Published in final edited form as:

Ind Eng Chem Res. 2011 July 11; 50(16): 9532–9538. doi:10.1021/ie200670g.

III. Co-electrodeposition/removal of copper and nickel in a spouted electrochemical reactor

Pengpeng Grimshaw, Joseph M. Calo*, and George Hradil

Brown University, School of Engineering, Providence, RI 02912, USA

Abstract

Results are presented of an investigation of co-electrodeposition of copper and nickel from acidic solution mixtures in a cylindrical spouted electrochemical reactor. The effects of solution pH, temperature, and applied current on metal removal/recovery rate, current efficiency, and corrosion of the deposited metals from the cathodic particles were examined under galvanostatic operation. The quantitative and qualitative behavior of co-electrodeposition of the two metals from their mixtures differs significantly from that of the individual single metal solutions. This is primarily attributed to the metal displacement reaction between Ni^0 and Cu^{2+} . This reaction effectively reduces copper corrosion, and amplifies that for nickel (at least at high concentrations). It also amplifies the separation of the deposition regimes of the two metals in time, which indicates that the recovery of each metal as a relatively pure deposit from the mixture is possible. It was also shown that nitrogen sparging considerably increases the observed net electrodeposition rates for both metals – considerably more so than from solutions with just the single metals alone. A numerical model of co-electrodeposition, corrosion, metal displacement, and mass transfer in the cylindrical spouted electrochemical reactor is presented that describes the behavior of the experimental copper and nickel removal data quite well.

1. Introduction

The co-removal/recovery of multiple metals from complex mixtures is of practical import in a number of applications, including electrowinning and the removal of multiple metal contaminants from water. Co-electrodeposition of copper and nickel and examination of the resultant alloy structures have been conducted in rotating cylinder electrodes for example.^{1,2,3} It has been shown that the co-electrodeposition of copper and nickel are not independent,¹ but that a displacement reaction occurs between deposited nickel metal and copper ion in solution.⁴ Bradley and Landolt⁵ reported on the electrodeposition-displacement reaction investigated with a pulsed current method. Bradley *et al.*⁶ and Scharfe *et al.*⁷ also studied the effects of metal displacement on electrodeposition. It has been shown that the properties of electrodeposited alloys differ from those of their cast analogs.^{8,9} Roy¹⁰ also reported on alloy structures formed using the displacement reaction. Shibahara *et al.*⁴ found that mixed-metal cubane-type clusters were involved in the displacement of a metal atom in the metal cluster by another metal atom, and Meuleman¹¹ reported that from one to four monolayers of nickel can be dissolved from Ni(Cu) layers by displacement and dissolution.

Copper electrodeposition from acidic solutions has been investigated in circulating particulate electrode systems.^{12,13,14,15} Nickel electrodeposition in the same experimental apparatus used here has also been investigated in our laboratory.¹⁶ Here we present results

*Corresponding Author: JMCalo@brown.edu. Tel: 401-863-1421. Fax: 401-863-9120.

on the *co-electrodeposition* of copper and nickel from mixtures in acidic solutions in a spouted electrochemical reactor. The effects of pH, temperature and nitrogen sparging on the net removal of the metals, corrosion and metal displacement rates of the co-deposited metals were investigated under galvanostatic conditions. These investigations were performed as part of the development of a Cyclic Electrowinning/Precipitation (CEP) system for the removal of complex mixtures of heavy metals at low concentrations from contaminated water.¹⁷

2. Experimental

2.1. Particulate Electrode System

The experimental spouted electrochemical reactor system and the experimental techniques used in the current work have been described elsewhere^{15,16} (the latter is an accompanying article), to which the reader is referred for the experimental details. As previously, the electrolyte solution was recirculated continuously from the solution holding tank through the draft tube in the spouted electrochemical reactor, and back again, while the conductive bed particles were circulated only in the spouted electrochemical reactor in a batchwise fashion. The particulate bed media were 2 mm diameter polymer beads, metallized with copper (Bead House LLC, CMC02.0/CP). The volume of conductive bed media used was 480 cm³, and the constant electrolyte solution flow rate used was 32.2 L min⁻¹.

