STUDIA UBB CHEMIA, LVI, 4, 2011 (p. 121 - 130)

NICKEL RECOVERY FROM ELECTRONIC WASTE
I. NICKEL RECOVERY FROM CATHODE RAY TUBES

BIANCA ROBOTIN[a], VASILE COMAN[a], PETRU ILEA[a, *]

ABSTRACT. The aim of the present study was the recovery of nickel from waste electrical and electronic equipment and particularly, from cathode ray tubes. The major nickel sources in cathode ray tubes are the electron gun and the nickel containing shadow mask. For the nickel recovery tests, the metallic components were chemically (H_2SO_4, HCl, $FeCl_3$ aqueous solutions) and electrochemically (H_2SO_4, HCl, NaCl aqueous solutions) solubilised. The obtained solutions were treated for selective nickel/iron separation. The resulted solutions were used for the electrowinning of nickel or nickel-iron alloys.

Keywords: *electronic waste, cathode ray tube waste, nickel recovery*

INTRODUCTION

Nowadays, resource recycling and environmental protection are central topics worldwide. Fast and continuous technological development in different areas leads to a massive accumulation of waste materials. Among these, an important class are the waste electrical and electronic equipments (WEEEs) [1-5]. WEEEs contain valuable materials, such as precious metals (Au, Ag, Pd, Pt), different useful metals (Cu, Ni, Zn, etc.), and a significant amount of chemical elements (Pb, Hg, Cr, Sn, Cd), which are hazardous for the environment and human health. Recycling of these materials is therefore an attractive alternative which aims at both recovering and reusing the metal values and avoiding the environmental risks [6].

Among WEEEs, cathode ray tubes (CRTs) recycling represents a major concern, mainly due to their large volume, toxicity of their material content, legislation (disposal restrictions) and recycling costs [7]. Moreover, the recent tendency of replacing CRT technology with liquid crystal, plasma, and light-emitting diode (LED) displays generates a massive accumulation of CRT waste. From the total weight of a TV set/computer screen, the CRT constitutes two thirds. The CRT components vary as a function of producer, model and fabrication year. The main materials used for CRT fabrication are glass and metal. Glass represents approximately 85 % of the total weight [8]

---

[a] Babes-Bolyai University, Faculty of Chemistry and Chemical Engineering, 11 Arany Janos Street RO-400028, Cluj-Napoca, Romania
[*] pilea@chem.ubbcluj.ro

and it has a negative impact on the environment when disposed improperly, due to its high content of heavy metals, especially Pb. Although numerous studies on glass recycling exist, an ultimate solution is still not obvious [8, 9]. Metals such as Fe, Ni, Co, Cr, Mn are found in the electron gun (EG) and in the shadow mask / aperture grill, depending on the used technology. In a CRT, the metallic components of an EG contain various amounts of nickel. On top of that, in some CRTs, there is another source of nickel, i.e. the shadow mask made of a nickel steel alloy (INVAR) with a low thermal expansion coefficient. To our knowledge, until now, there aren't any literature studies concerning the metal recovery and/or separation from CRTs, the main focus being on the recycling of the CRT glass [8, 9].

The current study focuses on nickel recovery from electronic waste, especially from CRTs. Nickel is an important metal, heavily utilized in industry mainly due to its anticorrosion properties [10]. At the same time, nickel could have a negative impact on the environment and human health if it contaminates the soil due to an improper disposal [11]. The recovery of nickel from WEEEs is therefore necessary for environmental reasons and, at the same time, could be economically feasible since nickel has an elevated price (18000 USD/tonne, October 2011, see: *http://www.metalprices.com*).

The extractive metallurgy of nickel can be the first place to look for technologies with direct application in the field of nickel recovery from electronic waste. The major nickel source on Earth is represented by the nickel ores (laterites and sulphides), which are extracted all over the world. The hydrometallurgical processes of obtaining the pure metal from its ores involve various leaching procedures. In the case of nickel, when using acid leaching, the main acids used are concentrated sulphuric and hydrochloric acid [10]. In the case of HCl, oxidizing agents, such as $FeCl_3$, are added to the mix [12], in order to facilitate the leaching process.

In our studies, the metallic composition of the EGs was determined, followed by a chemical and electrochemical solubilisation of the metallic components using different acid leaching agents and finally, nickel and iron were separated from the resulted solutions**.** The electrodeposition of nickel and nickel-iron alloys from the resulted solutions is currently under investigation.

