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II. Electrodeposition/removal of nickel in a spouted electrochemical reactor

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Abstract

An investigation is presented of nickel electrodeposition from acidic solutions in a cylindrical spouted electrochemical reactor. The effects of solution pH, temperature, and applied current on nickel removal/recovery rate, current efficiency, and corrosion rate of deposited nickel on the cathodic particles were explored under galvanostatic operation. Nitrogen sparging was used to decrease the dissolved oxygen concentration in the electrolyte in order to reduce the nickel corrosion rate, thereby increasing the nickel electrowinning rate and current efficiency. A numerical model of electrodeposition, including corrosion and mass transfer in the particulate cathode moving bed, is presented that describes the behavior of the experimental net nickel electrodeposition data quite well.

1. Introduction

Electrodeposition of nickel from aqueous solutions is important in a number of applications, including removal of nickel cations from water for reclamation and recycle, nickel production and purification, and electroplating. There are a number of reports in the literature related to nickel electrowinning,^{1,2,3,4,5,6} but not in spouted electrochemical reactors.

Packed beds have been used as electrowinning cathodes.^{7,8} However, the operating life of such systems is limited by agglomeration of the bed particles into a solid mass, and the concomitant unacceptable increase in pressure drop.^{9,10} Fluidized beds have also been used as cathodes for electrowinning.^{11,12,13} These types of systems offer good liquid-solid contacting and do not generally suffer from particle agglomeration. However, they generally exhibit poor electrical contact between particles, which is a function of bed expansion, inhomogeneous electrical potentials, and particle segregation effects.¹⁴ The existence of anodic or pseudo-anodic regions in fluidized bed electrodes that were not observed in unexpanded fixed beds of the same particles, has also been reported.^{15,16} In addition, the range of overpotentials tends to be spatially distributed in fluidized bed electrodes.¹⁰

The spouted or recirculating particulate electrochemical reactor incorporates many of the advantages of fixed and fluidized bed electrodes, while minimizing some of their disadvantages.¹⁷ In one series of investigations, copper^{18,19,20,21} and zinc²² electrowinning were investigated. A rectangular cell design with sidewall electrodes was employed in this work. The cathode particles were fluidized and separated from the adjacent anode by a membrane. With this arrangement, oxygen formed at the anode was prevented from participating in metal corrosion on the cathodic particles, which resulted in very high current efficiencies.

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Here we present results of nickel electrodeposition/removal in a cylindrical spouted electrochemical reactor. Results on simultaneous co-electrodeposition of copper and nickel in the same apparatus are presented in a related paper.²³ These investigations were performed as part of the development of a novel Cyclic Electrowinning/Precipitation (CEP) system for the effective removal of complex mixtures of heavy metals at low concentrations from contaminated water.²⁴

2. Experimental

2.1. Apparatus

A conceptual schematic of the spouted electrochemical reactor and flow system is presented in Figure 1. As shown, the liquid electrolyte is introduced as a high velocity jet at the center of the bottom of the conical vessel. This liquid jet entrains particles centripetally fed from the moving particulate bed and enters the draft tube. After passing through the draft tube, the entrained particles disengage from the liquid flow as the velocity decreases in the freeboard region, and then fall onto the inverted conical distributor. The collector/distributor cone channels the particles to the periphery of the vessel, where they fall onto the particulate moving bed cathode that transports them inward and downward back to the entrainment region. The distributor also serves to maintain a constant mean residence time of particles in the moving bed cathode on the conical vessel bottom where electrodeposition occurs. The pumping action provided by the spout circulates the particles through the vessel in a toroidal fashion - upwards in the spout, and downwards in the annular peripheral region. Materials, additional details of the construction and geometry of the spouted electrochemical reactor, and a drawing of the vessel body are available elsewhere.¹⁷

2.2. Materials and Analytical

The particulate bed media were 2 mm diameter polymer beads, metallized with copper (Bead House LLC, CMC02.0/CP). The standard fresh nickel sulfate solution used for the electrowinning experiments consisted of 70g $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, (>98% Aldrich) added to distilled and deionized water to a total volume of 18L, to produce an initial concentration of 0.015M Ni^{2+} . 150g of Na_2SO_4 (granular, >99% Aldrich) and 200g H_3BO_3 (used to suppress hydrogen evolution and stabilize pH in the vicinity of the cathode²⁵), were also added, as well as the requisite sulfuric acid (1M, Mallinkrodt) 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 (DO) concentration in the solution reservoir.