2.2. Materials

The fresh solutions used for all the experiments consisted of 70g CuSO₄·5H₂O, (>98% and 70g NiSO₄·6H₂O, (>98% Aldrich) added to distilled and deionized water to a total volume of 18L, to produce a solution 0.015M and 0.018M in Ni²⁺ and Cu²⁺, respectively. 150g of Na₂SO₄ (granular, >99% Aldrich) and 200g H₃BO₃ (used to suppress hydrogen evolution and stabilize the pH in the vicinity of the cathode¹⁸) were also added to the solution, as well as sufficient sulfuric acid (1M, Mallinkrodt) and/or potassium hydroxide (1M, Fisher Scientific) to attain the desired pH. An automatic pH controller (Barnant, model HD-PHP) was used to maintain constant pH with potassium hydroxide solution. For the metal corrosion experiments, sulfuric acid solution was used for pH control with the same controller. A portable dissolved oxygen meter (Hach, LDO™ HQ10) was employed to measure the dissolved oxygen concentration in the electrolyte solution during the experiments.

2.3. Analytical and Experimental Procedures

Copper and nickel ion concentrations, measured at 324.754 nm and 221.647 nm, respectively, were determined with an Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES; Jobin Yvon, JY2000). Five calibration standards were used covering the range of 1-7 ppm nickel in a matrix of 2% HNO₃, as well as a zero (blank) standard of the 2% HNO₃ matrix.

Nitrogen sparging of the electrolyte solution in the holding tank was investigated to reduce the dissolved oxygen concentration and nickel corrosion rates. The sparger system used for this purpose is also described in the accompanying paper.¹⁶

Liquid samples for analysis were taken from the solution holding tank. Tests showed that the concentrations from samples taken simultaneously from the solution holding tank and directly from the spouted vessel were essentially the same. This is consistent with the well-mixed nature of the spouted vessel and the solution holding tank, and the short mean residence time in the solution holding tank (on the order of 15s), in comparison to the characteristic reaction time in the spouted vessel.

Copper and nickel corrosion experiments were conducted by first operating in the electrowinning mode, and then turning off the feeder current while maintaining constant electrolyte flow and particle recirculation, and monitoring the dissolved metal ion concentrations as a function of time.

3. Co-Electrodeposition Model

An electrochemical model, based upon a general approach for modeling the behavior of recirculating electrochemical reactors,^{19,20} and the single metal model developed to correlate/predict copper¹⁵ and nickel¹⁶ behavior in single metal solutions, was extended to simulate the co-removal of copper and nickel behavior with pH and temperature.

The principal reactions assumed to occur during copper and nickel electrowinning from acidic aqueous solutions are:^{15,16}

In addition to the preceding, the model must also take into account metal corrosion in the presence of oxygen and $[\text{H}^+]$ which oxidizes deposited metal on the particles in acidic solutions *via* the same reactions as previously identified:

Also, as discussed above, it was found that the metal displacement reaction:

is important in describing the behavior of copper and nickel co-electrodeposition.

All the assumptions that were used in developing the models for the electrodeposition behavior of the single metals^{15,16} were retained in the current model, including mass transfer

resistance and kinetic formulations. For galvanostatic operation, the corresponding total cathodic current balance is given by:

$$i=i_1+i_2+i_3=\frac{(z_1F/a)k_1C_1}{(1+k_1/k_La)}+\frac{(z_2F/a)k_2C_2}{(1+k_2/k_La)}+(z_3F/a)k_3C_3 \quad (8)$$

where the subscripts are: 1 = copper; 2 = nickel; and 3 = hydrogen, respectively; z_i , i_i and C_i are the corresponding charge, cathodic current density, and bulk phase concentration; F is Faraday's constant; k_j is the electrochemical reduction rate constant, which depends on the electrode overpotential according to the Tafel approximation;^{15,16,21} k_L is the mass transfer coefficient given by Pickett²² for a single layer packed bed electrode, and a is the interfacial surface area per unit volume. The resultant mass balances for the two metal cations are:

$$\frac{dC_1}{dt} = -k'_1C_1 + k_{c1} - k'_dC_1 \quad (9)$$

$$\frac{dC_2}{dt} = -k'_2C_2 + k_{c2} + k'_dC_1 \quad (10)$$

in which $k'_i = k_i / (1 + k_i / k_L a)$. Also, it is assumed that the metal displacement reaction is first order in the copper cation concentration, C_1 , with the rate constant k_d , and the k_{ci} are the apparent corrosion rate constants for the two metals, which are zeroth order in the metal cation concentration, and first order in DO and $[H^+]$.^{15,16,23}

Tafel kinetics parameter values for the copper, nickel and hydrogen cathodic reactions are presented in Table 1.