RESULTS AND DISCUSSION

In our case, the first operation of the metal recycling process from electronic waste consisted of the manual dismantling of the monitors, when the plastic parts were separated from the cathode ray tube, the electrical wiring and the printed circuit boards contained within. In the next step, the CRT was broken down into pieces and the metallic parts were separated from the glass and ceramic components. The electron gun and shadow mask found inside the CRTs were further used for the solubilisation experiments.

Elemental composition determination of electron guns and shadow masks from CRTs

In order to perform an initial qualitative analysis of the elemental composition of an EG, the sample was investigated using X-ray diffraction (XRD). The XRD analysis result of a typical EG from a colour computer monitor is depicted in Figure 1. The results indicated the presence of Ni, Fe, Co and Cr.

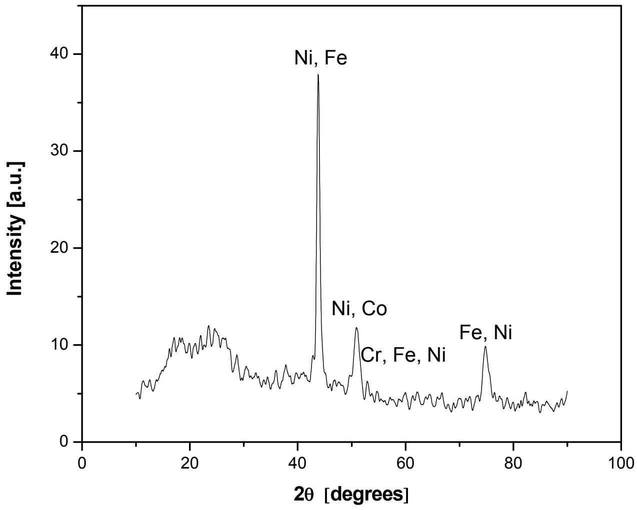

Figure 1. The XRD analysis of a typical EG from a colour monitor

The next stage was the quantitative elemental analysis of the EGs and shadow masks. For that purpose the EG was preliminarily subjected to a mechanical separation process into metallic, glass, and ceramic components, and the metallic parts were separated into magnetic (EGM) and non-magnetic (EGN) fractions. On average, an EG weighs around 18 g, out of which the EGM parts consist of approximately 45 %. In the case of shadow masks, it was noticed that the INVAR alloy was magnetic. The metallic parts from EG and shadow mask were solubilised in *aqua regia* and the resulted solutions were analysed by atomic absorption spectrometry (AAS). The elemental composition of the EG was estimated using five different samples, in order to establish an average composition. The tests were performed both on magnetically separated parts and non-separated ones. As mentioned before, the EG elemental composition is variable depending on the producer, model and manufacturing year. Therefore, the metal concentration varies as it is shown in Table 1.

As it can be seen in Table 1, a magnetic separation of the EG components generates two fractions with different concentration ratios Ni:Fe. The Ni content was higher in EGM (40 to 45 %), counting for 75 % of all Ni content in an EG. Moreover, the solubilisation of the EGN parts brings a high content of Cr in the solution, which is not the case with EGM.

Table 1. Typical elemental composition of the metallic parts of EGs and shadow masks from CRTs

CRT waste type	Ni	Fe	Cr	Mn	Co
	[%]				
EG	25-30	50-60	10-11	1.0-1.5	1-2
EGM	40-45	50-55	ND*	0.3-0.35	3-3.5
EGN	10-15	60-70	17-19	1.0-1.5	ND*
Shadow mask	36-40	60-64	ND*	ND*	ND*

*Not detected

These findings suggest different approaches for the Ni recovery from the magnetic and non-magnetic metallic parts of the EGs. As expected, the INVAR shadow mask has a content of Ni between 36 and 40 %. The experiments concerning the EG and INVAR solubilisation are presented below.

Metallic waste solubilisation

Chemical solubilisation

The EG waste chemical solubilisation was performed in sulphuric and hydrochloric acid respectively. Both acid solutions are used frequently in classical extraction methods of Ni from Ni containing ores [10]. Moreover, Ni electrowinning and electrorefining are performed using sulphate and chloride solutions, and even a mixture of the two. The solubilisation tests were performed using concentrated and diluted acid solutions.

