



Nickel Recovery from Printed Circuit Boards Using Acidophilic Bacteria

Anna MRAŽÍKOVÁ¹⁾, Renáta MARCINČÁKOVÁ²⁾, Jana KADUKOVÁ³⁾,
Oksana VELGOSOVÁ⁴⁾

¹⁾ RNDr.; Faculty of Metallurgy, Technical University in Kosice, Park Komenského 11, 042 00 Kosice, Slovak Republic; email: anna.mrazikova@tuke.sk

²⁾ RNDr.; Department of Material Science, Technical University in Kosice, Park Komenského 11, 042 00 Kosice, Slovak Republic; email: renata.marcincakova@tuke.sk

³⁾ Prof., RNDr., Ph.D.; Department of Material Science, Technical University in Kosice, Park Komenského 11, 042 00 Kosice, Slovak Republic; email: jana.kadukova@tuke.sk

⁴⁾ Doc. Ing., Ph.D.; Department of Material Science, Technical University in Kosice, Park Komenského 11, 042 00 Kosice, Slovak Republic; email: oksana.velgosova@tuke.sk

Summary

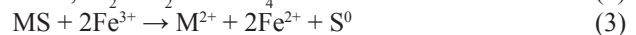
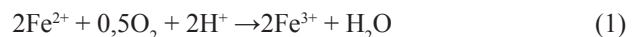
Electronic waste consists of a mixture of various metals particularly copper, aluminium, nickel, iron and steel. In addition to various hazardous materials, e-waste also contains valuable and precious materials but also different types of plastics and ceramics. Mechanical and pyrometallurgical recycling of electronic waste are not only energy and cost intensive but also generate atmospheric pollution through the release of dioxins and furans or high volumes of effluents. It is of real interest to find new technologies on metal recovery from e-waste which are not only economically appropriate but also environmentally friendly. One of the promising technologies for metal extraction from primary and secondary sources appears to be biohydrometallurgy. Acidophilic bacteria from genera *Acidithiobacillus* are among the most utilized bacteria in metal dissolution from low-grade ores and waste. The mixed bacterial culture of *Acidithiobacillus ferrooxidans* and *Acidithiobacillus thiooxidans* were investigated in nickel bioleaching from printed circuit boards (PCBs). As the leaching medium a nutrient medium with the initial pH 1.5 was used. Ferrous iron and elemental sulphur served as energy sources for microbial growth. The acidophilic bacteria were isolated from acid mine drainage water in Smolník in Slovakia and prior to bioleaching process they were grown in the presence of PCB waste. The highest nickel bioleaching efficiency (86 %) was reached on day 10 using the mixture of the acidophilic bacteria. In the absence of bacteria 36 % Ni at most was dissolved. The results from these studies demonstrate that nickel may be recovered from printed circuit boards by microbial leaching using mixed adapted consortium of mesophilic bacteria. Pre-adaptation of microorganisms to PCBs waste can enhance bioleaching process since this kind of waste is too toxic for them.

Keywords: bioleaching, electronic scrap, metals, *Acidithiobacillus ferrooxidans*, *Acidithiobacillus thiooxidans*

Introduction

Electronic waste can be defined as a mixture of various metals particularly copper, aluminium, nickel, iron and steel, attached to cover with or various types of plastics and ceramics (Ilyas et al., 2010). Recycling of the electronic waste is of a real importance not only from the waste treatment point of view but especially from the valuable metals recovery. Mechanical and pyrometallurgical recycling of electronic waste has been investigated by many researchers (Veit et al., 2007, Li et al., 2007, Wang et al., 2009). However, such processes require not only high energy and capital costs but generate atmospheric pollution through the release of dioxins and furans or high volumes of effluents (Veit et al., 2002, Wang et al., 2009). In the last decade, the biotechnology has been emerging as one of the most promising technologies for recovering metals from primary and secondary sources and wastes (Willner and Fornalczyk, 2013). The use of microorganisms appears to be economically the most appropriate method for recycling the valuable metals from the secondary resources. A bioleaching process offers a number of advantages compared to the conventional methods. These include low operating costs, minimization of the volume of chemical and/or biological sludge to be handled and high efficiency in detoxifying effluents. On the other hand, electronic scraps and PCBs waste have shown bacterial toxicity in the bi-