Liquid samples for analysis were obtained from the solution reservoir since tests showed that the concentrations from samples taken simultaneously from the reservoir 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 reservoir, and the very short mean residence time in the reservoir (on the order of 15s), in comparison to the characteristic reaction time in the spouted vessel. The solution reservoir was also thermostatted to maintain constant temperature to within $\pm 1^\circ\text{C}$.

Nickel ion concentrations, measured at 221.647 nm, were determined with an ICP Optical Emission Spectrometer (ICP-OES; Jobin Yvon, JY2000), and the total amount of metal removal was determined by difference. Five metal calibration standards were used, covering the range of 1-7 ppm in a matrix of 2% HNO_3 , as well as a zero (blank) standard of the 2% HNO_3 matrix.

2.3. Experimental Procedures

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.

Nitrogen sparging of the electrolyte solution in the reservoir was investigated to reduce the DO concentration and nickel corrosion rate. The sparger was constructed from 0.635 cm diameter nylon tubing arranged in a square, 16.5 cm on a side. About 2000 holes of 0.35 mm diameter were drilled through the sparger tubing. Based upon investigation of the characteristics of the sparger system, an operating flow rate of 2.8 standard L min⁻¹ of nitrogen was selected. It is noted that the performance of the system was not optimized. Indeed, mass transfer analysis suggests that it could be significantly improved to the point where it could almost eliminate nickel metal corrosion, thereby increasing the current efficiency.

Based upon our experimental and numerical spouted bed hydrodynamic studies,^{26,27,28} the constant volumetric flow rate and loading selected for the operation of the apparatus in this work were 32.2 L min⁻¹ and 480 cm³ of particles, respectively.

The spouted particulate electrode was operated galvanostatically. Typical average power requirements for this system at the metal, electrolyte and additive concentrations noted above at 10A was about 100W which varied by about 10% over the course of a typical experimental run.

3. Electrodeposition Model

A numerical model, based upon a general approach for modeling recirculating particulate electrochemical reactors,^{29,30} was formulated to simulate the behavior of net nickel removal behavior with pH and temperature. The principal reactions assumed to occur are:

Reaction (3) is the well-known oxygen reduction reaction,³¹ which is thermodynamically favored over the hydrogen formation reaction (2).³² However, the mechanism for this reaction includes four single-electron transfer steps,^{33,34} the first of which has a standard potential of -0.125V.³² Thus, it is expected that reaction (3) is actually less favored kinetically than reaction (2).^{35,36} Consequently, the latter was included as the primary, cathodic side reaction.

In addition to the preceding, it was observed that deposited nickel corrodes *via*:

analogous to that reported for copper corrosion.³⁷

Model development follows the same approach used in our previous work.¹⁷ Galvanostatic operation of the electrochemical system yields the total cathodic current:

$$i = i_1 + i_2 = \frac{(z_1 F/a) k_1 C_1}{(1 + k_1/k_L a)} + (z_2 F/a) k_2 C_2 \quad (6)$$

where: the subscripts 1 and 2 indicate Ni^{2+} and H^+ , 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_L is the mass transfer coefficient given by Pickett³⁸ for a single layer packed bed electrode, and a is the interfacial surface area per unit volume; and k_j is the electrochemical reduction rate constant. The mass balance for Ni^{2+} is:

$$\frac{dC_1}{dt} = -\frac{i_1 a}{n_1 F} + k_c \quad (7)$$

where k_c is the total corrosion rate, assumed to be zeroth order in Ni^{2+} at constant pH. The current density, i , is the effective reduction rate, given by the Tafel approximation as:³²

$$i \equiv z F C_j k_j = i_0 \exp(-\alpha F \eta / RT) \quad (8)$$

where i_0 is the exchange current density, α is the transfer coefficient, and $\eta = E - E_e$ is the overpotential, where E is the actual half-cell potential, and E_e is the equilibrium potential. Variation of the exchange current density, i_0 , with temperature is given by:³²

$$\frac{d(\ln i_0)}{dT} = \frac{\Delta H_0^*}{RT^2} \quad (9)$$

where ΔH_0^* is the enthalpy of activation at the equilibrium potential.³² The Tafel kinetics parameter values used in the model are presented in Table 1.

