

Preparation of high purity nickel film from industrial effluent by the distribution of charge over microelectrodes using newly designed free electrolytic diffusion approach

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Received 11 September 2007; received in revised form 7 January 2008; accepted 8 January 2008

Available online 16 January 2008

Abstract

The present work deals with the development of a newly designed free electrolytic diffusion approach (the distribution of charge over microelectrodes) for the purification of metals and was successfully applied for the purification of nickel from the industrial effluent containing high proportion of nickel. Atomic absorption spectrophotometer (AAS) analyzed the purified nickel deposited on working microelectrodes. The results obtained show that the purity of nickel was enhanced from 95% to 99.9% with traces of copper etc. It was concluded that distribution of charge over the microcathodes at a rate of 50 cycles per second (cps) shows better results for the production of high purity (HP) nickel as compared to 25 cycles per second (cps).

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Keywords: Free electrolysis; Microelectrode; Nickel purification; Thruster

1. Introduction

The effluent of nickel electroplating contains different wastes such as organic brightener, additives and toxic metals, i.e. nickel and its salts. Nickel pollution usually caused by several industrial processes such as electroplating, plastics manufacturing, nickel–cadmium batteries, fertilizers, pigments, mining and metallurgical [1–3]. While the nickel ion concentration in plating rinse can approach 2–900 mg/L, wastewater from paint and ink formulation, porcelain enameling, copper sulphate manufacture industries record effluent nickel ion concentrations that vary from 0 mg/L to 40 mg/L, 0.25 mg/L to 67 mg/L and around 22 mg/L [4]. Nickel and its compounds are carcinogenic and may constitute danger to human being and other lives [5].

When this effluent is released into Municipal sewage then it contaminates the rivers, streams, soils and causes environmental

problems. The toxic metals are accumulated in the edible tissues of plants. Finally these metals end up in the human body; consequently accumulation of nickel in plants beyond a certain limit can cause adverse effects on human health. Nickel causes blindness. Expectant mothers exposed to nickel were reported to be threatened with increasing incidents of abortions. The increased levels of nickel in food are associated with respiratory tracts problems [6], but there is another side of the picture as well that pure nickel and nickel alloys are used for a wide variety of applications. The major applications require corrosion and heat resistance, including aircraft gas turbines, steam turbine power plants, medical applications, and nuclear power systems, the chemical and petrochemical industries. The electronics industry accounts for approximately 6–8% of nickel consumption, which is a constantly growing share. A special nickel–iron alloy is widely used in lead frames, while Cu–Ni–Sn alloy is used in terminals, clips and springs. Pure nickel is also required for the hydrogenation as catalyst and other chemicals [7]. There are various methods, i.e. the anion exchange method, sublimation, reverse osmosis [8,9], evaporation, ion exchange [10] solvent extraction for the separation and refining, pyrometallurgical

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hydrometallurgical and electrometallurgical methods, selective volatilization and electro transport methods for purification of nickel [11].

The purification of nickel by conventional techniques like anion exchange is suitable but nickel does not form anionic chloro-complex species, thus it is entrained in the solution passing the ion-exchange column directly, while a large number of impurities (including Co and Fe) may be retained in the resin bed [14]. Purification of nickel by conventional aqueous chemical techniques and standard hydrometallurgical methods gives good results to a significant degree [15]. Purification of nickel by zone melting in an atmosphere of dry hydrogen eliminates carbon, oxygen, arsenic, antimony, zinc, sodium and a number of other minor impurity elements [16]. Therefore, zone melting of nickel was to be preceded by a different method of purification, one that is capable of eliminating cobalt, copper and iron. Instead of H_2 reduction after evaporation, nickel was electrodeposited from the purified ion-exchange effluent after separating the excess hydrochloric acid content in a simple cell containing no diaphragm between the anode and cathode compartments. The required range of acidity was pH 1–3 and the temperature was higher than $40^\circ C$ at a current density of approximately $10 A/dm^2$ to obtain a pure metallic deposit. Enhanced purification by the electro winning step was possible by applying a simple electrolysis at lower current densities, which dominantly deposits elements of a more noble character than nickel. The inert anode was conveniently made of platinum, while the starting cathode was made of a high purity (HP) nickel sheet [17]. The metal purified by the anion exchange procedure, electrodeposited directly or with periodic reverse pulsating current made up of cathodic cycles from the chloride–sulphate–boric acid electrolyte [18].