oleaching due to the presence of non – metallic components (Brandl, et al., 2001, Xiang et al., 2010, Zhu et al., 2011). The most studied and used group of microorganisms in metal extraction from low-grade ores and waste are genera from *Acidithiobacillus*. Among them bacteria of *Acidithiobacillus ferrooxidans* are major participants in consortia of microorganisms used for industrial recovery of copper (bioleaching or biomining) (Luptakova et al., 2002, Valdés et al., 2008, Bálintová et al., 2012). *A. ferrooxidans* and *A. thiooxidans* can grow and utilize ferrous iron or elemental sulphur and thus produce ferric ions (Eq. 1) or sulphuric acid (Eq. 2) that are important as leaching agents in metal recovery from primary and secondary sources (Eq. 3, 4, 5) (Lee and Pandey, 2011).



The present study was undertaken to evaluate the potential of metal - adapted mixed bacterial culture of *Acidithiobacillus ferrooxidans* and *A. thiooxidans* to solubilize nickel from printed circuit boards and to determine the relationship among the pH of the leaching media and percent-

ages of nickel release into the solution during the bioleaching process.

Materials and methods

The mesophilic chemolithotrophic bacterial culture of *A. ferrooxidans* and *A. thiooxidans*, used in the experiments was recovered from the acid mine drainage water in Smol-

nik and obtained from the Institute of Geotechnics of Slovak Academy of Science in Kosice, Slovakia. The mixed bacterial culture was cultured in 250 ml Erlenmeyer flask containing 200 ml the rich nutrient medium composed of KCl - 0,1 g, $(\text{NH}_4)_2\text{SO}_4$ - 2,0 g/l, K_2HPO_4 - 0,25 g/l, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ - 0,25 g/l, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ - 44,2 g/l, sulphur - 4 g/l and distilled water, 1000 ml (Kadukova et al., 2011). The

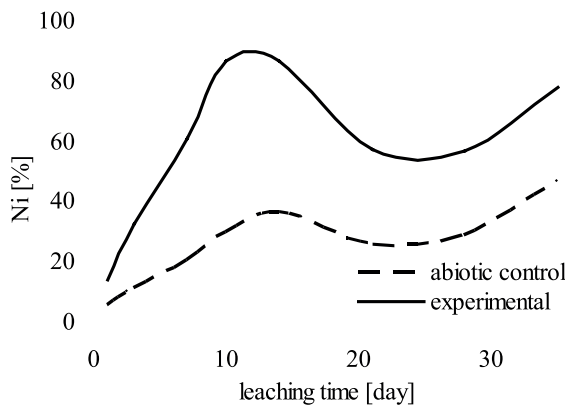


Fig.1 Percentage of nickel dissolved in bioleaching and abiotic control leaching.

Rys. 1 Udział niklu rozpuszczonego w procesie bioługowania i kontrolowanego ługowania chemicznego

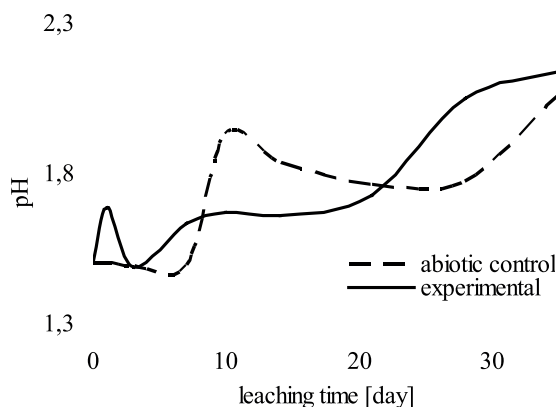


Fig. 2 The pH changes during bioleaching and abiotic control leaching

Rys. 2 Zmiany pH podczas bioługowania i kontrolowanego ługowania chemicznego

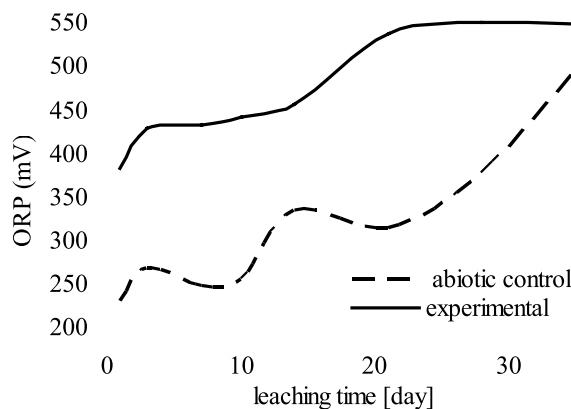


Fig. 3 The redox changes during bioleaching and abiotic control leaching.