The model solution methodology is also similar to that used previously.¹⁷ At constant current density, the transcendental current balance [Eq. (6)] is solved numerically for the cathodic potential, E . Eq. (7) is then solved for a time step using a Runge-Kutta 4th order method.⁴² These two steps are repeated alternately, moving forward in time, until the desired time is reached. Although nickel corrosion rates were measured, it was found that the best fits of the model to the experimental data were obtained by “adjusting” the corrosion rate as a model parameter. Measured corrosion rates were used as initial guesses, and corrosion rate values were adjusted so as to minimize the least squares deviation between the data points and the model predictions.

4. Results and Discussion

The effect of pH on nickel removal at 35°C is presented in Figure 2. As shown, the net rate increased with pH over this range, both with and without nitrogen sparging. In addition, it increases significantly with nitrogen sparging, especially at the lower pH values. The corresponding numerical simulations of nickel electrodeposition are also presented in this figure as the continuous curves. As shown, the model explains the experimental data reasonably well.

Nickel corrosion data as a function of pH at 35°C, both with and without nitrogen sparging, are presented in Figure 3. As shown, the corrosion rates under these conditions exhibit close to zeroth order behavior with respect to nickel ion concentration, and increase monotonically with decreasing pH at 35°C. The measured nickel corrosion rates (i.e., the slopes of the linear fits in Figure 3), as well as “fit” corrosion rates, determined as described above, are presented in Table 2. As shown, both sets of values agree reasonably well. A kinetic analysis of the data in Table 2 without nitrogen sparging, assuming first order dependence on DO concentration³⁷ from Figure 5, indicates that the apparent order with respect to $[H^+]$ is approximately unity as well, which is in agreement with the conclusions of Abd El Aal *et al.*⁴³ for nickel corrosion.

“Intrinsic” current efficiencies were determined from the instantaneous slopes (rates) of the net nickel removal curves, “corrected” for the corrosion rates (i.e., by addition of the corrosion rate to the observed rate). The corresponding current efficiencies for the nickel recovery data in Figure 2 are presented in Figure 4. As shown, the current efficiencies decrease with decreasing nickel ion concentration, as expected. Compared at the same concentration, the current efficiencies increased with pH over the range of experimental conditions investigated (i.e., pH 3.5–5.0). This is because the corrosion rate decreases with increasing pH, and the hydrogen formation side reaction at the cathode (Eq. (3)) becomes more inhibited. It is also noted that the current efficiencies were typically slightly lower at the beginning of each run. This is attributed to the initial presence of an oxide layer on the particle surfaces which increases the electrical resistance. This is consistent with the slightly elevated voltages and slight current oscillations that were typically observed during the very early stages of most experimental runs.

In Figure 5 are presented the DO concentrations during electrowinning at 35°C, 10A, as a function of pH, both with and without nitrogen sparging. As shown, without nitrogen sparging, the initial DO concentration was about 6.0 mg L⁻¹. (6.96 mg L⁻¹ is the equilibrium concentration in contact with air at 1 atm, 35°C.⁴⁴) With nitrogen sparging, the initial DO concentration in the electrolyte solution decreased to about 2.0 mg L⁻¹, which is well below the equilibrium value, and much less than that without nitrogen sparging. During electrowinning, the DO concentration increases rapidly to a maximum, and then either levels off (pH 3.5 and 4) or continues to decrease (pH 4.5 and 5). This behavior was qualitatively similar both with and without nitrogen sparging, except that the DO levels were significantly reduced (by as much as a factor of two) in the former case. It is noted that the oxygen behavior in Figure 5 at early times was monotonic with pH for both sets of data.

As indicated above, oxygen is produced primarily *via* the anodic reaction (4), and in the presence of H^+ can re-oxidize deposited nickel metal *via* reaction (6). The pseudo-steady DO level is controlled by the rates of the production and consumption reactions, as well as any mass transfer loss/gain while in contact with air in the freeboard of the solution reservoir. This qualitatively explains the relative asymptotic values for the two lower pH values in Figure 5. That is, as shown in Figure 3, the corrosion rate at pH 3.5 is significantly greater than that at pH 4, so it would be expected that more oxygen would be consumed in