Ewa and Marek [12] recovered cadmium and nickel from spent Ni–Cd batteries using hydrometallurgical techniques. Maximum total recoveries of cadmium and nickel from spent Ni–Cd batteries were 92% and 67%, respectively. Nagwan et al. [13] precipitated Cu(II), Ni(II) and Zn(II) ions from synthetic aqueous solutions as hydroxides by using cement by-pass kiln dust (CKD) leachate.

The present work deals with the preparation of high purity nickel film by distribution of charge over microcathodes using a newly designed free electrolytic diffusion apparatus (FEDA). FEDA is first time developed by us and is a compact apparatus consisting of one large cylindrical platinum anode having a longitudinal slit for the migration of cations, an array of anodes to overcome the resistance and a number of microelectrodes (1–10 in numbers in this experiment) on which current passes at different cycle per seconds (cps) as programmed with thruster. The separation of the cations took place due to variation in the transport number; electrolytic diffusion and cations get deposited on their respective microcathode. Our work is distinguished from the existing conventional techniques in this regard that instead of using a single cathode (with or without rotating disc electrodes) in simple electrolysis a set of 12 microcathodes was used, at which charge distributes, at the rate of 25 cps and 50 cps, respectively.

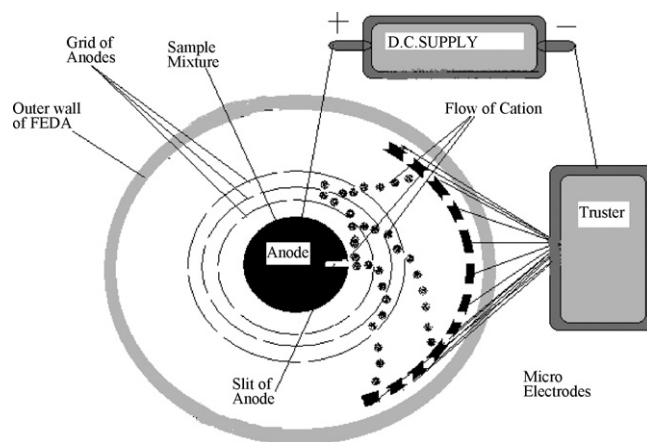


Fig. 1. Free electrolytic diffusion apparatus.

2. Experimental

2.1. Designing of free electrolytic diffusion apparatus

The concept of designing and working of the free electrolytic diffusion apparatus has been taken from existing electro analytical techniques like electrogravimetry (calculation of weight of deposit before and after electro deposition), voltametry (use of microelectrodes), electrophoresis (passage of metallic cations in a gel when subjected in an electric field) and electroplating (electrodeposition of a thin metallic film on the cathode).

The apparatus (Fig. 1) used in this work consists of a large cylindrical hollow anode (containing sample mixture) made of platinum with side longitudinal slit. The width of slit was 1 mm and 5 mm long. It was filled with cellulosic material to pass the metallic cations outside the cylinder. Cylindrical platinum anode was further surrounded by an array of anodes for the eddy diffusion of metallic cations toward the microcathodes (made of graphite) as programmed with the thruster. The thruster distributed the charge over the microcathodes at a frequency of 25 cps and 50 cps, respectively at and applied current (1–10 A).

2.2. Sample preparation

Sample solutions were prepared with deionized water with the resistivity being more than $10^5 \Omega m$. The provided sample was dissolved in a hydrochloric acid solution, prepared from commercial special grade HCl and dissolved in deionized water. After the anion exchange separation, the highly purified $NiCl_2$ solution was evaporated to dryness to obtain anhydrous $NiCl_2$. The anhydrous salt was re-dissolved in 0.1N HCl and subjected to a specially designed free electrolytic diffusion apparatus and programmed with thruster at 25 cps and 50 cps, respectively. Experiments were performed at room temperature and pH 3.0. The pH was adjusted at 3.0 by using boric acid buffer.

2.3. Standard calibration solution preparation

Standard solutions used were provided by Health Safety and Environmental Training Center, Lahore, Pakistan. Different dilutions of deposited metal were prepared and their absorbance

compared with standard. After this the standard deviation values at λ 232 nm and λ 341.5 nm wavelengths were calculated, respectively.