Solubilisation tests in concentrated H_2SO_4 (approx. 18 M) revealed the inefficiency of using this strong acid solution as solubilisation medium due, most probably to, the formation of a passive layer on the metallic surface. A more diluted solution (2 M) of H_2SO_4 proved to be more efficient in dissolving the metallic waste. The results showed that after 12 days, 44.3 % (4.7 g) of the 10.6 g of EG waste were dissolved in 100 ml of 2 M H_2SO_4 solution. If we consider a linear evolution of the solubilisation process, this result translates in a solubilisation rate of 16.3 mg of waste per hour. The same leaching agent (2 M H_2SO_4) was used for comparison in the electrochemical solubilisation tests, described in the next section.

The next approach was to use different concentrations of HCl: 1, 2, 4, 6 and 12 M. When using concentrated HCl (above 6 M) the EG waste can be totally dissolved in a reasonable time period, but toxicity and handling issues arise. The diluted HCl solutions were much less efficient as leaching agents for this type of metallic waste (results not shown).

The low solubilisation efficiencies in mineral acids (H_2SO_4 and HCl) lead to the use of an oxidising agent in acidic media, more precisely $FeCl_3$ in HCl. The solubilisation tests were carried out using both the separated metallic waste (EGM and EGN) and the non-separated waste. In this case small quantities of waste were used (approximately 1 g) and, for quantification reasons, the tests were stopped after 11 days, before the end of the process. The amount of oxidant needed was stoichiometrically calculated and added in 100 % excess in the 1 M HCl solution. The obtained results are depicted in Figure 2.

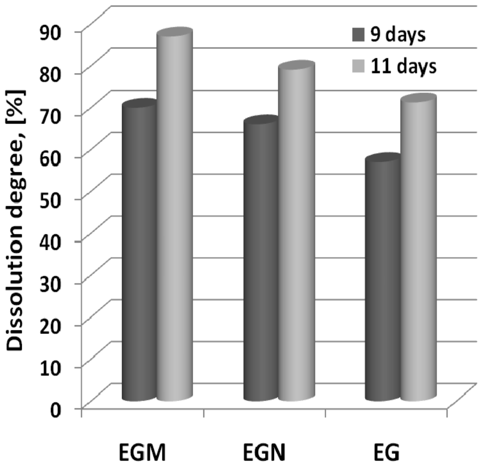

Figure 2. Solubilisation degree of the EGs metallic parts at two different times, by using 0.04 M $FeCl_3$ containing 1 M HCl.

As can be seen from Figure 2, after 9 days approximately 60 % of the non-separated waste was dissolved while, apparently, the magnetic separation produced an increase of the dissolved quantity percentage (approximately 10 %) for both EGM and EGN. At the end of the test, after 11 days, it was found that 87 % of EGM, 79.1 % of EGN and 71.3 % of EG were dissolved, keeping the trend observed after 9 days. Considering the duration and the experimental conditions, the differences between the three cases can be considered within the limits of acceptable experimental errors and they cannot be assigned to a positive effect of magnetic separation. The calculated solubilisation rate in this case is several times lower than for 2 M H_2SO_4, being situated between 2.7 and 3.3 mg of EG waste per hour.

The results of the chemical solubilisation tests show that, although some approaches are very efficient in dissolving the waste, the procedure takes a very long time and consumes large quantities of concentrated mineral acids. Moreover, handling and toxicity issues arise. In order to partially eliminate the handling concerns, a more diluted acidic media or an oxidizing agent present (e.g. $FeCl_3$) can be used successfully.

In order to improve the solubilisation degree of these wastes and to shorten the time spent for this operation, the next experiments were performed in an electrochemical reactor, using the metallic waste as anode.

Electrochemical solubilisation

The electrochemical solubilisation (ECS) tests were performed on the INVAR shadow mask and on the magnetic parts (EGM) of the EG respectively. The magnetic parts were used due to the high concentration of Ni and the possibility to avoid the contamination with Cr of the resulted solutions. In the next sections the focus will be only on the solutions resulted from the solubilisation of EGM and/or INVAR shadow mask.

The solubilisation of the metallic waste was carried out in three different acidic solutions: 2 M H_2SO_4, 1 M HCl and 0.1 M NaCl (pH = 1) respectively. The tests were carried out in an electrochemical cell with an electrolyte volume of 500 cm^3. The electrodes consisted of two graphite plates (1 cm thickness and 70 cm^2 surface area), with parallel horizontal placement inside the cell. The upper electrode was used as cathode and the metallic waste was placed on the bottom plate, in electrical contact with the anode. The cell was placed on a magnetic stirrer which proved to be very useful for maintaining the electrical contact between the magnetic metallic parts and the graphite anode and at the same time for providing a controlled stirring of the metallic pieces. All ECS experiments were performed at room temperature, under galvanostatic conditions (applied current values between 0.5 and 2 A).

