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METALS LEACHING FROM WASTE PRINTED CIRCUIT BOARDS. PART I: EFFICIENCY AND SELECTIVITY IN $FeCl_3$ AND $CuCl_2$ ACIDIC SOLUTIONS

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ABSTRACT. The leaching of metals from waste printed circuit boards (WPCBs) was investigated in different leaching systems using $FeCl_3$ or $CuCl_2$ as oxidants. The influence of solution speciation on the redox equilibria and process performances was studied in unstirred 1 M HCl solutions. The efficiency of these systems was compared on the basis of the extent of leaching of individual metals and total metal dissolution. It has been found that in chloride medium the leaching efficiency reaches a plateau at 0.4 M $CuCl_2$ concentration, while for $FeCl_3$ it is continuously increasing even at concentrations four times higher.

Keywords: *waste printed circuit boards, leaching systems, $FeCl_3$ and $CuCl_2$*

INTRODUCTION

In the recent years, the lifespan of consumer electronic devices has become relatively short, due to the rapid changes in equipment features and capabilities. This creates a large stream of waste electric and electronic equipment (WEEE) [1, 1]. Printed circuit boards (PCBs) are a key component in electronic equipments, representing about 3 % of the total amount of WEEE. In general, WPCBs contain approximately 30 % metals and 70 % non-metal materials [2, 3]. The typical metals in PCBs consist of copper (20 %), iron (8 %), tin (4 %), nickel (2 %), lead (2 %), zinc (1 %), silver (0.2 %), gold (0.1 %), and palladium (0.005 %) [2-7]. Hence, recycling of electronic waste is an important topic not only from the point of waste treatment but also from the recovery aspect of valuable materials. Therefore, in the past few years many investigations have been made to develop eco-friendly technologies with cost effective processing and without any negative impact on the environment [1, 2-8].

Electronic waste recycling technologies have several preliminary steps in order to separate and concentrate the valuable materials and thus increase the performance of the recycling process. The most important pre-treatments are mechanical processing, specific gravity separation, magnetic and

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electrostatic separation [5-8]. These are followed by pyrometallurgical and hydrometallurgical technologies which are the main industrial scale processes for metal recovery from WEEE [5, 7]. Pyrometallurgical processing, especially open burning, incineration and smelting were the traditional methods for metal recovery from e-waste in the last two decades [2, 5, 7, 8]. These methods are simple but have major disadvantages like: non-selectivity, hazardous operating conditions and emission of toxic gases (dioxin, brominated flame retardants) and fumes metals (Hg, Pb and Cd) [1, 5-9]. The hydrometallurgical method is more predictable, and more easily controlled. The most important steps in hydrometallurgical processing consist of a series of acid or caustic leaching of metals from the WEEE depending upon the composition of the WPCBs and the variable chemical properties of the metals. The use of aerated cyanide leaching system for gold and silver has been banned in some countries due to environmental concerns [10]. This has resulted in the increase in research activities with non-cyanide ligands and more efficient oxidant than air [11-14]. However there are issues that need to be solved, such as: increasing leaching rate and selectivity while reducing the reagent consumption [8].

The aim of this work was to study the leaching of metals from WPCBs in acidic $FeCl_3$ or $CuCl_2$ solutions. The efficiency of the dissolution processes was evaluated based on the experimental results and possible redox equilibriums.

RESULTS AND DISCUSSION

The influence of oxidant concentration on overall metal dissolution

Analyzing the literature data for the Fe-Cl-H_2O and Cu-Cl-H_2O systems [15-20] it was found that, depending on chloride concentration, the following chemical species can be present in the solution: $FeCl_2^+$, Fe^{2+}, $CuCl_2(aq)$, $CuCl^+$, $CuCl_2^-$ and $CuCl_3^{2-}$. For the Fe^{3+}/Fe^{2+} redox couple, Cl^- concentration is ranging from 1.3 to 5.8 M, as a result, the predominant chemical species are $FeCl_2^+$ and Fe^{2+}. In the case of Cu^{2+}/Cu^+ when chloride concentration is lower than 2 M the predominant chemical species are $CuCl^+$ and $CuCl_2^-$, while at higher concentrations, $CuCl_2(aq)$ and $CuCl_3^{2-}$ are the predominant.