2.4. AAS determination

Every microcathode was weighed before and after the electrodeposition using a sensitive analytical balance. The scratchings of deposit were dissolved in the extra pure conc. HNO_3 (Merck grade) and made its dilutions up to 1000 times. These dilutions were run in atomic absorption spectrophotometer (AAS) (AAnalyst 100) at λ_{max} 232 nm and λ_{max} 341.5 nm, respectively. The values obtained were compared with the standards values. A graph between concentration and absorption was plotted to know the concentration of desired metal and then finally determined the percentage purity of metallic deposit on each microcathode, respectively.

3. Results and discussion

3.1. Effect of addition of boric acid

Our work indicates that the addition of a modifier such as boric acid enhanced the electro winning from high quality nickel deposits while inorganic additives showed the little influence on the current efficiency. Increasing either nickel concentration or electrolyte temperature improved the current efficiency, while decreasing the pH significantly reduced the current efficiency. Similar results were reported by Holm and Keefe [19] and Lupi et al. [20].

3.2. Cell designs and mass transfer limitations

Conventional filter press cells with flat-plate electrodes can handle the high metal ion concentrations, while lower concentrations require specialized methods and cell designs with high specific electrode surface area and with high mass transfer regimes. The performance of electrochemical processes was dependent upon the specific area of the electrode or membrane at which these processes occur and mass transfer limitations take place.

Liquid convection, diffusion and migration can determine mass transfer limitations. If the concentration of the supporting electrolyte was higher by a factor 10 than the concentration of the selected species to be oxidized or reduced and the migration of the selected species could be neglected. Its transport rate is then determined by diffusion and in stationary state given by Fick's first law:

$$i = nFD \left(\frac{dc}{dx} \right)_{x=0} \quad (1)$$

In order to overcome the mass transfer limitation we enhanced the efficiency of FEDA by arranging a grid of anodes around the cylindrical platinum anode. It not only directed the nickel cations toward respective microcathode but also leaving behind the impurities.

3.3. Charge distribution and electrodeposition

In general, during electrolysis cations present in the electrolytic cell are deposited at the cathode at their respective electrode potentials. The purity of the metallic deposit reaches up to 90%. Different parameters, which influence the structure, geometry and purity of metallic deposit on cathode like temperature, pH, supporting electrolytes and electrode potentials have been reported but literature is silent about the distribution of charge over microcathodes to study its effects on the purity of metallic deposit. So in this research we have studied the effect of charge distribution over the microcathodes to obtain pure metallic deposit at 25 cps and 50 cps, respectively.

3.4. ICP analysis of nickel chloride

The starting material was an industrial effluent. It was analyzed by inductive couple plasma (ICP). ICP analysis showed that 95% nickel was present as a major element, 2.4% copper as major impurity and Mg, Al, Si, Na, K, Ca, Cr, Fe, Co, Zn, Bi and Pb are the minor impurities while As and Sb, are in traces less than 0.01 ppm (Table 1).

3.5. Effect of charge distribution at the rate of 25 cps

Table 2 shows the results of distribution of charge at the rate of 25 cycles per seconds (cps) on the separation and purification of nickel from the mixture. In this experiment total 10 microcathodes were arranged around the array of anodes in a circular fashion as shown in the Fig. 1 and as programmed with thruster at 25 cps. The deposit was analyzed by AAS (AAnalyst 100) using the PerkinElmer, Aldrich and self-prepared standards following AAS manual respectively. The percentage purity of nickel decreased from cathodes 1–8 gradually and then increased rapidly as shown in Fig. 2. The reason might be the presence of

Table 1
ICP analysis of nickel chloride solution at 25 cps and 50 cps

Serial #	Element	Concentration (mg/L)	Concentration (mg/L) at 25 cps	Concentration (mg/L) at 50 cps
1	Mg	0.15	0.1	0.1
2	Al	0.18	0.1	0.01
3	Si	0.1	0.01	0.01
4	K	0.3	0.12	0.02
5	Ca	0.1	0.01	0.01
6	Cr	0.1	0.01	0.01
7	C	0.01	0.01	0.01
8	O	0.01	0.01	0.01
9	Na	0.01	0.02	0.01
10	Fe	0.2	0.1	0.05
11	Co	0.1	0.01	0.01
12	Ni	95	99.19	99.55
13	Cu	2.4	0.89	0.41
14	Zn	0.1	0.01	0.01
15	Bi	0.1	0.01	0.01
16	As	0.01	0.01	0.01
17	Sb	0.01	0.01	0.01
18	Pb	0.1	0.01	0.01