the former case, resulting in a lower DO concentration, as observed. However, this does not explain the almost linear decrease in DO concentration at the two higher pH values. At these two pH values, the nickel ion concentration is quite low when the decrease in DO occurs. Consequently, it appears that another oxygen “sink” develops at the cathode under these conditions. Although the bulk solution is acidic, Ji *et al.*⁴ have shown that the pH near the cathode surface is always greater than that of the bulk electrolyte, and that under certain conditions this can cause the formation of insoluble hydroxides at cathode surfaces. Cui and Lee⁵ also found that nickel hydroxide deposited on the cathode surface was stable. In the current experiments at the highest pH of 5, a grey-green color of the solution was clearly visible in the vicinity of the particulate cathode bed. This can be attributed to nickel hydroxide formation near the cathodic particles. However, as shown in Figure 2, nickel electrodeposition was still quite rapid under these conditions, and the particle surfaces appeared to remain similar in color to that during nickel electrowinning at lower pH values. Thus even when conditions were such that the pH in the vicinity of the particles was sufficiently high to form hydroxide, it did not accumulate on particle surfaces to impede nickel reduction. This is attributed to the mechanical, “self-polishing” action of the particles abrading against one another in the moving bed cathode that causes any incipient hydroxide deposits to be continually removed from the particle surfaces. It is noted that this would probably not occur under similar conditions on static cathode surfaces (i.e., in fixed beds) upon which hydroxide formation could impede nickel electrowinning under otherwise similar conditions.

A half-cell reaction that increases pH in the vicinity of the cathode, and consumes oxygen is:

and it is catalyzed by nickel.⁴⁵ Thus, when the nickel ion concentration decreases sufficiently, reaction (10) would tend to become more effective at the cathode. This is consistent with all the experimental observations: i.e., higher effective pH near the cathode; the development of an additional oxygen sink at the cathode; and the presence of catalytic metallic nickel. In addition, it was observed that when the nickel ion concentration decreased to low levels, the amount of hydroxide introduced by the pH controller in the reservoir decreased to essentially zero, which is also consistent with reaction (10). Another cathodic reaction that would increase the pH locally and decrease the DO concentration is reaction (3). Both of these reactions would tend to become more important as the bulk nickel ion concentration decreases.

In Figure 6 is presented the behavior of nickel electrowinning as a function of temperature at pH 4 and 10A, with and without nitrogen sparging. As shown, nitrogen sparging increases the current efficiency and accelerates net nickel electrodeposition. Sparging seemed to be somewhat more effective in increasing the nickel removal rate at lower temperatures. The results of numerical simulations of net nickel electrodeposition are also presented in this figure as the continuous curves. As shown, the simulations explain the experimental data reasonably well.

In Table 3 are presented nickel corrosion rates obtained from the measurements in comparison to the “fit” corrosion rates, as explained above, as a function of temperature at constant pH 4. It is noted that although the “fit” values are generally of the same order as the measured values, they tend to be consistently larger, which may reflect enhanced corrosion due to effects such as the occurrence of local anodic zones in the moving bed cathode.⁴⁶

The corresponding DO concentrations are presented in Figure 7. As shown, the initial DO concentrations prior to beginning electrodeposition were 7.6, 6.0, 4.9, and 4.4 mg L⁻¹ at 30°C, 35°C, 40°C, and 45°C, respectively, without nitrogen sparging, which is expected from equilibrium considerations for water in contact with air at 1 atm. The data with nitrogen sparging also show increasing initial DO concentrations with temperature, but at lower levels, below expected equilibrium values. During electrowinning, the DO concentration increases rapidly, and then levels out to a relatively constant asymptotic value. For the data without nitrogen sparging, the observed pseudo-steady asymptotic values were not monotonic with temperature; i.e., the approximate average asymptotic values were about 9.2, 9.7, 6.8, and 6.0 mg L⁻¹ for 30°C, 35°C, 40°C, and 45°C, respectively. This behavior is consistent with the DO balance:

$$d[O_2]/dt = k_a - k_c[H^+][O_2] - k_L a([O_2] - [O_2]_{eq}), \quad (11)$$

where the terms on the right hand side are, respectively, anodic oxygen production *via* reaction (4), oxygen consumption at the cathode due to reaction (8) (corrosion), and oxygen transport to/from air in the solution reservoir. The pseudo-steady DO concentration is then given by:

$$[O_2]_s = (k_a + k_L[O_2]_{eq}) / (k_c[H^+] + k_L) \quad (12)$$

At low temperatures, for sufficiently high anodic oxygen production rate and low corrosion rate, Eq. (12) reduces to:

