal calomel reference electrode (whose standard electrode potential is 0.2676 V), a distant counterelectrode,
Table I. Standard electrode potentials with and without complexing by chloride, at 25°C.

<table>
<thead>
<tr>
<th>reaction</th>
<th>$U^0$, volt</th>
<th>noncomplexed</th>
<th>with chloride</th>
</tr>
</thead>
<tbody>
<tr>
<td>ferrous/ferric</td>
<td>0.771</td>
<td>0.745</td>
<td></td>
</tr>
<tr>
<td>cuprous/copper</td>
<td>0.521</td>
<td>0.233</td>
<td></td>
</tr>
<tr>
<td>cupric/copper</td>
<td>0.337</td>
<td>0.3355</td>
<td></td>
</tr>
<tr>
<td>cuprous/cupric</td>
<td>0.153</td>
<td>0.438</td>
<td></td>
</tr>
<tr>
<td>ferric/iron</td>
<td>-0.036</td>
<td>-0.0523</td>
<td></td>
</tr>
<tr>
<td>ferrous/iron</td>
<td>-0.440</td>
<td>-0.451</td>
<td></td>
</tr>
</tbody>
</table>
and a bulk solution of the same composition as the process stream. Deposition of copper from this electrochemical cell can be analyzed by applying dilute-electrolytic-solution theory with constant physical properties.\textsuperscript{22,24} The results of this analysis include concentration profiles of the ionic species within the diffusion layer on the electrode, current-potential curves, and current efficiencies for this system.

For convenience, the current density distribution was assumed to be uniform on the surface of the electrode. Newman\textsuperscript{25} showed how one should calculate the current distribution on a rotating-disk electrode, but consideration of the problem treated here at that level of sophistication is beyond the scope of this work. However, the results to be presented are applicable at the center of the disk.

Newman\textsuperscript{26} also showed that for the rotating-disk electrode, on which one electrode reaction occurs at its limiting value, the governing equations for electrolytic mass transfer are the same as those for other flow configurations. Consequently, the assumption that the results reported here are also applicable to other flow configurations\textsuperscript{26} should be a reasonable first approximation.

Governing Equations

The material-balance equations for the concentrations of the ionic species within the diffusion layer on a rotating-disk electrode are\textsuperscript{27}

\[
\left( \frac{D_i}{D_R} \right) c_i'' + 3 \zeta \frac{2}{R} c_i' + \left( \frac{z_i u F}{D_R} \right) \left( c_i \phi'' + c_i' \phi' \right) = 0 ,
\]  

(6)
where the prime denotes differentiation with respect to the dimensionless distance $\xi$. For the rotating disk

$$\xi = y/\delta ,$$  

(7)

where $y$ is the normal distance from the surface and $\delta$ is the thickness of the diffusion layer, expressed as

$$\delta = \left( \frac{3D_R}{a\nu} \right)^{1/3} \left( \frac{y}{\nu} \right)^{1/2} ,$$  

(8)

with $a = 0.51023262$. The position of the reaction plane, the ionic species concentration profiles, and the potential distribution can be determined by solution of these equations together with the condition of electroneutrality

$$\sum_i z_i c_i = 0 ,$$  

(9)

and the following boundary conditions.

The boundary conditions in the bulk solution are that

$$c_i \rightarrow c_{i\infty} \text{ as } \xi \rightarrow \infty .$$

At an arbitrary position, $\Phi$ can be specified, corresponding to the arbitrary zero of potential. At the reaction plane the boundary conditions are:

a. The total flux of each element (Cu, Fe, and Cl) as well as the flux of $H^+$ and dissolved $H_2$ is continuous.
b. The concentration of both the cuprous and the ferric species is zero.

c. The fluxes of ferric and cuprous species to the reaction plane are equal.