In order to compare the three leaching media, identical quantities of INVAR (around 5 g), were dissolved under galvanostatic conditions (2 A) for the same period of time (2.5 h). The calculated current efficiency was higher than 90 % in all cases. The main differences between the three acidic solutions are detailed below.

In the case of 1 M HCl, a thin green coloured deposit with low adherence was observed on the cathode surface at the end of the experiment. When working under galvanostatic conditions, the reaction taking place at the cathode is hydrogen evolution. If the dissolved metals reach a certain concentration and the potential of the cathode allows for it, the hydrogen evolution is partially replaced by the electrodeposition of the metals (in our case Ni and Fe). Moreover, in an unbuffered medium, the hydrogen evolution reaction changes the local pH at the cathode surface especially, and it can induce the precipitation of Fe and Ni hydroxides, hence the appearance of a coloured precipitate/deposit.

In 0.1 M NaCl (pH = 1) the local pH change effect resulted very soon in a large quantity of precipitate around the cathode. The experiment was stopped after approximately 2 hours and the solution and precipitate were analysed by AAS. The final pH of the solution reached a value around 4, where all Fe(III) should precipitate as $Fe(OH)_3$. The analysis of the precipitate (washed and dried) showed a surprisingly high amount of Ni (45 % of the total Ni-Fe content), although the Ni percentage in INVAR is 36 % and Ni precipitation should occur at higher pH values. The explanation could be the fast precipitation due to high local pH changes. The amount of metal left in the solution was less than half (45 %) of the whole dissolved quantity with a Ni/Fe ratio of 1/2.5. In our opinion this medium can be used for ECS only with a strict control of pH, e.g. by addition of concentrated HCl.

The best results from our perspective were those obtained for 2 M H_2SO_4 solution. In this case no deposit or precipitate was observed at the cathode. This fact suggests us to use the same solution for more successive solubilisation tests (e.g. 3), the final concentration of metal in the solution arriving at ~30 g/L. Even at this concentration the cathodic deposition of Ni/Fe didn't occur. The current efficiency was higher compared to HCl and NaCl, reaching approximately 95 %. A parallel test was run, under identical experimental conditions but in absence of electrolysis current, in order to evaluate the contribution of the chemical solubilisation. The result showed that in the same period of time, 2.5 hours, in 2 M H_2SO_4, less than 0.5 % of the total metallic waste was solubilised. The chemical solubilisation rate for pure INVAR in 2 M H_2SO_4 was lower (9 mg/hour) than that for EG wastes (see Section 2.1).

In the case of EGM waste, the results in 2 M H_2SO_4 and 1 M HCl were similar to those for INVAR, with a high current efficiency in both cases (higher than 90 %). Some ECS tests were performed at lower current values (e.g. 0.5 A) when, for a similar amount of used total charge (10 hours), the current efficiency was higher, reaching 99 % in the case of HCl.

Compared with the chemical solubilisation, a higher efficiency of the ECS of the metallic waste in diluted acidic solutions (e.g. 2 M H_2SO_4, 1 M HCl and even 0.1 M HCl) was clearly noticed (hours *vs.* days). In the case of HCl, the chemical solubilisation was efficient only when the concentration of the acid was above 6 M. It was also demonstrated that the ECS is feasible in 0.1 M NaCl (pH = 1), when the pH is maintained at low values by adding acid or by buffering the acidic solution.

Fe-Ni separation from solutions / Iron precipitation

The solution resulted from the solubilisation of the EG waste contains a large amount of Fe ions. If the final purpose is to obtain a relatively pure deposit of Ni, Fe must be separated from the solution before any electrowinning experiments. Another alternative would be the tuning of the experimental parameters (solution composition, pH, temperature, current density) in order to obtained Ni-Fe alloys with a useful composition (e.g. INVAR).

Various studies offer multiple alternatives for Fe removal, the simplest being the precipitation of Fe^{3+} by controlling the temperature and pH of the solution [13-15]. In the case of low concentrations of Fe ions, an extraction using specific solvents could be employed [16, 17], too. Unfortunately, these agents are usually very costly and couldn't justify economically their employment for our purposes (considering Ni and Fe prices), except for low (traces) Fe amounts in the solution.