Table 2
Percentage purity achieved by using free electrolytic diffusion apparatus at 25 cps

Cathode #	Weight of metal deposit (g)	Concentration from graph (mg/L)			Average concentration \pm S.D. $((a+b+c)/3) \pm$ S.D.	Percentage purity			Average percentage purity \pm S.D. $((x+y+z)/3) \pm$ S.D.
		<i>a</i>	<i>b</i>	<i>c</i>		<i>x</i>	<i>y</i>	<i>z</i>	
1	0.1054	10.48	10.52	10.51	10.50 \pm 0.017	99.43	99.81	99.72	99.65 \pm 0.162
2	0.1265	12.61	12.53	12.55	12.56 \pm 0.034	99.68	99.05	99.2	99.31 \pm 0.269
3	0.0986	9.80	9.82	9.75	9.79 \pm 0.029	99.39	99.59	98.88	99.29 \pm 0.299
4	0.1086	10.76	10.81	10.72	10.76 \pm 0.037	99.07	99.53	98.71	99.11 \pm 0.335
5	0.1271	12.58	12.59	12.55	12.57 \pm 0.017	98.97	99.05	98.74	98.92 \pm 0.131
6	0.1233	12.32	12.3	11.98	12.20 \pm 0.193	99.91	99.83	97.16	98.97 \pm 1.565
7	0.1479	14.78	14.76	14.26	14.60 \pm 0.294	99.93	99.79	96.41	98.71 \pm 1.993
8	0.1258	12.55	12.56	12.36	12.49 \pm 0.113	99.76	99.84	98.25	99.28 \pm 0.896
9	0.1663	16.61	16.53	16.45	16.53 \pm 0.065	99.87	99.39	98.91	99.39 \pm 0.289
10	0.1155	11.54	11.5	11.51	11.52 \pm 0.017	99.91	99.57	99.65	99.71 \pm 0.145

a = concentration of an electrodeposit according to the AAS manual; *b* = concentration of an electrodeposit according to the PerkinElmer standard; *c* = concentration of an electrodeposit according to the Aldrich standard; *x* = percentage purity of an electrodeposit w.r.t AAS manual; *y* = percentage purity of an electrodeposit w.r.t PerkinElmer standard; *z* = percentage purity of an electrodeposit w.r.t Aldrich standard.

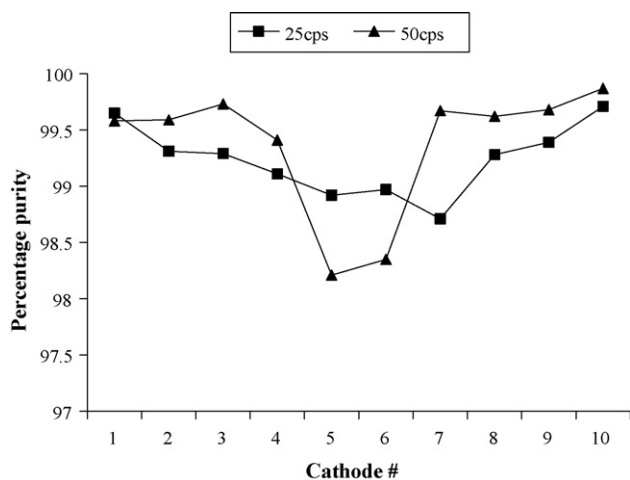


Fig. 2. Cathode wise percentage purity for nickel at 25 cps and 50 cps.

major impurity copper; since the copper is more electro active than nickel so it might be deposited on the cathodes 1–8, after the decrease of copper concentration in the sample solution nickel electrodeposition suddenly increased. The presence of copper

also affects the purity level of nickel as shown in Fig. 2. The graph relates the standard deviation with electrodeposits on cathodes. At 25 cps, due to slow distribution of charge maximum standard deviation is observed from ± 0.1 to ± 2.0 as shown in Fig. 3.