$$[O_2]_s \approx k_a / k_L \quad (13)$$

From this expression, if the anodic reaction is activated, the pseudo-steady DO concentration will increase with temperature, just as observed between 30°C (9.2 mg L⁻¹) and 35°C (9.7 mg L⁻¹). As the temperature increases further, the corrosion rate eventually becomes larger than the mass transfer rate, such that the pseudo-steady DO concentration then becomes:

$$[O_2]_s \approx k_a / k_c[H^+] \quad (14)$$

Thus, if the effective corrosion activation energy is greater than that for anodic DO production, the pseudo-steady DO concentration will decrease with increasing temperature, just as observed at 35°C (9.7 mg L⁻¹), 40°C (6.8 mg L⁻¹), and 45°C (6.0 mg L⁻¹), without nitrogen sparging.

The situation with nitrogen sparging is somewhat different. In this case, the DO removal rate in the solution reservoir is much greater and approximately constant, and Eq. (12) becomes:

$$[O_2]_s = (k_a - k_s) / k_c[H^+] \quad (15)$$

where k_s is the oxygen removal rate by nitrogen sparging. In this case, since k_s is not activated, it is expected that the DO concentration will decrease monotonically with temperature, in agreement with the corresponding data in Figure 7. Eqns. (14) and (15) also suggest that at constant temperature, the steady DO concentration will increase with increasing pH. This behavior is observed in Figure 5 at early times at 35°C.

The effect of the feeder current on nickel electrowinning at pH 4.0 and 35°C is presented in Figure 8, both with and without nitrogen sparging. As expected, the nickel removal rate increases significantly with feeder current, and the current efficiency decreases. Also, nitrogen sparging improved the net nickel removal rate, especially as the current increased. The model results show the correct trends. However, at the highest current of 15A, the data show a significant difference between operation with and without sparging, while the model shows somewhat less of a difference. This is attributed to the fact that the model uses a simple constant corrosion rate approximation that does not explicitly take into account the effects of the variability of the DO concentration, as well as the possibility of increased importance of additional cathodic oxygen sinks when the nickel cation concentration becomes very low.

4. Conclusion

The spouted electrochemical reactor exhibited good performance for the removal of nickel from acidic solutions. It was determined that, in general, the rate of nickel electrowinning increases with increasing pH and temperature, over the experimental range investigated. Nitrogen sparging of the electrolyte solution was effective in reducing the dissolved oxygen concentration, suppressing the nickel corrosion reaction, and, thereby, improving the net nickel recovery rate. The effects of nitrogen sparging were somewhat more effective at higher pH, lower temperature, and higher feeder currents.

The electrochemical kinetics of net nickel removal in the spouted electrochemical reactor was reasonably well described by a batch Tafel kinetics model, incorporating a constant corrosion rate as an approximation.

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References

1. Epelboin I, Wiart R. Mechanism of the Electrocrystallization of Nickel and Cobalt in Acidic Solution. *J Electrochem Soc.* 1971; 118:1577–1582.
2. Epelboin I, Jousselin M, Wiart R. Impedance measurements for nickel deposition in sulfate and chloride electrolytes. *J Electroanal Chem.* 1981; 119(1):61–71.
3. Zeller RL III, Landau U. The Effect of Hydrogen on the Ductility of Electrodeposited Ni-P Amorphous Alloys. *J Electrochem Soc.* 1990; 137(4):1107–1112.
4. Ji J, Cooper WC, Dreisinger DB, Peter E. Surface pH measurements during nickel electrodeposition. *J Appl Electrochem.* 1995; 25(7):642–650.
5. Cui CQ, Lee JY. Nickel deposition from unbuffered neutral chloride solutions in the presence of oxygen. *Electrochim Acta.* 1995; 40(11):1653–1662.
6. Lantelme F, Seghioer A. Model of nickel electrodeposition from acidic medium. *J Appl Electrochem.* 1998; 28:907–913.
7. Simonsson D. A flow-by packed bed electrode for removal of metal ions from wastewaters. *J Appl Electrochem.* 1984; 14(5):595–604.