Considering the calculated equilibrium potentials (vs. NHE) for the standard redox systems (Fe^{3+}/Fe^{2+}, Cu^{2+}/Cu^+, Cu^{2+}/Cu, Cu^+/Cu):

$$Fe^{3+} + e^- \leftrightarrow Fe^{2+} \qquad E^0 = 0.775\ V \qquad (1)$$

$$Cu^{2+} + 2e^- \leftrightarrow Cu \qquad E^0 = 0.337\ V \qquad (2)$$

$$Cu^{2+} + e^- \leftrightarrow Cu^+ \qquad E^0 = 0.167\ V \qquad (3)$$

$$Cu^+ + e^- \leftrightarrow Cu \qquad E^0 = 0.506\ V \qquad (4)$$

The dissolution of metals involves the following redox reactions and equilibrium potentials for the oxidants:

$$FeCl_2^+ + e^- \leftrightarrow Fe^{2+} + 2Cl^- \qquad E^0 = 0.702\ V \tag{5}$$

$$CuCl^+ + 2e^- \leftrightarrow Cu + Cl^- \qquad E^0 = 0.318\ V \tag{6}$$

$$CuCl^+ + Cl^- + e^- \leftrightarrow CuCl_2^- \qquad E^0 = 0.466\ V \tag{7}$$

$$CuCl_2^- + e^- \leftrightarrow Cu + 2Cl^- \qquad E^0 = 0.169\ V \tag{8}$$

$$CuCl_{2\,(aq)} + 2e^- \leftrightarrow Cu + 2Cl^- \qquad E^0 = 0.319\ V \tag{9}$$

$$CuCl_{2\,(aq)} + Cl^- + e^- \leftrightarrow CuCl_3^{2-} \qquad E^0 = 0.428\ V \tag{10}$$

$$CuCl_3^{2-} + e^- \leftrightarrow Cu + 3Cl^- \qquad E^0 = 0.209\ V \tag{11}$$

Comparing the standard reduction potential value of the Fe^{3+}/Fe^{2+} redox couple in chloride, eq. (5), and chloride free medium eq. (1) it can be seen that the formation of $FeCl_2^+$ does not influence significantly the oxidant power of Fe^{3+} ions. Similarly, for the Cu^{2+}/Cu redox couple the potential was not notably modified in chloride solution due to the low stability of Cu (II) chloro-complexes. Quite the opposite happens in the case of Cu^{2+}/Cu^+ (eq. 7, 10) for which the redox potential is shifted to more positive values, in the presence of chloride ions. This can be attributed to the formation of very stable Cu (I) chloro-complexes which, accordingly to the Nernst equation, will determine the increase of the redox potential. Figure 1 shows that the dependency of the global dissolution degree (defined as the ratio between the amount of dissolved metals and total amount of metals in the WPCB sample) on the oxidant concentration is more pronounced in the case of $FeCl_3$ than for $CuCl_2$.

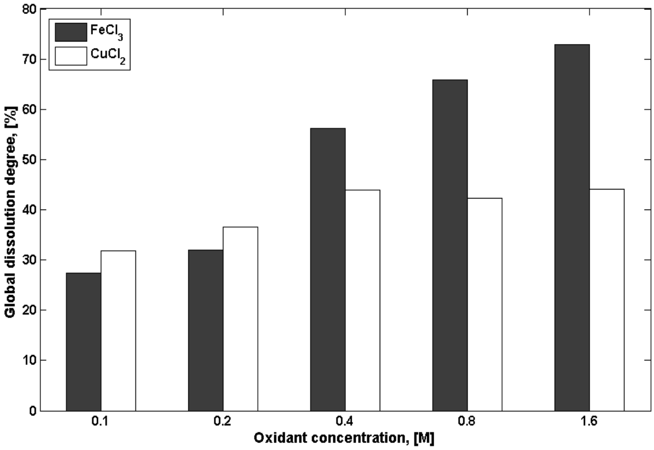

Figure 1. Global dissolution degree of metals in 1 M HCl using $FeCl_3$ and $CuCl_2$ as oxidants.