Our initial approach aimed at a selective precipitation of iron from the solution. The solution used for this purpose was that resulted from the ECS of an EGM sample under galvanostatic conditions (0.5 A) in 1 M HCl, as described above (see Section 2.2). A complete solubilisation of approximately 5.3 g of waste was finished in 10 hours. The resulted solution had the composition shown in

Table 2, with a Ni to Fe ratio in the solution of 1 to 1.2 and traces of Co and Mn. Iron could be partially separated by precipitating Fe^{3+} by raising the solution pH, stepwise, from 2 to 4 (adding NaOH). It was observed that the ratio Ni to Fe was changed to 2:1 with small losses of Ni in the precipitate (Table 2). The results show that by this simple approach a percentage of approximately 55 % of Fe was removed from the solution. The resulted solution could be used for Ni-Fe alloys electrodeposition, with high Ni content [18].

Table 2. Metal concentrations of the samples resulted by selective precipitation of iron (NaOH addition)

Sample	Ni		Fe		Co		Mn	
	[g/L]	[%]	[g/L]	[%]	[g/L]	[%]	[g/L]	[%]
Solution	9.02	44.40	11.00	51.30	0.39	1.90	0.19	0.90
Precipitate	-	4.50	-	94.10	-	0.05	-	0.04
Filtrate	8.60	64.70	4.20	33.40	0.38	0.80	0.18	0.70

In order to separate more iron from the solution, Fe^{2+} needs to be oxidised to Fe^{3+}. This can be accomplished either chemically (by using oxygen, chlorine or an oxidiser such as sodium persulphate) or electrochemically (by anodic oxidation at a convenient electrode material). Our first approach was the oxidation with air at high temperature. The temperature of the solution was kept constant at 85 ^{0}C for four hours at a pH value around 3.5 and the aeration was performed using a peristaltic pump. The results in this case have shown a removal efficiency of Fe of about 85 %.

The complete removal of Fe^{3+} from a synthetic sulphate based solution containing 1:1 Ni and Fe (~ 10 g/L each) was obtained by precipitating Fe^{3+} at pH 3.5 and 80 ^{0}C. The pH was controlled by adding a solution of 10 % Na_2CO_3. The reaction time was four hours and the analysis of the filtrate showed that there was virtually no Fe left in the solution. The nickel loss in the precipitate was estimated to be around 4.4 % of the initial dissolved quantity.

Nickel and nickel-iron alloys can be electrodeposited on different materials (steel, copper, nickel, carbon) using conventional methods both from sulphate and chloride media in a relatively broad range of acidic solutions (pH between 2 and 4); the influence of different parameters (solution composition, pH, temperature, and current density) on the Ni and Ni-Fe alloys electrowinning is under current study and the results will be presented in future publications.

CONCLUSIONS

Nickel recovery from electronic waste is important both economically and for environmental reasons. The current research aimed at a concrete aspect of WEEE recycling, i.e. the solubilisation of the Ni containing metallic parts of CRTs (EG and shadow mask) and the purification of the obtained aqueous solutions.

The results of our current studies lead us to the following conclusions:

Chemical solubilisation of the metallic EG wastes from CRTs takes a very long time (solubilisation rates in the mg/hour range) and sometimes consumes large quantities of concentrated mineral acids;

The chemical solubilisation can be improved when an oxidizing agent such as $FeCl_3$ is used (see for example the case of diluted HCl);

Electrochemical solubilisation is much faster (hours *vs.* days) and can be performed in less acidic conditions with high efficiencies. Current efficiencies over 90% were obtained in all experimental conditions, even for the highest applied current value (2 A);

Iron can be partially or totally separated from the resulted solutions *via* the oxidation of Fe^{2+} to Fe^{3+}, followed by Fe^{3+} precipitation at controlled pH and temperature;

The resulted solutions, depending on the residual Fe concentration, can be used for the electrodeposition of nickel and/or nickel-iron alloys. The composition of the alloys can be controlled by tuning the experimental electroextraction conditions.

EXPERIMENTAL SECTION

Reagents

The main leaching media used for experiments were 2 M H_2SO_4, 1 M HCl, 0.1 M NaCl in HCl (pH = 1) and 0.04 M $FeCl_3$ in 1 M HCl. All chemicals were of analytical grade and were used as received. All solutions were prepared with double distilled water (Double D Still, JENCONS, England).