8. Chu AKP, Fleischmann M, Hills GJ. Packed bed electrodes. I. Electrochemical extraction of copper ions from dilute aqueous solutions. *J Appl Electrochem.* 1974; 4(4):323–330.
9. Houghton RW, Kuhn AT. Mass-transport problems and some design concepts of electrochemical reactors. *J Appl Electrochem.* 1974; 4(3):173–190.
10. Ferreira BK. Three-dimensional electrodes for the removal of metals from dilute solutions – a review. *Mineral Processing & Extractive Metal Rev.* 2008; 29:330–371.
11. Sequeira, CAC.; Marques, FDS. *Electrochemical Engineering: I ChemE Symposium Series No 112.* Vol. 112. NY/London: Hemisphere Pub. Corp.; 1989. Effect of current on gold electrowinning with a fluidized bed electrode; p. 297–306.
12. Backhurst JR, Goodridge F, Coulson JM, Plimley RE. A preliminary investigation of fluidized bed electrodes. *J Electrochem Soc.* 1969; (116):1600–1607.
13. Germain S, Goodridge F. Copper deposition in a fluidized bed cell. *Electrochim Acta.* 1976; 21(8): 545–550.
14. Fleischmann M, Oldfield JW, Tennakoon L. Fluidized bed electrodes. IV. Electrodeposition of copper in a fluidized bed of copper-coated spheres. *J Appl Electrochem.* 1971; 1(2):103–112.
15. Coeuret F. The fluidized bed electrode for the continuous recovery of metals. *J Appl Electrochem.* 1980; 10:687–696.
16. Hadzismajlovic, DzE; Popov, KI.; Pavlovic, MG. The visualization of the electrochemical behaviour of metal particles in spouted, fluidized and packed beds. *Powder Tech.* 1996; 86(2): 145–148.
17. Shirvanian PA, Calo JM. Copper recovery in a particulate spouted bed electrode. *J Appl Electrochem.* 2005; 35(1):101–111.
18. 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.
19. 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.
20. Stankovic VD, Stankovic S. An investigation of the spouted bed electrode cell for the electrowinning of metal from dilute solutions. *J Appl Electrochem.* 1991; 21(2):124–129.
21. Masterson IF, Evans JW. Fluidized bed electrowinning of copper: experiments using 150 ampere and 1000 ampere cells and some mathematical modeling. *Metall Mat Trans B.* 1982; 13B:3–13.
22. Jiricny V, Roy A, Evans JW. Electrodeposition of zinc from sodium zincate/hydroxide electrolytes in a spouted bed electrode (SBE). *Metall Mat Trans B.* 2000; 31B(4):755–766.
23. Grimshaw P, Calo JM, Shirvanian PA, Hradil G III. Co-electrodeposition/removal of copper and nickel from acidic solution mixtures with a spouted electrochemical reactor. *Ind Eng Chem Res.* 2011 submitted.
24. 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.
25. 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.
26. Shirvanian, PA. PhD Dissertation. Division of Engineering, Brown University; 2003. Electrolytic Recovery of Metals in a Spouted Vessel Reactor: An Experimental and Simulation Approach.
27. Shirvanian PA, Calo JM. Hydrodynamic scaling of a rectangular spouted vessel with a draft duct. *Chem Eng J.* 2004; 103(1-33):29–34.
28. Shirvanian PA, Calo JM, Hradil G. Numerical simulation of fluid-particle hydrodynamics in a rectangular spouted vessel. *Int J Multiphase Flow.* 2006; 32:739–753.
29. Scott K. Reactor Modelling for Electrochemical Processes. *J Chem Tech Biotechnol.* 1992; 54:257–266.
30. Walker ATS, Wragg AA. The modeling of concentration-time relationships in recirculating electrochemical reactor systems. *Electrochim Acta.* 1977; 22(10):1129–1134.
31. Larminie, J.; Dicks, A. *Fuel Cell Systems Explained.* John Wiley & Sons Ltd.; Chichester: 2000.
32. Rieger, PH. *Electrochemistry.* Prentice-Hall; Englewood Cliffs, NJ: 1987.