The boundary conditions at the rotating-disk electrode are that the normal component of the flux of species $i$ evaluated at the electrode surface is equal to the sum of its reaction rates:

$$
N_i = -z_i u_i F c_i \frac{d\phi}{dy} - D_i \frac{dc_i}{dy}
$$

$$
= - \sum_{j=1}^{m} \frac{s_{ij}}{n_j F}
$$

where $m$ is the number of reactions occurring at the electrode and $s_{ij}$ and $n_j$ are the stoichiometric coefficient of species $i$ and the number of electrons transferred in electrode reaction $j$ when written in the abstract form

$$
\sum_{i} s_{ij} z_i^{+} + n_j e^{-}
$$

The current density due to reaction $j$, $i_j$, was approximated by the Butler-Volmer equation:

$$
i_j = i_{o j} \left[ \exp \left( \frac{\alpha_{ij} F}{RT} \eta_{sj} \right) - \exp \left( - \frac{\alpha_{ij} F}{RT} \eta_{sj} \right) \right],
$$

where the composition dependence of the exchange current density was assumed to have the form
The symbol $i_{oj,\text{ref}}$ represents the exchange current density evaluated at the reference concentration of the ionic species, with $c_{i,\text{ref}} = 1 \text{ M}$, and at unit relative activity of the metallic species. In equation 13, $i$ ranges over the ionic species and $k$ over the metallic species. The relative activity of iron was taken to equal its mole fraction in the deposit, and the relative activity of copper was set equal to unity since little iron was expected to be deposited. Thus, $a_{Fe}$ was set equal to $0.5 i_3/i_2$, and the activity coefficient was ignored. The activity coefficient of iron should be greater than unity since iron and copper are not completely miscible, and consequently the deposition rate of iron should be even lower than that calculated here.

The transfer coefficients $\alpha_{aj}$ and $\alpha_{cj}$ are taken to sum to $n_j$. The exponents for both ionic and metallic species were given the values

$$\gamma_{ij} = q_{ij} + \frac{\alpha_{cj}}{n_j} s_{ij},$$

where $q_{ij} = -s_{ij}$ for a cathodic reactant and is zero otherwise.

The surface overpotential for reaction $j$ is

$$\eta_{sj} = V - \phi_o - U_{j,o},$$
where $V$ is the potential of the rotating disk, $\phi_0$ is the potential of the solution just outside the diffuse part of the double layer as measured by a reference electrode of a given kind, and $U_{j,0}$ is the theoretical open-circuit potential for reaction $j$ at the composition prevailing at the electrode surface -- again relative to the reference electrode of a given kind. For a normal calomel reference electrode,

$$U_{j,0} = U_j^0 - U_{\text{cal}}^0 - \frac{RT}{n_j F} \left[ \sum_i s_{ij} \ln \left( \frac{c_i^0}{\rho_i^0} \right) + \sum_k s_{kj} \ln a_k \right]$$

$$+ \frac{RT}{F} \ln \left( \frac{c_{\text{Cl}^-}^0}{\rho_{\text{Cl}^-}^0} \right).$$  

(16)

Here, $c_{\text{Cl}^-}^\lambda$ is the concentration of chloride ion in the reference electrode compartment, and the concentrations must be expressed in moles/liter if the usual tabulations of standard electrode potentials $U_j^0$ are to be used. Note that possible activity-coefficient corrections to the concentrations of the ionic species have been ignored.

Solution Technique

Equations 6 and 9 together with the above boundary conditions constitute a boundary-value problem involving coupled, ordinary, nonlinear, differential equations. The governing equations and boundary conditions were cast in finite-difference form accurate to order $h^2$, where $h$ is the dimensionless distance between mesh
points, and solved by a numerical solution technique developed by Newman. An interesting aspect of this problem is the unknown reaction plane position. In conditions b and c there is one more boundary condition than would be needed for a fixed plane position. Consequently, the plane position \( L \) must be treated as an unknown constant. To use the same computer subroutines, the treatment of this unknown constant was similar to that used by Newman for the eigenvalues of the Graetz problem.

Parameter values used to obtain numerical results are presented in Table II. Mobilities were calculated from the tabulated diffusion coefficients by means of the Nernst-Einstein relation, \( u_i = D_i / RT \). For the transfer coefficients, \( \alpha_{cj} = 0.5 \), and the exchange current densities, \( i_{0j,ref} \), for reactions 1 and 3 were given the value \( 10^{-3} \text{ A/cm}^2 \) while values of \( 5 \times 10^{-3} \) and \( 5.89 \times 10^{-3} \text{ A/cm}^2 \) were used for reactions 2 and 4, respectively.

Results

Results are presented for four cases. In case one, only reaction 1, the reduction of the cupric species to cuprous species, is permitted to occur at the electrode (see Table II). In the remaining cases, reactions 1, 2, 3, and 4 occur at the electrode. These separate cases emphasize the significance of multiple electrode reactions and the significance of the ratio of the bulk concentration of cupric species to ferric species. Table II gives the bulk concentrations for each case.