The model solution methodology is similar to that used previously,^{15,16} modified for the metal displacement reaction, as follows. An initial estimate of the metal displacement reaction rate constant was determined by fitting the Cu and Ni data to polynomials. From these fits, values of C_1 , C_2 , and dC_1/dt at the nickel maximum where $dC_2/dt = 0$, were found. From the sum of Eqns. (9) and (10), evaluated at the nickel maximum, and the experimental value (slope) measured from the Ni corrosion data, $(k'_dC_1 + k_{c2})_{\text{exp}}$:

$$k'_d = \frac{k'_2C_2 \Big|_{\text{max}} - (k'_dC_1 + k_{c2})_{\text{exp}}}{(C_1 \Big|_{\text{max}} - C_1 \Big|_{\text{exp}})} \quad (11)$$

$$k_{c2} = k'_2C_2 \Big|_{\text{max}} - k'_dC_1 \Big|_{\text{max}} \quad (12)$$

The sum of the slopes of the linear corrosion data for copper and nickel yield the value $(k_{c1} + k_{c2})_{\text{exp}}$, and

$$k_{c1} = (k_{c1} + k_{c2})_{\text{exp}} - k_{c2} \quad (13)$$

Using these values for k_d' , k_{c1} , and k_{c2} , the model was then solved for the copper and nickel cation concentrations in the following manner. For constant current density, i , beginning with the initial metal ion concentrations, C_{10} and C_{20} , the transcendental current balance [Eq. (8)] is solved to yield the cathodic potential, E . Eqns. (9) and (10) are then solved for the first time step using a Runge-Kutta, 4th order method.²⁸ These two steps are then repeated alternately, moving forward in time, until the desired time is reached.

A sum of least squares method was devised to determine the “best fit” set of parameter values for k_{c1} , k_{c2} , and k_d' . First, assuming the measured copper and nickel corrosion rates, the rate of the metal displacement reaction was adjusted to minimize the sum of least squares deviation of the initial portion of the nickel removal curve up to the nickel maximum where it is dominant. Next, the copper corrosion rate was adjusted to provide the “best fit” for the copper removal curve. The same was then done for the nickel removal curve. This process was repeated with the new fit corrosion rates until the resultant parameter values converged.

4. Results and Discussion

Results for co-electrodeposition of copper and nickel as a function of pH at 40°C are presented in Figure 2, and as a function of temperature at constant pH 4 in Figure 3, without nitrogen sparging. In these plots, the data points are the measured values, and the curves are the model results for copper and nickel, respectively. As shown, the model results are in reasonable agreement with the data. Copper deposits first and nickel second, consistent with their respective standard reduction potentials. The behavior of the copper and nickel overpotentials, $\eta = E - E_e$, determined from the model, reflect these observations, exhibiting a larger, negative overpotential for copper than nickel over the entire experiment. A sharp change in the overpotential occurs for both metals over the region where copper deposition cuts off. For example, at pH 4, 40°C, 10A, copper initially deposits very rapidly up to about 110 min, which is where the nickel maximum occurs. Over this region, the overpotential for copper increases slightly (averaging about -230 mV), while that for nickel is positive and decreases slightly (averaging about +150 mV). Over the region where copper electrodeposition ceases (*ca.* 110 – 130 min), both the copper and nickel overpotentials are negative and decrease rapidly (*i.e.*, become more negative) as nickel begins to electrodeposit. The model results also indicate that the copper electrodeposition rate constant and the mass transfer coefficient become approximately equal (*i.e.*, $k_L a/k_1 = 1$) at about 110 min, while the same occurred for nickel (*i.e.*, $k_L a/k_2 = 1$) at about 400 min.