Rys. 3 Zmiany potencjału redoks podczas bioługowania i kontrolowanego ługowania chemicznego

initial pH was adjusted to 1.5 with 10M H₂SO₄ or 10% NaOH. To obtain metal – adapted bacteria 1g electronic waste in the form of printed circuit boards was added to the mixed bacterial culture and incubated at 30°C. The process acclimation lasted 2 weeks and bacterial growth was monitored by pH and ORP changes. Prior the bioleaching process 10 ml of the metal - adapted bacteria were transferred to 200 ml fresh nutrient media with pH = 1.5 for 5 days. Afterwards 2 g of electronic waste with the particle size of 1- 1000 mm was added. The sample was regularly withdrawn on days: 1, 3, 7, 10, 14, 21, 28, 35 to determine the concentration of nickel dissolved by atomic absorption spectrophotometer (Perkin Elmer 3100). The results of AAS of PCBs before bioleaching revealed the presence of Cu (19.21%), Zn (1.17%), Ni (0.32%), Al (1.73%). Simultaneously, abiotic control leaching under the same conditions but without any bacteria was carried out.

Results and discussion

Percentages of nickel solubilized in leaching solution by mixed culture of *A. ferrooxidans* and *A. thiooxidans* are shown in Fig. 1. In the nickel bioleaching process the highest bioleaching rate was observed in the first 10 days, when 86 % Ni was dissolved. After that time, nickel concentration rapidly decreased up to day 21, however, on the following days the increase of nickel solubilization was observed. The similar time-course of nickel dissolution was observed in the abiotic control leaching.

The highest nickel leaching rate was observed in the first 14 days, when 36% Ni at most was dissolved.

Fig. 2 depicts the pH changes during the nickel bioleaching and abiotic control leaching period. Initially, a rapid increase in pH was observed in the first 3 days of bioleaching that was in coincident with alkaline nature of electronic waste. Consequently, the pH started increasing

owing to hydrolysis of the metal ions, which were released in the solution. In the abiotic control leaching the pH value was more or less stable in the first 7 days which indicates typical chemical leaching of nickel from the waste.

ORP changes over the time in the bioleaching and abiotic control leaching experiments are plotted in Fig. 3. During the Ni bioleaching process the redox value started at 380 mV and immediately increased up to 440 mV measured on day 3. Afterwards it remained more or less stable up to day 14, and then it started gradually increased again. On day 35 the redox potential reached value of 549 mV. The curve of redox potential in the abiotic leaching was the similar to that in the bioleaching; however, ORP values were much lower. Redox potential started at 227 mV and on day 14 it reached only the value of 330 and consequently it rapidly ascended with increase of the leaching time.

Conclusion

The results from these studies demonstrate that nickel can be recovered from electronic scrap by microbial leaching using mesophilic chemolithotrophic bacterial culture of *A. ferrooxidans* and *A. thiooxidans*. Time-course of the nickel dissolution and nickel bioleaching efficiency as well, were the highest during the first 14 days (86%) compared to the abiotic control leaching when 35% Ni at most was released. This pattern shows that the leaching of nickel from the electronic scrap owing to chemical oxidation was insignificant and major contribution is of bioleaching for nickel dissolution in case of electronic scraps.

Acknowledgements

The work was fully supported by a grant from the Slovak National Grant Agency under the VEGA Project 1/0235/12.

Literatura - References

1. Bálintová, M. et al. *Úprava kyslých banských vôd*. Košice, Stavebná fakulta, Technická univerzita, 2012, s 131
2. Brandl, H. et al. *Computer-munching microbes: metal leaching from electronic scrap by bacteria and fungi*, *Hydrometallurgy*, 59, 2001, p.319-326
3. Ilyas, S. et al. *Column bioleaching of metals from electronic scrap*. *Hydrometallurgy*. 101, 2010, p.135 – 140
4. Kadukova, J. et al. *Návody na cvičenia zo Základov biotechnológií*, *Hutnícka fakulta, Technická univerzita v Košiciach, Košice*, 2011, p.129
5. Lee J., et al. *Bio-processing of solid wastes and secondary resources for metal extraction – A review*. *Waste Management*, 22, 2012, p.3-18
6. Li, J. *Recycle technology for recovering resources and products from waste printed circuit boards*, *Environmental Science and Technology*, 41, 2007, p. 1995-2000