Experimental setups

The composition of EGs was established by XRD on a Shimadzu diffractometer XRD-6000 assembled in Bragg-Brentano $\theta/2\theta$ with a goniometer which operates at atmospheric pressure with Ni filters using CuK_α radiation (λ = 1.5418 Å). The standard calibration was made with quartz powder. Data acquisition conditions were: 40 KV operating potential at a 30 mA current. The peaks qualitative identification was realized using the JCPDS (Joint Committee on Powder Diffraction Standards) database.

The EGs elemental composition was determined by solubilisation in *aqua regia* and Atomic Absorbtion Spectrometry (AAS) measurements using an Atomic Absorption Spectrometer (AAS) Avanta 9500 (GBC, Australia).

For electrochemical solubilisation tests, an electrochemical reactor (electrolyte volume of 500 cm^3) with plane parallel graphite electrodes was used. Saturated $Ag|AgCl_{KCl}$ reference electrodes were used for all experiments.

A PC equipped with a PCI 6221 E data acquisition board (National Instruments, USA) was used to drive a DXC236 potentiostat/galvanostat (Wenking, Germany). The LabView 6.1 software (National Instruments, USA) was used for the process control and data acquisition.

ACKNOWLEDGMENTS

BR and VC wish to thank for financial support the projects co-financed by the Sectoral Operational Program For Human Resources Development 2007 – 2013 - contract no.: POSDRU/88/1.5/S/60185 – “Innovative doctoral studies in a Knowledge Based Society” and - contract no.: POSDRU/89/ 1.5/S/60189 – “Postdoctoral Programs for Sustainable Development in a Knowledge Based Society”, respectively.

Authors are grateful to Dr. Oana Ponta for XRD analysis and Dr. Sorin-Aurel Dorneanu for his help and assistance.

REFERENCES

1. R. Widmer, H. Oswald-Krapf, D. Sinha-Khetriwal, M. Schnellmann, H. Böni, *Environmental Impact Assessment Review,* **2005**, *25*, 436.
2. B.R. Babu, A.K. Parande, C.A. Basha, *Waste Management & Research,* **2007**, *25*, 307.
3. B.H. Robinson, *Science of the Total Environment*, **2009**, *408*, 183.
4. F.O. Ongondo, I.D. Williams, T.J. Cherrett, *Waste Management,* **2011**, *31*, 714.
5. M. Bigum, T.H. Christensen, in *Solid Waste Technology & Management, Vol. 1 & 2* (Ed.: T.H. Christensen), John Wiley & Sons, Ltd, Chichester, UK, **2010**.
6. L.E. Macaskie, I.P. Mikheenko, P. Yong, K. Deplanche, A.J. Murray, M. Paterson-Beedle, V.S. Coker, C.I. Pearce, R. Cutting, R.A.D. Pattrick, D. Vaughan, G. van der Laan, J.R. Lloyd, *Hydrometallurgy,* **2010**, *104*, 483.
7. C. Nnorom, O. Osibanjo, M.O.C. Ogwuegbu, *Resources, Conservation and Recycling,* **2011**, *55*, 275.
8. F. Andreola, L. Barbieri, A. Corradi, I. Lancellotti, *Waste Management and Research,* **2005**, *23*, 314.
9. S. Herat, *CLEAN - Soil, Air, Water,* **2008**, *36*, 19.
10. D.E.G. Kerfoot, in *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH Verlag GmbH & Co. KGaA, **2000**.
11. E. Denkhaus, K. Salnikow, *Critical Reviews in Oncology/Hematology,* **2002**, *42*, 35.
12. K.H. Park, D. Mohapatra, B.R. Reddy, *Separation and Purification Technology,* **2006**, *51*, 332.
13. K. Wang, J. Li, R.G. McDonald, R.E. Browner, *Hydrometallurgy,* **2011**, *109*, 140.
14. Y. Chang, X. Zhai, B. Li, Y. Fu, *Hydrometallurgy,* **2010**, *101*, 84.
15. S. Agatzini-Leonardou, P.E. Tsakiridis, P. Oustadakis, T. Karidakis, A. Katsiapi, *Minerals Engineering,* **2009**, *22*, 1181.
16. R.K. Mishra, P.C. Rout, K. Sarangi, K.C. Nathsarma, *Hydrometallurgy,* **2011**, *108*, 93.
17. M.-S. Lee, K.-J. Lee, *Hydrometallurgy,* **2005**, *80*, 163.
18. I. Tabakovic, V. Inturi, J. Thurn, M. Kief, *Electrochimica Acta*, **2010**, 55, 6749.