For electrodeposition of just copper from acidic solutions in the same apparatus used in the current work, it was found that the net rate increased with increasing pH and decreasing temperature,¹⁵ while for solutions containing just nickel, the behavior with pH was similar, but the net rate *increased* with temperature over the range of parameter values investigated.¹⁶ As shown in Figures 2 and 3, for co-electrodeposition, copper generally behaved as previously, except with a much more rapid net removal rate. Nickel behavior, however, was more complex, such that the maximum net electrodeposition rate occurred at about pH 4. Also, from the results in Figure 3 at constant pH 4, the maximum co-electrodeposition rates occurred at a temperature of about 30°C for copper and about 40°C for nickel.

The nickel maxima observed at relative concentration ratios (C_i/C_{i0}) of about 1.05 - 1.2 in Figures 2 and 3 are attributed to the metal displacement (oxidation) reaction of Ni^0 by Cu^{++} [Eq. (7)]. Metal displacement reactions are well known^{29,30} and are used commercially in applications such as the “cementation” of silver,³¹ for example. These reactions can also result in significant quantitative and qualitative differences between the electrochemical removal of metals from single metal aqueous solutions and from solutions of multiple metal mixtures.

From the preceding, the metal displacement reaction between copper ion and nickel metal [Eq. (7)] can effectively decrease/reverse the net rate of copper corrosion, accelerate the rate of copper removal, increase the net rate of nickel corrosion, at least initially, and also amplify the separation of the deposition regimes of the two metals in time. The latter suggests that the recovery of each metal as a relatively pure deposit layer may be possible by using such strategies as employing different sets of particulate electrodes at the appropriate times, for example.

In addition to the nickel maxima evident in Figures 2 and 3, the effects of the displacement reaction between copper and nickel are quite evident in the metal corrosion experiments as well. In Figure 4 are presented corrosion results at 40°C as a function of solution pH without nitrogen sparging. As noted, the concentration of nickel ion increases with time at all the pH values, while the concentration of copper ion also increases with time at low pH (2.5 and 3.0). With increasing pH, however, the rate (i.e., the slope) decreases to zero, and the copper ion concentration thereafter decreases with time with increasing pH; and increasingly so with pH.

At pH 4, the copper concentration only decreases with time, and the rate (slope) becomes more negative with increasing temperature in the absence of an applied current. This behavior is directly attributable to the metal displacement reaction. With the current off, the electrodeposition rate terms are zero, and the resultant expressions can be solved to yield:

$$C_1 = (C'_{10} - \frac{k_{c1}}{k'_d}) \exp(-k'_d t) + \frac{k_{c1}}{k'_d} \quad (14)$$

$$C_2 = (C'_{10} + C'_{20}) - \frac{k_{c1}}{k'_d} + (k_{c1} + k_{c2})t - (C'_{10} - \frac{k_{c1}}{k'_d}) (\exp(-k'_d t)) \quad (15)$$

where C'_{10} and C'_{20} are, respectively, the copper and nickel cation concentrations at the point where the feeder current is turned off. From Eq. (14), it can be concluded that the copper cation concentration can exhibit two regimes of behavior, depending on the relative magnitudes of k_{c1} and k'_d : corrosion rate-control for $k'_d \gg k_{c1}$ where the copper cation concentration increases with time after current shut-off; and displacement rate control for $k_{c1} \ll k'_d$ where the copper cation concentration decreases with time after current shut-off. The results here demonstrate both types of behavior depending on temperature, pH, and copper cation concentration at the time of current shut-off. If the argument of the exponential is relatively small, the resultant behavior will be approximately linear in time; i.e.,

$$C_1 = C'_{10} + (k_{c1} - k'_d C'_{10})t \quad (16)$$

$$C_2 = C'_{20} + (k_{c2} + k'_d C'_{10})t \quad (17)$$

From Figure 4, the corrosion data are indeed approximately linear in time, consistent with these expressions, and thus the kinetics are close to zeroth order, at least over this timescale.

Experimentally determined net corrosion rates for copper and nickel from experiments without nitrogen sparging are summarized in Table 2, along with the final “best fit” parameter values determined from the model, as described above. As shown, the experimental rates obtained by shutting off the current agree reasonably well with the values obtained from the model fits. The “fit” net corrosion values were consistently less than the measured values, but were quite close for the constant pH 4 data; however, they differ a bit more (by about a factor of 2-3 or so) for the isothermal 40°C data as a function of pH. This supports our conclusion that the essential elements of the system are reasonably well captured by the simple model.