33. Dong Q, Santhanagopalan S, White RE. Simulation of the Oxygen Reduction Reaction at an RDE in 0.5 M H₂SO₄ Including an Adsorption Mechanism. *J Electrochem Soc.* 2007; 154(9):A888–A899.
34. Mustain WE, Prakash J. Kinetics and mechanism for the oxygen reduction reaction on polycrystalline cobalt-palladium electrocatalysts in acid media. *J Power Sources.* 2007; 170(1):28–37.
35. Tamamushi R. On the Mechanism of the Reduction Process of the Hydrogen Ion at the Dropping Mercury Electrode. I. Theoretical Part. *Bull Chem Soc Japan.* 1952; 25(5):287–293.
36. Tamamushi R. On the Mechanism of the Reduction Process of the Hydrogen Ion at the Dropping Mercury Electrode. II. Experimental Part—The Limiting Current of the Hydrogen Wave. *Bull Chem Soc Japan.* 1952; 25(5):293–298.
37. Ives DJG, Rawson AE. Copper Corrosion. II. Kinetic Studies. *J Electrochem Soc.* 1962; 109(6):452–457.
38. Pickett, DJ. *Electrochemical Reactor Design.* 2nd. Elsevier; Amsterdam: 1979.
39. 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.
40. 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.
41. Conway, BE. *Electrochemical Data.* Elsevier; Amsterdam: 1952.
42. Nakamura, J. *Applied Numerical Methods With Software.* Prentice Hall; Upper Saddle River, NJ: 1991.
43. Abd El Aal EE, Zakria W, Abd El Haleem SM. Anodic dissolution of nickel in acidic chloride solutions. *J Mater Eng Perform.* 2003; 12:172–178.
44. Eaton, AD.; Clesceri, LS.; Rice, EW.; Greenberg, AE.; Franson, MAH. *Standard Methods for the Examination of Water and Wastewater.* 12th. American Public Health Association; New York: 1965. p. 408
45. Verma A, Basu S. Direct alkaline fuel cell for multiple liquid fuels: Anode electrode studies. *J Power Sources.* 2007; 174(1):180–185.
46. Huh T, Evans JW. Electrical and Electrochemical Behavior of Fluidized Bed Electrodes. *J Electrochem Soc.* 1987; 134(2):308–317.

Figure 1.
Schematic of spouted particulate electrode apparatus and flow system.

Figure 2. Net nickel removal as a function of solution pH at 10A, 35°C, without (—) and with (- - -) nitrogen sparging.

Figure 3. Nickel ion concentration (offset by initial nickel ion concentration, C_0) due to corrosion from the particles with the feeder current off, as a function of solution pH at 35°C, without (—) and with (- - -) nitrogen sparging.

Figure 4. "Intrinsic" current efficiencies for the data presented in Figure 1, without (—) and with (- - -) nitrogen sparging.

Figure 5. Dissolved oxygen concentration during nickel recovery as a function of pH, at 10A, 35°C, without (—) and with (- - -) nitrogen sparging.

Figure 6. Net nickel recovery as a function of solution temperature at 10A, pH 4, without (—) and with (- - -) nitrogen sparging.

Figure 7. Dissolved oxygen concentration during nickel recovery at 10A, pH 4, as a function of temperature, with (— — —) and without (—) nitrogen sparging.

Figure 8.
Net nickel recovery at 35°C, pH 4, as a function of applied current, with and without (—) nitrogen sparging.

Table 1Tafel kinetics parameter values for nickel electrowinning.³²

Cathodic Reaction	Transfer coefficient, α	Exchange current density, i_0 (A m ⁻²)	Equilibrium enthalpy of activation, ΔH_0^* (kJ mol ⁻¹)	T(°C)
(Ni ²⁺ /Ni)	0.49 [39]	0.068 [39]	37.2 [40]	25
(H ⁺ /H ₂)	0.63 [41]	0.002 [41]	42.2 [41]	20

Table 2

Measured and “fit” nickel corrosion rates (35°C, 10A).

pH	Nickel corrosion rate without (w/o) nitrogen sparging ($\times 10^6$ mol L ⁻¹ min ⁻¹)		Nickel corrosion rate with nitrogen sparging ($\times 10^6$ mol L ⁻¹ min ⁻¹)	
(35°C, 10A)	Measured	“Fit”	Measured	“Fit”
3.5	57	38	22	21
4.0	12	29	2.6	10
4.5	4.1	17	1.6	3.4
5.0	2.8	10	1.2	0.9

Table 3

Measured and “fit” nickel corrosion rates (pH 4, 10A).

Temperature (°C)	Nickel corrosion rate without nitrogen sparging ($\times 10^6$ mol L ⁻¹ min ⁻¹)		Nickel corrosion rate with nitrogen sparging ($\times 10^6$ mol L ⁻¹ min ⁻¹)	
(pH 4, 10A)	Measured	“Fit”	Measured	“Fit”
30	10.2	24	1.6	8.6
35	12.1	29	2.6	10
40	13.4	40	3.6	14
45	18.4	45	4.5	16