3.6. Effect of charge distribution at the rate of 50 cps

Table 3 shows the results of distribution of charge at the rate of 50 cycles per seconds (cps) on the separation and purification of nickel from the mixture. In this experiment total 10 microcathodes were also arranged around the array of anodes in a circular fashion as shown in Fig. 1 and programmed with thruster at 50 cps. The deposit was analyzed by AAS (AAAnalyst 100) using the PerkinElmer, Aldrich and self-prepared standards following AAS manual respectively. The percentage purity of nickel almost remains constant up to the cathodes 1–4, while it suddenly decreased at the cathode no. 6 and then increased gradually and again became constant as shown in Fig. 2. The sudden decreases in nickel purity at 50 cps at cathode no. 6–7 might be due to presence of copper a major impurity. Other impurities

Table 3
Percentage purity achieved by using free electrolytic diffusion apparatus at 50 cps

Cathode #	Weight of metal deposit (g)	Concentration from graph (mg/L)			Average concentration \pm S.D. $((a+b+c)/3) \pm$ S.D.	Percentage purity			Average percentage purity \pm S.D. $((x+y+z)/3) \pm$ S.D.
		<i>a</i>	<i>b</i>	<i>c</i>		<i>x</i>	<i>y</i>	<i>z</i>	
1	0.1123	11.21	11.18	11.16	11.18 \pm 0.020	99.82	99.56	99.37	99.58 \pm 0.184
2	0.1152	11.49	11.45	11.50	11.48 \pm 0.021	99.74	99.39	99.65	99.59 \pm 0.148
3	0.1261	12.60	12.58	12.55	12.58 \pm 0.020	99.92	99.76	99.52	99.73 \pm 0.164
4	0.1192	11.78	11.86	11.91	11.85 \pm 0.053	98.83	99.49	99.92	99.41 \pm 0.448
5	0.1456	14.36	14.25	14.29	14.30 \pm 0.056	98.62	97.87	98.14	98.21 \pm 0.380
6	0.1053	10.31	10.41	10.35	10.36 \pm 0.050	97.91	98.86	98.29	98.35 \pm 0.478
7	0.1220	12.18	12.14	12.19	12.17 \pm 0.021	99.75	99.43	99.83	99.67 \pm 0.173
8	0.1136	11.31	11.29	11.35	11.32 \pm 0.025	99.56	99.39	99.92	99.62 \pm 0.221
9	0.1051	10.46	10.47	10.50	10.48 \pm 0.017	99.52	99.62	99.91	99.68 \pm 0.165
10	0.1134	11.28	11.32	11.33	11.31 \pm 0.022	99.47	99.82	99.91	99.87 \pm 0.045

a = concentration of an electrodeposit according to the AAS manual; *b* = concentration of an electrodeposit according to the PerkinElmer standard; *c* = concentration of an electrodeposit according to the Aldrich standard; *x* = percentage purity of an electrodeposit w.r.t AAS manual; *y* = percentage purity of an electrodeposit w.r.t PerkinElmer standard; *z* = percentage purity of an electrodeposit w.r.t Aldrich standard.

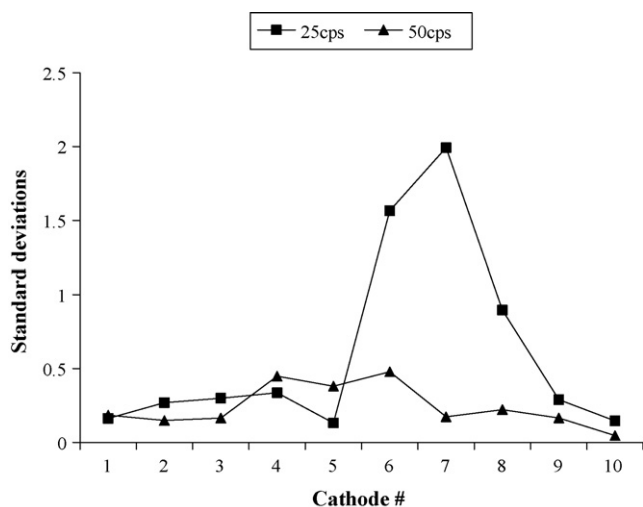


Fig. 3. Cathode wise standard deviation for nickel at 25 cps and 50 cps.

remaining left after the charge distribution at the rate of 50 cps were Co, Fe, Pb, Zn and Cu. At 50 cps, standard deviation ranges from 0.1 to 0.5 only. This range is very small as compared to the range obtained at 25 cps. The cathodes profile showing percentage purity and standard deviation (Figs. 2 and 3) clearly show that distribution of charge at the rate of 50 cps shows better results as compared to 25 cps.