For the isothermal copper data (@40°C) at low pH (3.0 and 3.5), the corrosion rate is greater than the metal displacement rate, while the reverse is true at higher pH (4.0 and 4.5) where the corrosion rates are less. Consequently, the resultant slopes for the isothermal “corrosion” data for copper exhibit a transition from positive to negative with increasing pH. As a function of temperature at a constant pH of 4, the copper behavior is dominated by metal displacement, such that the “corrosion” curves exhibit only negative slopes. These slopes become increasingly negative with increasing pH, reflective of the Arrhenius temperature dependence of the displacement rate constant. This differs from the behavior observed in acidic solutions containing just copper¹⁵ or nickel,¹⁶ in which it was found that the corrosion rates were always positive; i.e., the metal ion concentrations always increased with time when the current was turned off. For nickel, however, both the corrosion and displacement reactions act in the same direction to monotonically increase the concentration of nickel ion in solution, such that the resultant slopes can only be positive, as previously discussed. As shown in Table 2, the corrosion rates for nickel increase monotonically with temperature and decreasing pH.

Fricoteaux and Douglade³² and Pourbaix³³ found that Cu₂O formation can occur at pH ≥ 3.0 *via*:

The deposited cuprous oxide would then further inhibit the metal displacement reaction. The higher the pH, the more facile the production of copper oxide, which may at least partially explain why the nickel displacement reaction rate decreases with increasing pH. A power law fit of the displacement reaction rate constant data as a function of pH from Table 2, indicates that the rate constant is proportional to $[\text{H}^{+}]^{-0.72}$ at 40°C. Also, from the results in Table 2, the metal displacement reaction rate constant is Arrhenius temperature-dependent with an apparent activation energy of 47.2 kJ/mol at a constant pH of 4.

The behavior of the DO concentration data with time, corresponding to the electrodeposition data in Figures 2 and 3, is presented in Figure 5. As shown, upon initiation of electrowinning, the DO concentration increases rapidly, exhibits a maximum, and then gradually decreases again. This behavior is similar to that observed for nickel electrodeposition alone.¹⁶ The DO concentration increases up to pH 4, and then decreases with increasing pH beyond that point. Also, as shown, it first increases with temperature (at

constant pH 4) to 40°C, and then decreases thereafter. This behavior can be understood in terms of the model presented here, as discussed elsewhere.¹⁶

In Figure 2 it is noted that the net copper electrodeposition rate increases with *increasing* pH and *decreasing* temperature. This was also noted in previous work with just copper in solution.¹⁵ This differs somewhat from the behavior of solutions with just nickel present, where the electrodeposition rate increases with both *increasing* pH and temperature.¹⁶ These observations are attributed to the relative effectiveness of the net electrodeposition rate in comparison to the corrosion rate. In the case of nickel, the corrosion rate increases with both temperature and decreasing pH, but not as rapidly with temperature as observed for copper.

As was found for both copper and nickel solutions, sparging with an inert gas reduces the dissolved oxygen concentration and, consequently, the corrosion rate.^{15,16} In Figure 6 are presented co-electrodeposition data with nitrogen sparging for copper/nickel solutions as a function of pH at 40°C, 10A. The data from Figure 2 for pH 4, 40°C, 10A, are also presented for comparison. As shown, nitrogen sparging considerably increases the observed net electrodeposition rates for both metals – considerably more so than was observed from solutions with just the single metals alone.^{15,16}

Corrosion rate results following co-electrodeposition of copper and nickel are summarized in Table 3. As shown, the total corrosion rates for both metals were reduced by about a factor 2-3 with nitrogen sparging. The reduction in corrosion rates increases the negative slopes of the copper curves, and decreases the positive slopes of the nickel curves, decreasing the inhibition of the displacement reaction which accelerates copper and nickel removal rates to a greater degree than shown in Figures 2 and 3 without nitrogen sparging.