Hence, an increase of oxidant concentration by 16 times (0.1-1.6 M) enhances the global dissolution degree 2.6 times for $FeCl_3$ and 1.5 times for $CuCl_2$. This can be easily explained by considering the different standard reduction potentials eq. (1-11) of the studied redox systems Fe^{3+}/Fe^{2+},

Cu^{2+}/Cu^{+}, Cu^{2+}/Cu. As a result, at the same oxidant concentration Fe^{3+} is a more powerful oxidizing agent than Cu^{2+} or Cu^{+} in both chloride and chloride free mediums, due to the higher redox potential. However, the experimental results show that at low oxidant concentrations (0.1-0.2 M) it appears that $CuCl_2$ is more efficient oxidant in the dissolution of metals than $FeCl_3$.

In order to explain these results the influence of mass transport on the dissolution rate has to be considered. Since the leaching experiments are realized in stationary solutions the mass transport of the reactants and products will occur only by diffusion. Therefore the transport intensity of different chemical species is dependent on the diffusion coefficient which in turn depends on the molar volume (bulk) of the ions. Based on the discussions regarding the speciation of Fe^{3+}/Fe^{2+} and Cu^{2+}/Cu^{+} in aqua chloride medium it is obvious that the intensity of the mass transport will depend on the complexation of Fe^{3+}, Cu^{2+} and Cu^{+}. For this reason in the case of $FeCl_3$ the mass transport has the same rate throughout the experiments thanks to the formation of only one chloro-complex ($FeCl_2^+$) while for Cu^{2+}/Cu^{+} there are two situations. At lower $CuCl_2$ concentrations than 0.4 M the chemical species involved in the leaching process are $CuCl^+$ and $CuCl_2^-$, while at higher concentrations than 0.4 M the transport of $CuCl_{2(aq)}$ and $CuCl_3^{2-}$ has to be considered.

It is clear that the transport of copper chloro-complexes is even slower as the concentration of chloride ions increases due to the formation of more bulk species. Also, comparing the copper chloro-complexes with $FeCl_2^+$ it seems like at oxidant concentrations lower than 0.4 M the diffusion of Cu^{2+} is faster than that of Fe^{3+} because the $CuCl^+$ ion is smaller than $FeCl_2^+$ ion. For oxidant concentrations higher than 0.4 M the transport of Cu^{2+} is still the fastest due to the formation of $CuCl_{2(aq)}$ neutral species which diffuse more easily than $FeCl_2^+$ ions.

In order to reveal the chemical species which diffuse from the reaction zone to the bulk and their influence on the metals dissolution rate is essential to identify the reactions from which they have been resulted. Analyzing the possible redox reactions eq. (1-11) it is obvious that in the case of Fe^{3+}/Fe^{2+} there is a single main redox reaction eq. (5) which generates small ions (Fe^{2+}, Cl^-) as reaction products. In contrast, the Cu^{2+} can be reduced by parallel reactions to Cu or Cu^+ depending on the $CuCl_2$ concentration and the molar ratio between the $CuCl_2$ and the metals from the WPCB sample. Therefore at low $CuCl_2$ concentrations (0.1-0.4 M) the Cu^{2+} ion is reduced by two competitive reactions eq. (6, 7). The redox equilibrium constant for eq. (6, 7) can be defined by the following equations:

$$K_1 = \frac{k_1}{k_{-1}} = e^{-\frac{\Delta_r G_1}{RT}} = \frac{[Cl^-]}{[CuCl^+]} = 5.72 \cdot 10^{10} \qquad (12)$$

$$K_2 = \frac{k_2}{k_{-2}} = e^{-\frac{\Delta_r G_2}{RT}} = \frac{[CuCl_2^-]}{[CuCl^+][Cl^-]} = 7.63 \cdot 10^7 \qquad (13)$$

where K_1, K_2 are the redox equilibrium constants for eq. (6, 7); k_1, k_2 forward rate constants; k_{-1}, k_{-2} backward rate constants; $\Delta_r G_1$, $\Delta_r G_2$ standard free energy of reaction expressed in KJ/mol; *R* - universal gas constant in J/(mol K); *T* - temperature in K.