Figure 2 displays the dependence of the electric potential \( \Phi \) on the dimensionless distance from the electrode \( \xi \) for case one.
Table II. Parameter values.

<table>
<thead>
<tr>
<th>species</th>
<th>$10^5 D_i$</th>
<th>$c_{i\infty}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>cm$^2$/s</td>
<td>mol/l cases 1 and 2</td>
</tr>
<tr>
<td>CuCl$_3^{2-}$</td>
<td>$0.6^a$</td>
<td>0</td>
</tr>
<tr>
<td>CuCl$^+$</td>
<td>$0.6^a$</td>
<td>3</td>
</tr>
<tr>
<td>FeCl$_2^+$</td>
<td>$0.739^b$</td>
<td>0</td>
</tr>
<tr>
<td>FeCl$_2^{2+}$</td>
<td>$0.896^b$</td>
<td>1:5</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>$2.032^c$</td>
<td>6.1</td>
</tr>
<tr>
<td>H$^+$</td>
<td>$9.312^c$</td>
<td>0.1</td>
</tr>
<tr>
<td>H$_2$</td>
<td>$3.8^d$</td>
<td>$4.155 \times 10^{-10}$</td>
</tr>
</tbody>
</table>

T = 298.15 K \quad \nu = 0.010049 \text{ cm}^2/\text{s} \\
\rho_o = 0.99707 \text{ g/cm}^3 \quad \Omega = 261.8 \text{ rad/s}

$^a$ Taken from reference 3L.

$^b$ Because of a lack of data, the diffusion coefficients of the ferrous and ferric species were taken to be the same as those of ferrocyanide and ferricyanide ions, respectively, as given in table 75-1 of reference 22.

$^c$ Taken from table 75-1 of reference 22.

$^d$ This value was arbitrarily selected for this work (see John Newman and Limin Hsueh, "Currents Limited by Gas Solubility," Industrial and Engineering Chemistry Fundamentals, 9 (1970), 677-679).
Figure 2. Dependence of the electric potential on the dimensionless distance from the electrode when $V - \Phi_0 = -0.3545$ V and reaction 1 alone occurs at the electrode.
Two quantities of interest, $\phi_0$ and $\tilde{\phi}_0$, are illustrated in this figure. The potential in the solution at the electrode surface (just outside the diffuse double-layer) $\phi_0$ and the potential of the working electrode $V$ are used to form the potential difference $V - \phi_0$, which is related to the driving force for the electrode reaction (see equation 15).

The electric potential in the solution outside of the diffusion layer, $\tilde{\phi}$, extrapolated to the electrode surface is designated as $\tilde{\phi}_0$. Its value may be obtained by extrapolating Ohm's law,

$$i_T = \sum_{j=1}^{m} i_j = -\kappa_\infty \frac{d\tilde{\phi}}{dy}, \quad (17)$$

to the electrode surface from the bulk by using the previously calculated value of $i_T$ and the conductivity $\kappa_\infty$ of the bulk solution. The potential difference $V - \tilde{\phi}_0$ represents an alternative driving force for the electrode reaction. We might write for the total overpotential

$$\eta_{s_j} + \eta_{c_j} = V - \tilde{\phi}_0 - U_{j,\infty}, \quad (18)$$

where $\eta_{c_j}$ is the concentration overpotential for reaction $j$ and $U_{j,\infty}$ is the theoretical open-circuit potential for reaction $j$ at the bulk solution composition and the alloy composition of the deposit.

There is a difference between $\tilde{\phi}_0$ and $\phi_0$ because the conductivity varies with position in the diffusion layer and is not equal to $\kappa_\infty$ and because there exists a diffusion potential due to
the concentration variations and the different diffusion coefficients of the various species (see equation 125-7 of reference 22). These factors are accounted for when one solves simultaneously the coupled equations 6 and 9 across the diffusion layer to obtain the potential distribution in figure 2.

Figure 3 depicts the calculated concentration profiles of the ionic species within the diffusion layer that were obtained at the same potential difference. In this figure, the dimensionless distance from the electrode at which the concentration of both the cuprous and the ferric species is zero indicates the position of the reaction plane.