In Figure 7 are presented the sum of the copper and nickel cation concentrations as a function of time (at 40°C, 10A) with pH as a parameter from the results in Figure 2. Summation of the differential mass balances for the two cations [Eqns. (9) and (10)] eliminates the metal displacement reaction terms, so that these curves represent the net effect of just metal electrodeposition and corrosion. As shown, the resultant curves are approximately linear over the entire range, with a slope that gradually increases with pH, except for the data with pH 4.5. This behavior is attributed to galvanostatic operation under conditions where the operating current is less than the limiting current. Under these conditions, it has been shown that the concentration of the metal cations decreases linearly with time.^{20,34} The increasing (negative) slope with pH is attributed to diminution of the net corrosion rate with pH, with the exception of the slope for pH 4.5, where the effects of corrosion are minimal, but where the net metal electrodeposition rate is also slowing.

5. Conclusion

The spouted electrochemical reactor system exhibited good performance for the co-electrodeposition of copper and nickel from acidic aqueous mixtures. The quantitative and qualitative behavior of the removal of the metals from their mixtures was significantly different from that of the corresponding single metal solutions. This is attributed primarily to the metal displacement reaction between Ni and Cu²⁺. The latter effectively eliminated the copper corrosion reaction and augmented that for nickel, at least initially. It also amplified the separation of the deposition regimes in time for both metals, indicating that the recovery of each as a relatively pure metal deposit was possible under certain conditions. It was shown that nitrogen sparging considerably increases the observed net electrodeposition rates for both metals – considerably more so than from solutions with just the single metals alone.^{15,16} These data have been useful in the design and operation of a cyclic

electrowinning/precipitation (CEP) system for the removal of complex heavy metal mixtures from contaminated water.¹⁷

The electrochemical kinetics of the spouted bed particulate electrode was reasonably well described by a batch kinetic model based on the Tafel equations, incorporating a constant corrosion rate as an approximation, and the metal displacement reaction. The kinetic rate constant of the Ni-Cu²⁺ reaction was found to be Arrhenius temperature dependent with an apparent activation energy of 47.2 kJ/mol at a constant pH of 4, and a negative order dependence on pH.

Acknowledgments

This work was supported by grant #5 P42 ES013660 from the National Institute of Environmental Health Sciences (NIEHS), NIH. The authors also wish to thank Dr. D. Murray and Mr. J.R. Orchard of the Geological Sciences Department of Brown University for analytical assistance.

References

1. Landolt D. Electrochemical and materials science aspects of alloy deposition. *Electrochim Acta*. 1994; 39(8-9):1075–1099.
2. Chassaing E, Vu Quang K. Mechanism of copper-nickel alloy electrodeposition. *J Appl Electrochem*. 1987; 17(6):1267–1280.
3. Glibin VP, Kuznetsov BV, Vorobyova TN. Investigation of the thermodynamic properties of Cu–Ni alloys obtained by electrodeposition or by casting. *J Alloys Compounds*. 2005; 386:139–143.
4. Shibahara T, Asano T, Sakane G. Metal Replacement Reactions of Mixed-Metal Cubane-Type Clusters [Mo₃MS₄(H₂O)₁₀]4+ (M = Fe, Ni). *Polyhedron*. 1991; 10(19):2351–2352.
5. Bradley PE, Landolt D. A surface coverage model for pulse-plating of binary alloys exhibiting a displacement reaction. *Electrochim Acta*. 1997; 42(6):993–1003.
6. Bradley PE, Roy S, Landolt D. Pulse-plating of copper–nickel alloys from a sulfamate solution. *J Chem Soc Faraday Trans*. 1996; 92:4015–4019.
7. Scharfe RR, Sastri VS, Chakrabarti CL. Kinetics of Displacement of Ni(II) by Cu(II) in Bis(dithiocarbamate)nickel(II). *Can J Chem*. 1972; 50:3384–3386.
8. Bories C, Bonino JP, Rousset A. Structure and thermal stability of zinc–nickel electrodeposits. *J Appl Electrochem*. 1999; 29(9):1045–1051.
9. Vorobyova TN, Bobrovskaya VP, Sviridov VV. The composition and structure of electrodeposited copper–tin alloy films. *Met Finishing*. 1997; 95(11):14–20.
10. Roy S. Electrodeposition of compositionally modulated alloys by a electrodeposition–displacement reaction method. *Surf Coat Tech*. 1998; 105(3):202–205.
11. Meuleman WRA, Roy S, Péter L, Varga I. Effect of Current and Potential Waveforms on Sublayer Thickness of Electrodeposited Copper-Nickel Multilayers. *J Electrochem Soc*. 2002; 149(10):C479–C486.
12. Jiricny V, Roy A, Evans JW. Copper electrowinning using spouted bed electrodes: Part I. Experiments with oxygen evolution or matte oxidation at the anode. *Metall Mat Trans B: Proc Metall Mat Proc Sci*. 2002; 33B(5):669–676.
13. Jiricny V, Roy A, Evans JW. Copper electrowinning using spouted-bed electrodes: Part II. Copper electrowinning with ferrous ion oxidation as the anodic reaction. *Metall Mat Trans B: Proc Metall Mat Proc Sci*. 2002; 33B(5):677–683.
14. Evans JW, Ding R, Doyle FM, Jiricny V. Copper electrodeposition onto extended surface area electrodes and the treatment of copper-containing waste streams. *Scand J Metall*. 2005; 34(6):363–368.
15. Shirvanian PA, Calo JM. Copper recovery in a particulate spouted bed electrode. *J Appl Electrochem*. 2005; 35(1):101–111.
16. Grimshaw P, Calo JM, Shirvanian PA, Hradil G II. Electrodeposition/removal of nickel from acidic solutions with a spouted electrochemical reactor. *Ind Eng Chem Res*. 2011 submitted.