7. Luptakova, A. et al. *Minerálne biotechnológie II., Sulfuretum v prírode a v priemysle, VŠB - Technická univerzita Ostrava, 2002*
8. Valdés, J. et al. *Acidithiobacillus ferrooxidans metabolism: from genome semence to industrial applications. BMC Genomics, 2008, 9:597*
9. Veit, H.M. et al. *Using mechanical processing in recycling printed circuit boards, JOM, 54, 2002, p. 45-47*
10. Veit, H.M. et al. *Waste multilayer ceramic capacitors, Hydrometallurgy, 2007, p. 89-95*
11. Wang, J. et al. *Bioleaching of metals from printed wire boards by Acidithiobacillus ferrooxidans and Acidithiobacillus thiooxidans and their mixture. Journal of Hazardous Material, 172, 2009, p.1100-1105*
12. Willner, J., Fornalczyk, A. *Extraction of metals from electronic waste by bacterial leaching, Environment Protection Engineering, 2013, 1, p. 197-208*
13. Xiang, Y. et al. *Bioleaching of copper from waste printed circuit boards by bacterial consortium enriched from acid mine drainage, Journal of Hazardous Materials, 184, 2010, p. 812-818*
14. Zhu, N. et al. *Bioleaching of metal concentrates of waste printed circuit boards by mixed culture of acidophilic bacteria, Journal of Hazardous Materials, 192, 2011, p. 614-619*

Odzysk niklu z płytek układów drukowanych z użyciem bakterii kwasolubnych

Odpady elektroniczne składają się z mieszaniny różnych metali szczególnie miedzi, aluminium, niklu, żelaza i stali. Oprócz różnych materiałów niebezpiecznych, odpady elektroniczne zawierają również cenne i szlachetne materiały, ale również różne rodzaje tworzyw sztucznych i ceramiki. Recykling mechaniczny i pirometalurgiczny odpadów elektronicznych są nie tylko energochłonne i kosztowne, ale także generują zanieczyszczenia powietrza poprzez uwalnianie dioksyn i furanów oraz dużej ilości ścieków. Szczególnie ważnym jest więc znalezienie nowych technologii w zakresie odzysku metali z odpadów elektronicznych, które są nie tylko właściwe z ekonomicznego punktu widzenia, ale również przyjazne dla środowiska naturalnego. Jedną z obiecujących technologii ekstrakcji metali ze źródeł pierwotnych i wtórnych wydaje się być biohydrometalurgia. Kwasolubne bakterie z rodzaju *Acidithiobacillus* są jednymi z najczęściej wykorzystywanych bakterii w rozpuszczaniu metalu z rud niskiej jakości oraz odpadów. Mieszana kultur bakterii *Acidithiobacillusferrooxidans* i *Acidithiobacillusthiooxidans* zbadana została w procesie bioługowania niklu z obwodów drukowanych (PCB). Jako czynnik ługujący zastosowano pożywkę o pH początkowym 1,5. Jony żelaza (II) i siarka elementarna służyły jako źródło energii dla wzrostu drobnoustrojów. Kwasolubne bakterie wyizolowano z kwaśnej drenażowej wody kopalnianej w Smolniku na Słowacji i przed procesem ługowania biologicznego były hodowane w obecności odpadów PCB. Najwyższą skuteczność bioługowania niklu (86%) osiągnięto w dniu 10 stosując mieszaninę kwasolubnych bakterii. W przypadku braku bakterii rozpuszczano maksymalnie 36% Ni. Wyniki tych badań wskazują, że nikiel można odzyskać z płytek obwodów drukowanych przez wymywanie z użyciem mieszaniny przystosowanych drobnoustrojów - bakterii mezofilnych. Wstępna adaptacja drobnoustrojów do odpadów PCB może poprawić proces ługowania biologicznego, ponieważ ten rodzaj odpadów jest dla nich zbyt toksyczny.

Słowa kluczowe: bioługowanie, złom elektroniczny, metale, *Acidithiobacillus ferrooxidans*, *Acidithiobacillus thiooxidans*