By comparing the redox equilibrium constants values of the two reactions it is evident that the ratio between the forward and backward rate constants is 750 times higher for the cementation of copper than for the reduction of $CuCl^+$ to $CuCl_2^-$. This means that $CuCl^+$ is consumed much faster when it is reduced to Cu than when it is reduced to $CuCl_2^-$. Given that the both mass transport and redox reaction are much faster in the case of eq. (6) it can be concluded that the contribution of eq. (7) to the dissolution of metals can be neglected in the range of 0.1-0.4 M $CuCl_2$ concentration.

It is also important to reveal that the increase of $CuCl_2$ concentration will affect the rate of copper cementation until the whole surface of the metals is covered by Cu. This also results from the experimental data showed in Figure 1, which confirm that the metals dissolution achieves a maximum at 0.4 M after which the increase of $CuCl_2$ concentration does not affect the dissolution rate due to the fact that the contact between the reagents is blocked by the cemented copper. In order to continue the dissolution of metals it is necessary to dissolve the cemented copper first. This can occur by eq. (14) at chloride concentrations below 2 M and by eq. (15) at chloride concentrations higher than 2 M:

$$Cu + 3Cl^- + CuCl^+ \leftrightarrow 2CuCl_2^- \qquad K_3 = 1.01 \cdot 10^5 \qquad (14)$$

$$Cu + 4Cl^- + CuCl_{2\,(aq)} \leftrightarrow 2CuCl_3^{2-} \qquad K_4 = 5.13 \cdot 10^3 \qquad (15)$$

The equilibrium constants values obtained for eq. (14, 15) indicates that the dissolution of cemented copper is less favored than the dissolution of metals through copper cementation eq. (12, 13) and is diminished by the increase of chloride concentration. Furthermore, the discussions regarding the influence of mass transport and thermodynamic equilibriums on the dissolution of metals explains why Cu^{2+} is more efficient at lower oxidant concentration than Fe^{3+}. Since the dissolution of metals in the case of $CuCl_2$ occurs only by cementation eq. (6, 8) it is evident that $CuCl_2$ can oxidize twice as much metal than $FeCl_3$. For this reason, as it is shown in Fig. 1, the global dissolution degree of metals is a bit higher for $CuCl_2$ when the oxidant concentration is ranging from 0.1-0.2 M. As for higher oxidant concentrations than 0.2 M, $FeCl_3$ turns out to be more efficient because the dissolution of metals with Fe^{3+} is not hindered by the formation of a solid phase like in the case of copper cementation.

The influence of oxidant concentration on individual metal dissolution

The individual dissolution degree was determined for each metal at the studied oxidant concentrations (0.1-1.6 M). Comparing the experimental results from Table 1 it is obvious that the leaching rate of Zn and Ni differ not only in values but also in their evolution with oxidant concentration.