17. Grimshaw P, Calo JM, Hradil G. Cyclic Electrowinning/Precipitation (CEP) System for the Removal of Heavy Metal Mixtures From Aqueous Solutions. *Chem Eng J*. 2011 submitted.
18. Kelly JJ, Goods SH, Talin AA, Hachman JT. Electrodeposition of Ni from Low-Temperature Sulfamate Electrolytes (2006). *J Electrochem Soc*. 2006; 153(5):C318–C324.
19. Scott K. Reactor Modelling for Electrochemical Processes. *J Chem Tech Biotechnol*. 1992; 54:257–266.
20. Walker ATS, Wragg AA. The modeling of concentration-time relationships in recirculating electrochemical reactor systems. *Electrochim Acta*. 1977; 22(10):1129–1134.
21. Rieger, PH. *Electrochemistry*. Prentice-Hall; Englewood Cliffs, NJ: 1987.
22. Pickett, DJ. *Electrochemical Reactor Design*. 2nd. Elsevier; Amsterdam: 1979.
23. Ives DJG, Rawson AE. Copper Corrosion. II. Kinetic Studies. *J Electrochem Soc*. 1962; 109(6): 452–457.
24. Cifuentes L, Simpson J. Temperature dependence of the cathodic and anodic kinetics in a copper electrowinning cell based on reactive electrodialysis. *Chem Eng Sci*. 2005; 60:4915–4923.
25. Mohanty US, Tripathy BC, Singh P, Das SC. Effect of Cd²⁺ on the electrodeposition of nickel from sulfate solutions. Part II. Polarisation behaviour. *J Electroanal Chem*. 2004; 566:47–52.
26. Son SH, Chung DW, Kwon DC, Lee HK. A kinetic study on the electrodeposition of Ni-Cr alloy on copper for embedded resistor layer in PCB. *Adv Mat Res*. 2008; 47-50:754–757.
27. Conway, BE. *Electrochemical Data*. Elsevier; Amsterdam: 1952.
28. Nakamura, J. *Applied Numerical Methods With Software*. Prentice Hall; Upper Saddle River, NJ: 1991.
29. Massé N, Piron DL. Simulation of Copper Cementation (Metal Displacement Reactions). *J Electrochem Soc*. 1993; 140(10):2818–2824.
30. Ritchie IM, Roberston SG. A capacitance study of the silver(I)/copper displacement reaction. *J Appl Electrochem*. 1999; 27(1):59–63.
31. Timur S, Cetinkaya O, Ertürk S, Orhan G. Investigating silver cementation from nitrate solutions by copper in forced convection systems. *Miner Met Process*. 2005; 22(4):205–210.
32. Fricoteaux P, Douglade J. A study of electroless displacement of cobalt by copper during the electrochemical preparation of Cu–Co alloy multilayers by pulse polarization. *Surf Coat Tech*. 2004; 184(1):63–68.
33. Pourbaix, M. *Atlas des equilibres electrochimiques it 25°C*. Gauthiers-Villars & Cie; Paris: 1963.
34. Stankovic VD, Wragg AA. Modelling of time-dependent performance criteria in a three-dimensional cell system during batch recirculation copper recovery. *J Appl Electrochem*. 1995; 25(6):565–573.