The calculated current density due to reaction 1 alone, \( \dot{i}_1 \), normalized by the current density predicted by the Levich equation\(^3\)

\[
i_{LD} = 0.62048 \frac{n_1 F c R_0}{s_{RL}} (\Omega V)^{1/2} \left( \frac{D_R}{\nu} \right)^{2/3},
\]

is presented in figure 4, as a function of the potential differences \( V - \Phi_0 \) and \( V - \Phi_0 \).

Figure 5 displays the calculated concentration profiles for case two with \( V - \Phi_0 = -0.3493 \) V.

In figure 6 the dimensionless position of the reaction plane \( L/\delta \) is presented as a function of the potential difference \( V - \Phi_0 \) for cases 1 and 2.

The total predicted dimensionless current density for case 2 is plotted in figure 7 as a function of the potential difference \( V - \Phi_0 \).
Figure 3. Dependence of the concentration of the various species on the dimensionless distance from the electrode for case 1 with $V - \phi_0 = -0.3545$ V.
Figure 4. The dimensionless current density when reaction 1 alone occurs at the electrode as a function of the potential differences $V - \Phi_0$ and $V - \phi_0$. 
Figure 5. Concentration profiles of the various species near the electrode for case 2 with $V - \phi_0 = -0.3493 \text{ V}$. 
Figure 6. Dependence of the dimensionless reaction plane position on $V - \hat{\Phi}_o$ for cases 1(---) and 2(---).
Figure 7. Dependence of the dimensionless current densities on $V - \Phi_0$ for case 2.
The current densities due to reactions 1 and 2 for case 2 are also plotted in figure 7. (The current density due to reactions 3 and 4 were too small to be plotted conveniently on figure 7.) These calculated current densities were used to calculate the current efficiency, $100 \times 2i_2/i_T$, as a function of the potential difference $V - \Phi_o$, which is plotted in figure 8. Also shown in figure 8 are the current efficiencies for cases 3 and 4.

Finally, the dependence of the relative surface concentration of the cupric, cuprous, and chloride species on $V - \Phi_o$ is presented in figure 9.

Discussion

The potential profile and the concentration profiles shown in figures 2, 3, and 5 are not smooth at the reaction plane because of the assumption that $K$ is infinite.

Consider first case one, where the only electrode reaction is the reduction of cupric to cuprous ions. The latter diffuse away from the electrode to the reaction plane, where they reduce ferric to ferrous ions, with regeneration of cupric. Some of the cuprous species also escapes by radial convection. The concentration profiles in figure 3 illustrate these processes. As the electric driving force is increased, the concentration of the limiting reactant, the cupric species, approaches zero, and the concentration of the product cuprous species at the electrode increases. Consequently, the position of the reaction plane moves away from the electrode, as also shown in figure 6. The position of the reaction plane is determined by a
Figure 8. Dependence of the current efficiency on $V - \Phi_0$.

$r = \frac{c_{\text{CuCl}^+}}{c_{\text{FeCl}^2+}}$, $r = 2, 1, \text{and} 0.5$ for cases 2, 3, and 4, respectively.
Figure 9. Dependence of the relative surface concentration of some of the ionic species present in the system on $V - \Phi_0$ for case 2.
balance of the transport of cuprous species from the electrode and the transport of ferric species from infinity. The ferrous species, the product of the plane reaction, also has accumulated toward the disk surface. The chloride ion is produced by reaction 5 at the plane and consumed by reaction 1 at the electrode, and the consequences of this are observed in the concentration profiles.

The current density for reaction 1 can exceed substantially the limiting value for convection and diffusion of the cupric species as given by the Levich equation. Figure 4 shows ratios as high as 2.12. This enhancement is due to ionic migration of the limiting reactant and the regeneration of the cupric species at the reaction plane. Since the cupric species is positively charged, it is attracted toward the cathode according to the potential distribution in figure 2. This effect of migration also accounts for the maximum in the concentration of the cupric species at the reaction plane and for the increase of concentration of the ferrous species toward the electrode (see figure 3), where this species is neither produced nor consumed. The effect of the reaction plane is, in essence, to bring the bulk concentration of the limiting reactant closer to the electrode, since the cupric species is produced at the plane by reaction 5, and this serves to increase the concentration gradient at the electrode.

Another way to think about this effect is to realize that the reduction of ferric to ferrous, which occurs at the plane, requires a supply of electrons from the electrode. The indirect supply of these electrons through the transport of cuprous species from the electrode to the plane contributes to a higher current density for
reaction 1. In fact, the reduction of ferric to ferrous requires a smaller electric driving force than the reduction of cupric to cuprous (see table I). When the reaction-plane distance has decreased to zero, the reduction of ferric to ferrous can proceed directly on the electrode, and the analysis would actually become simpler.