Table 1. Individual dissolution degree of Zn, Ni and Cu in 1 M HCl using different oxidant concentrations

Oxidant concentration, M	**Individual dissolution degree, %**				
	Zn		**Ni**		**Cu**
	$FeCl_3$	**$CuCl_2$**	**$FeCl_3$**	**$CuCl_2$**	**$FeCl_3$**
0.1	93.3	92.5	18.1	26.9	52.8
0.2	93.2	89.3	22.1	33.7	71.1
0.4	95.3	71.6	51.1	43.9	91.9
0.8	95.1	64.1	65.2	43.5	90.7
1.6	94.2	64.1	74.9	45.3	90.8

First of all, this difference between Zn and Ni appears due the fact that Ni being a more noble metal than Zn the reaction with the oxidants occurs slower. It is also important to notice that the rate of the dissolution process also depends on the structure in which the two metals are present in the WPCBs. While Ni is used as thin layers in the corrosion protection of electric contacts and components, Zn is used as Cu-Zn alloys (brass). Therefore the dissolution of Zn is influenced by both oxidant concentration and Cu dissolution rate, while for Ni it depends only on the concentration of the leaching agents. In consequence the dissolution rate of Ni increases with the increase of $FeCl_3$ concentration due to the large contact area between the reactants, while for Zn the process is slightly affected, since the leaching of Zn, out of the brass lattice, leads to a porous structure in which the process can be limited by mass transport. However due to the fact that $FeCl_3$ dissolves efficiently even copper (Table 1) the dissolution degree of Zn is very high and practically limited not by diffusion but through the redox equilibrium established between the Fe^{3+} and the two metals. The pores influence on Zn dissolution is also sustained by the literature date [21] available for the dezincification of Cu-Zn alloys in various corrosive environments.

Similarly for the experiments with $CuCl_2$ it can be observed, from Table 1 that the dissolution degree of Zn and Ni varies in opposite direction with the increase of oxidant concentration. For Zn the dissolution rate decreases while for Ni increases with an increase of $CuCl_2$ concentration. This can be easily explained in view of the discussions regarding the global dissolution of the metals and the literature date [21] concerning the dezincification of Cu-Zn alloys. Considering that the dissolution of Zn involves the cementation of Cu it is clear that the number and size of the pores becomes even lower as the concentration of $CuCl_2$ is higher, reaching a minimum when the pores (access to Zn) are completely blocked by cemented copper [21]. Therefore the dissolution of Zn in this case is limited by the mass transport in the pores due to the fact that $CuCl_2$ dissolves much slower copper from the pores walls than $FeCl_3$.

In other situations, concurrently with the dissolution process can occur the cementation of the same metal on less noble ones, due to the different standard reduction potentials of the metals. Such an example is the dissolution of silver and lead, which even if are very different in terms of chemical reactivity, their dissolution processes are similarly affected by the cementation on more reactive metals such as Ni and Zn. Therefore the accumulation rate of Ag^+ and Pb^{2+} ions in the solution is given by the difference between the rate of their dissolution and cementation.

In the case of $CuCl_2$ the leaching processes for Ag and Pb are more complicated because their cementation and dissolution is influenced by the cementation of copper as well. In contrast, when $FeCl_3$ is used, the dissolution and cementation of Ag and Pb is not affected so differently, because the reduction of Fe^{3+} those not involve the formation of a new phase. Therefore, at the same oxidant concentration the amount of Ag^+ and Pb^{2+} ions in the solution is higher for the $CuCl_2$ experiments than for the $FeCl_3$. This is also sustained by the experimental results obtained for Ag and Pb, as it is showed in Fig. 2-3.

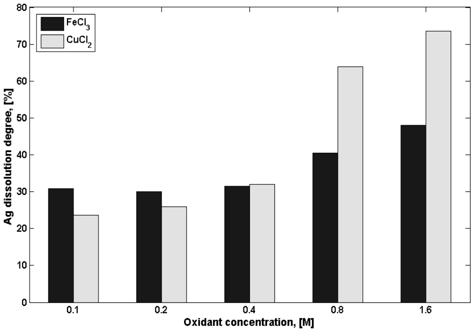

Figure 2. Individual dissolution degree of Ag in 1 M HCl using different concentrations of $FeCl_3$ and $CuCl_2$.