Figure 1. Galvanostatic co-electrodeposition of copper and nickel in the spouted particulate electrode as a function of solution pH at 40°C, 10A without nitrogen sparging.

Figure 2. Galvanostatic co-electrodeposition of copper and nickel in the spouted particulate electrode as a function of solution temperature at pH 4, 10A without nitrogen sparging.

Figure 3.

Copper and nickel ion concentrations during “corrosion” studies with no applied current as a function of solution pH at 40°C, without nitrogen sparging.

Figure 4. Corresponding dissolved oxygen concentrations for the Cu/Ni co-electrodeposition data presented in Figures 1 and 2.

Figure 5. Normalized copper and nickel concentrations at a constant solution temperature of 40°C as a function of solution pH with nitrogen sparging. The bold solid and dashed curves without data symbols are the data for copper and nickel removal/recovery without nitrogen sparging at pH 4, 40°C, 10A, from Figure 1 for comparison.

Figure 6. Normalized sum of copper and nickel ion concentrations from Figure 1 as a function of pH at 40°C, 10A.

Table 1Tafel kinetics parameter values used in the Cu/Ni co-electrodeposition model.²¹

Cathodic Reaction	Transfer coefficient, α	Exchange current density, A m ⁻²	Enthalpy of activation (kJ mol ⁻¹)	T(°C)
Cu ²⁺ /Cu	0.74 [24]	2.3 [24] [†]	41.7 [24] [†]	25
Ni ²⁺ /Ni	0.49 [25]	0.068 [25]	37.2 [26]	25
H ⁺ /H ₂	0.63 [27]	0.002 [27]	42.2 [27]	20

[†] Calculated from data in Reference [24].

Table 2

Measured and “Fit” net copper and nickel corrosion rates without nitrogen sparging.

	Measured Net “Corrosion” Rate ($\times 10^5 \text{ mol L}^{-1} \text{ min}^{-1}$)			“Fit” Net “Corrosion” Rate ($\times 10^5 \text{ mol L}^{-1} \text{ min}^{-1}$)			Cu(II)/Ni Displacement Rate Constant (min^{-1})
	Cu	Ni	Cu + Ni ($k_{\text{C1}} + k_{\text{C2}}$)	Cu	Ni	Cu + Ni ($k_{\text{C1}} + k_{\text{C2}}$)	
T(°C)	pH 4, 10A						
30	-1.6	2.5	0.9	-0.2	0.8	0.6	0.002
40	-1.9	3.2	1.3	-0.1	1.1	1.0	0.003
50	-2.5	3.9	1.4	-0.2	1.5	1.3	0.004
60	-3.9	5.5	1.6	-0.7	2.2	1.5	0.012
pH	40°C, 10A						
3.0	2.6	4.6	7.2	0.01	2.3	2.4	0.006
3.5	1.1	3.6	4.7	0.05	1.8	1.8	0.004
4.0	-1.9	3.2	1.3	-0.2	1.1	0.9	0.003
4.5	-2.0	2.6	0.6	-0.3	0.6	0.3	0.002

Table 3

Measured net copper and nickel “corrosion” rates with nitrogen sparging.

	Measured Net “Corrosion” Rate ($\times 10^5 \text{ mol L}^{-1} \text{ min}^{-1}$)		
	Cu	Ni	Cu + Ni ($k_{C1} + k_{C2}$)
T(°C)	pH 4, 10A		
30	-2.2	2.6	0.4
40	-2.4	2.8	0.4
50	-3.1	3.3	0.2
60	-4.5	5.2	0.7
pH	40°C, 10A		
2.5	1.4	3.5	4.9
3.0	0.7	3.4	4.1
3.5	-0.03	2.9	2.8
4.0	-2.4	2.8	0.4
4.5	-2.6	2.8	0.2