Figure 4 shows that $\phi_o - \phi$, the difference between the potential drop through the diffusion layer and that obtained by extrapolation with the bulk conductivity, is relatively small compared with the scale of potentials over which the current rises toward its limiting value. For the situation in figure 2, $\phi_o - \phi$ has the value of 19.9 mV.

For case two, we must now consider the additional effects associated with the possibility of depositing copper and iron on the electrode and also the possibility of evolving hydrogen gas at the electrode. The deposition of copper by reaction 2 consumes cuprous ions produced through reaction 1, and consequently less of the cuprous species remains to diffuse back into the solution. Comparison of the concentration profiles in figures 3 and 5 shows this reduction of the cuprous concentration at the surface. The reaction plane is now much closer to the electrode, as also depicted in figure 6. Comparison of the predicted reaction plane positions at small values of $-(V - \phi_o)$ for cases 1 and 2, as shown in figure 6, reveals that the reaction plane is further from the electrode in case 2, a result which is due to the dissolution of deposited copper according to reaction 2.
The current densities in figure 7 reflect the difference in the potentials of the two copper reactions (see table I). The current density due to reaction 1 is well along toward a limiting current -- the same limit shown in figure 4 -- before the current density due to reaction 2 becomes significant. The slight increase in the current density due to reaction 1 above the initial plateau is due to the increasingly larger concentration gradient of the limiting reactant as the reaction plane moves closer to the electrode (compare figures 3 and 5). The cupric species produced at the reaction plane can no longer escape by radial convection. Furthermore, the current density due to reaction 2 will increase the potential gradients and enhance further the migration of cupric ions toward the electrode from the bulk solution.

In order to avoid contamination of the deposit with iron, the electric driving force should not be made too large, according to the standard electrode potentials in table I. For example, the current density for reaction 3 is very small and can be used to estimate that less than $10^{-5}$ atom percent of the deposit is iron for values of $V - \Phi_o$ more positive than about $-0.51$ V. However, this estimate is probably high because the activity of iron was taken to equal the atom fraction, with neglect of the activity coefficient. Since the activity coefficient is greater than unity, the deposition of iron would be further impeded.

For such low rates of reaction 3, the low current efficiencies in figure 8 are mainly due to two causes: (1) "leakage" of cuprous...
species away from the electrode by radial convection and (2) consumption of cuprous species at the reaction plane. The latter is equivalent to the indirect current required for reduction of ferric to ferrous at the plane. Because the reduction of cupric and ferric species occurs at a lower electric driving force than reaction 2, the current efficiency increases with an increase in the electric driving force and approaches about 70.5, 55.7, and 39.5 percent for cases 2, 3, and 4, respectively. The maximum possible current efficiency is determined mainly by the ratio of ferric and cupric concentrations in the bulk solution. At still larger values of the electric driving force, the current efficiency would decrease due to the deposition of iron by reaction 3 and the evolution of hydrogen according to reaction 4.

For some cases the range of acceptable operating potential differences may be determined by the solubility limit of the cuprous species (approximately 1 M in the solutions studied here) and the maximum tolerable iron contamination of the deposit or hydrogen gas evolution. For case 2, figure 9 (also see figure 5) shows that operating at potential differences more positive than about -0.35 V could lead to undesirable precipitation of cuprous species. (For cases 3 and 4, \( \Phi_o - V \) should be at least 0.32 and 0.275 V, respectively, to avoid CuCl precipitation.) At the other extreme in the range of acceptable operating potential differences for case 2, the current density due to reaction 3 may be used to predict that the iron contamination of the deposited alloy would exceed \( 10^{-5} \) atom percent for \( V - \Phi_o \) values more negative than about -0.52 V. Further
reduction of $V - \tilde{\phi}_o$ would lead eventually to hydrogen gas evolution.
(The value of $V - \tilde{\phi}_o$ at which this may begin to occur for case 4
was predicted to be approximately $-0.789 \text{ V}$, for example.)

Another limiting situation is associated with the bulk chloride
concentration. Since chloride ions are consumed and liberated at
the electrode at rates which depend on $V - \tilde{\phi}_o$, a minimum in the
surface concentration of chloride ions exists, as shown in figure 9.
The implication of this minimum is that, for some bulk compositions,
the chloride ion concentration would vanish at the electrode, a
condition which may be considered undesirable because the complexing
of the species would be no longer ensured.