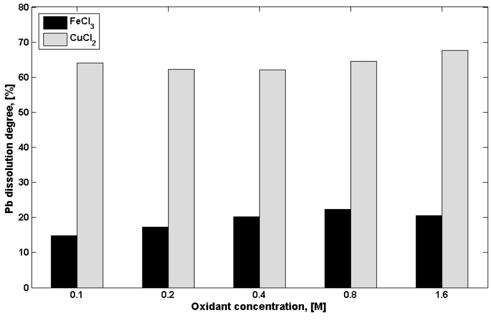

Figure 3. Individual dissolution degree of Pb in 1 M HCl using different concentrations of $FeCl_3$ and $CuCl_2$.

Also, comparing the dissolution degree for Ag and Pb it seems like the difference between the efficiency of the two oxidants is greater in the case of Pb. This is caused by the fact that silver can also react with the cemented copper while lead being a more reactive metal than copper is cementing only on Ni or Zn.

Differently from the previous metals, the reduction potential of Au^+ and Au^{3+} in the presence of chloride ions is still higher than the ones obtained for the oxidants. As a result the chemical dissolution of gold is not possible in these experimental conditions. The presence of dissolved gold (Fig. 4) can be attributed to the formation of colloidal gold through the detachment of very small gold particles from the surface of dissolving metals. In consequence to achieve higher gold dissolution degrees it is necessary to use a more efficient ligand than chloride ions.

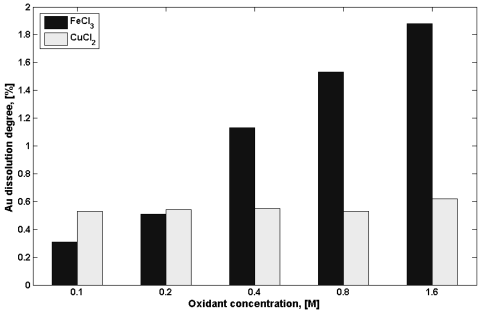

Figure 4. Individual dissolution degree of Au in 1 M HCl using different concentrations of $FeCl_3$ and $CuCl_2$.

CONCLUSIONS

The experimental results proved that the dissolution of metals from WPCBs occurs efficiently in acidic $FeCl_3$ and $CuCl_2$ solutions. However, the efficiency and selectivity of the leaching systems is very different and strongly depends on the oxidant concentration and solution speciation. The main differences between the oxidants are caused by the fact that the dissolution process with $CuCl_2$ is limited not by the redox equilibrium like for $FeCl_3$, but through the cementation of copper which blocks the surface of the metals. Nevertheless, until the metals are completely covered with copper the leaching process with $CuCl_2$ gives superior performances than the one with ferric chloride. For this reason the global metal dissolution degree is higher for copper chloride at oxidant concentrations below 0.2 M, while at higher concentrations $FeCl_3$ is more efficient, because it does not block the metals surface like cemented copper. In contrast the selectivity of the leaching systems is not modified significantly, compared to each other, with the increase of oxidant concentration. Therefore further investigations will be performed in the presence of more efficient ligands (thiourea, thiosulfate, and thiocyanate) in order to enhance the dissolution of metals and the selectivity of the process.

EXPERIMENTAL

Leaching tests were carried out using a special type of PCBs in which the support was made of a ceramic material and the conductive pathways between the electronic components consist of thin layers of Au, Ag and Pb. The solid material was characterized using XRD and EDAX.

The elemental assay of digested material in aqua regia was conducted using atomic absorption spectroscopy (Avanta PM, GBC-Australia). The mass of the WPCBs used in these experiments was 18.8 g. In order to ensure a large contact area between the reactants, they were crushed to smaller pieces (3.1-3.8 cm^2) in a preliminary mechanical step. Then Al was removed selectively from each sample by leaching the WPCBs with 50 mL solution of unstirred 2.5 M NaOH for 24 h. Next, the aluminium free samples were used to determine the extent of dissolution of overall and individual metals in different solutions. The oxidants used were hydrochloric acid and ferric (III)-chloride (Fluka) or copper (II)-chloride (Merck). All leaching experiments were conducted in 100 ml unstirred solution, at room temperature, over a period of 72 h. To prevent the precipitation of metal ions in all experimental situations the pH was kept in strong acid medium by using 1 M HCl acid (Merck). The solid:liquid ratio in the leaching experiments was 1:5. The concentration of metals in the leaching solutions and in the residue at the end of the experiments was determined by atomic adsorption spectroscopy.