4. Conclusion

Previous research described the effect of rotation of disc electrode on the geometry and structure of electrodeposits, but this work for the first time proved that rotation of charge at higher cycles per seconds over the multi cathode system could be employed for the separation and purification of nickel harmful wastes. Usually distribution of charge at the rate of 50 cps shows better results as compared to 25 cps. The results obtained show that the purity of nickel was enhanced from 95% to 99.9% with traces of copper etc.

Acknowledgements

Author is thankful to Mr. Arshad Mahmood (Senior Chemist) Health Safety and Environmental Training Center, Town Ship,

Lahore for providing the international standards (PerkinElmer and Aldrich) for AAS analysis. Author is also thankful to Sajad Hassan Shah (Project Director HEC) for providing financial assistance.

References

- [1] M.I. Kefala, A.I. Zouboulis, K.A. Matis, Biosorption of cadmium ions by Actinomycetes and separation by flotation, *Environ. Pollut.* 104 (1999) 283–293.
- [2] P. Kaewsarn, Q. Yu, Cadmium(II) removal from aqueous solutions by pre-treated biomass of marine alga *Padina sp.*, *Environ. Pollut.* 112 (2001) 209–213.
- [3] J.K. Park, Y.B. Jin, H.N. Chang, Reusable biosorbents in capsules from *Zoogloea ramigera* cells for cadmium removal, *Biotechnol. Bioeng.* 63 (1999) 116–121.
- [4] J.W. Patterson, *Waste Water Treatment*, New York, Science Publishers, New York, 1977.
- [5] B. Volesky, *Biosorption of Heavy Metals*, CRC Press Inc., Boca Raton, Florida, 1990.
- [6] Othmer Kirk, *Encyclopedia of Chemical Technology*, 6, second ed., Jehn wildly and sons, Inc., 1969.
- [7] C.S. Lin, P.C. Hsu, L. Chang, C.H. Chen, Thermomechanical properties and fatigue of nanocrystalline Ni/Cu, *J. Appl. Electrochem.* 31 (2001) 925–933.
- [8] Z. Amjad (Ed.), *Reverse Osmosis: Membrane Technology, Water Chemistry, and Industrial Applications*, Van Nostrand Reinhold, New York, 1993.
- [9] M. Mulder, *Basic Principles of Membrane Technology*, Kluwer Academic, Dordrecht, 1996.
- [10] F. Helfferich, *Ion Exchange*, Dover Publications Inc., New York, 1995.
- [11] Y. Waseda, M. Issihiki, *Purification Process and Characterization of Ultra High Pure Metals*, Springer-Verlag, Berlin, Heidelberg, New York, 2002, pp. 39–61 (Chap. No. 2).
- [12] Rudnik Ewa, Nikiel Marek, Hydrometallurgical recovery of cadmium and nickel from spent Ni–Cd batteries, *Hydrometallurgy* 89 (1–2) (2007) 61–71.
- [13] Nagwan G. Zaki, I.A. Khattab, N.M. Abd El-Monem, Removal of some heavy metals by CKD leachate, *J. Hazard. Mater.* 147 (1–2) (2007) 21–27.
- [14] M. Nardin, A.M. Wache, V.Q. Kinh, *Mem. Sci. Rev. Metal* 66 (1969) 312.
- [15] N. Zubryckyj, W. Kunda, D.J.I. Evans, *J. Electrochem. Soc.* 116 (1969) 542.
- [16] R.R. Sodden, V.J. Albano, *J. Electrochem. Soc.* 115 (1968) 766.
- [17] M. Dinu, *Metalurgia (Bucharest)* 35 (1983) 599.
- [18] P.T. Tang, U.S. Patent 6,036,833. March 14 (2000).
- [19] M. Holm, T.J.O. Keefe, Evaluation of nickel deposition by electrochemical impedance spectroscopy, *J. Appl. Electrochem.* 30 (2000) 1125–1132.
- [20] C. Lupi, M. Pasquali, A. DellEra, Studies concerning nickel electrowinning from acidic and alkaline electrolytes, *Minerals Eng.* 19 (12) (2006) 1246–1250.