Summary and Conclusion

The results of this work are that one can predict for this
system: 1) the location of a hypothesized reaction plane; 2)
reasonable concentration profiles for the ionic species; 3) realistic
current-potential curves; 4) current efficiencies of about 70.5
55.7 and 39.5 percent for cases 2, 3, and 4, respectively; and
5) a copper product that can be at least 99.99999 percent pure.
Consequently, the design of an electrochemical cell to remove the
copper directly from the model process stream appears to be feasible
provided that problems with the physical structure of the copper
deposit can be avoided.
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Notation

\( a \) constant = 0.51023262
\( a_k \) relative activity of metal \( k \) in the deposit
\( c_i \) concentration of species \( i \), mol/l
\( c_{i,0} \) concentration of species \( i \) at the electrode surface, mol/l
\( c_{i,\infty} \) concentration of species \( i \) in the bulk solution, mol/l
\( c_{i,\text{ref}} \) reference concentration of species \( i \), mol/l
\( D_i \) diffusion coefficient of species \( i \), cm\(^2\)/s
\( D_R \) diffusion coefficient of the limiting reactant \((\text{CuCl}^+)\), cm\(^2\)/s

\( F \) Faraday's constant = 96,487 C/mol
\( h \) mesh size
\( i_j \) current density due to reaction \( j \), A/cm\(^2\)
\( i_T \) total current density, A/cm\(^2\)
\( i_{o,j} \) exchange current density, A/cm\(^2\)
\( i_{o,j,\text{ref}} \) reference exchange current density, A/cm\(^2\)
\( i_{LD} \) limiting current density due to diffusion (see equation 18), A/cm\(^2\)
\( K \) equilibrium constant for reaction 5, (kg/mol)\(^2\)
\( L \) position of the reaction plane, cm
number of rotating-disk electrode reactions

\( M_i \)

symbol for the chemical formula of species \( i \)

\( n_j \)

number of electrons transferred in reaction \( j \)

\( N_i \)

normal component of the flux of species \( i \), \( \text{mol/cm}^2 \cdot \text{s} \)

\( R \)

universal gas constant = \( 8.3143 \text{ J mol}^{-1} \text{K}^{-1} \)

\( s_{ij} \)

stoichiometric coefficient of species \( i \) in reaction \( j \)

\( T \)

absolute temperature, \( \text{K} \)

\( u_i \)

mobility of species \( i \), \( \text{cm}^2 \text{ mol}^{-1} \text{s}^{-1} \)

\( U_{j,o} \)

theoretical open-circuit potential for reaction \( j \) at the surface composition, \( \text{V} \)

\( U_j \)

standard electrode potential for reaction \( j \), \( \text{V} \)

\( U_{\text{cal}} \)

standard electrode potential of the calomel reference electrode, \( \text{V} \)

\( V \)

potential of the rotating-disk electrode, \( \text{V} \)

\( y \)

normal distance from the disk, \( \text{cm} \)

\( z_i \)

charge number of species \( i \)

\( \alpha_{aj} \)

anodic transfer coefficient for reaction \( j \)

\( \alpha_{cj} \)

cathodic transfer coefficient for reaction \( j \)

\( \gamma_{ij} \)

exponent in composition dependence of exchange current density

\( \delta \)

diffusion layer thickness, \( \text{cm} \)

\( \eta_{cj} \)

concentration overpotential for reaction \( j \), \( \text{V} \)

\( \eta_{bj} \)

surface overpotential for reaction \( j \), \( \text{V} \)

\( \kappa_{\infty} \)

bulk solution conductivity, \( \text{ohm}^{-1} \text{cm}^{-1} \)

\( \nu \)

kinematic viscosity of the solution, \( \text{cm}^2/\text{s} \)

\( \xi \)

dimensionless distance from the disk
\( \rho_0 \)  pure solvent density, g/cm\(^3\)
\( \phi \)  potential in the solution, V
\( \phi_0 \)  potential in the solution adjacent to the electrode surface, V
\( \tilde{\phi} \)  potential in the solution outside the diffusion layer, V
\( \tilde{\phi}_0 \)  potential in the bulk solution extrapolated to the surface of the rotating-disk electrode, V
\( \Omega \)  rotation speed of the disk, rad/s
References


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