The XRD analysis of the ceramic support shows that, instead of copper based boards a mixture of oxides (Al_2O_3, SiO_2) was used to manufacture the non-conductive substrate. Also the elemental composition of the ceramic substrate determined by EDAX indicates the presence of Al (51.89 %), Si (11.46 %) and O (35.69 %). The metallic composition of the WPCBs determined by atomic absorption spectroscopy, after the pretreatment with NaOH, is shown in Table 2.

Table 2. Chemical composition (%) of the studied WPCB samples*

Ag	Au	Cu	Ni	Pb	Zn	Ceramic material
0.14	0.11	0.45	2.2	0.05	0.40	96.65

* Average data obtained from five different WPCB samples

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REFERENCES

1. I. Bereketli, M.E. Genevois, Y.E. Albayrak, M. Ozyol, *Expert Systems with Applications,* **2011**, *38*, 71.
2. H.Y. Kang, J.M. Schoenung, *Resources, Conservation and Recycling*, **2005**, *45*, 368.
3. K. Huang, J. Guo, Z. Xu, *Journal of Hazardous Materials*, **2009**, *164*, 399.
4. L. Longa, S. Sun, S. Zhong, W. Dai, J. Liu, W. Song, *Journal of Hazardous Materials*, **2010**, *177*, 626.
5. S. Ilyas, M.A. Anwar, S.B. Niazi, M.A. Ghauri, *Hydrometallurgy*, **2007**, *88*, 180.
6. W. Jiang, L. Jia, X. Zhen-Ming, *Journal of Hazardous Materials*, **2009**, *161*, 257.
7. R.V. Murugan, S. Bharat, A.P. Deshpande, S. Varughese, P. Haridoss, *Powder Technology*, **2008**, *183*, 169.
8. Y.J. Park, D.J., Fray, *Journal of Hazardous Materials*, **2009**, *164*, 1152.
9. J. Wang, J. Bai, J. Xu, B. Liang, *Journal of Hazardous Materials*, **2009**, *172*, 1100.
10. J. Cui, L. Zhang, *Journal of Hazardous Materials*, **2008**, *158*, 228.
11. G. Hilson, A.J. Monhemius, *Journal of Cleaner Production,* **2006**, *14*, 1158.
12. D. Feng, J.S.J. Van Deventer, *Hydrometallurgy*, **2011**, *106*, 38.
13. E.Y. Kim, M.S. Kim, J.C. Lee, J. Jeong, B.D. Pandey, *Hydrometallurgy*, **2011**, *107*, 124.
14. O.N. Starovoytov, N.S. Kim, K.N. Han, *Hydrometallurgy*, **2007**, *86*, 114.
15. O. Tsydenova, M. Bengtsson, *Waste Management*, **2011**, *31*, 45.
16. L. Barbieri, R. Giovanardi, I. Lancellotti, M. Michelazzi, *Environmental Chemistry Letters,* **2010**, *8*, 171.
17. B. Beverskog, *SKI Rapport 98*, Sweden, **1998**.
18. M.D. Muir, G. Senanayake, *Hydrometallurgy*, **2003**, *14*, 279.
19. G. Senanayake, D.M. Muir, *Metallurgical and Materials Transactions B*, **1988**, *19*, 37.
20. B.R. Tagirov, I.I. Diakonov, O.A. Devina, A.V. Zotov, *Chemical Geology*, **2000**, *162*, 193.
21. N.J. Welham, K.A. Malatt, S. Vukcevic, *Hydrometallurgy*, **2000**, 57, 209.
22. P.R. Roberge, *Handbook of Corrosion Engineering*, McGraw-Hill, New-York, **2000**, 451.