STUDY OF Ni AND Cd BIOLEACHING FROM SPENT Ni-Cd BATTERIES

OKSANA VELGOSOVÁ, JANA KADUKOVÁ, RENÁTA MARCINČÁKOVÁ

Technical University in Košice, Faculty of Metallurgy, Department of Material Science, Letná 9, Košice 04200, Slovak Republic (oksana.velgosova@tuke.sk)

Abstract: In the present work the Ni and Cd extraction from the electrode material of spent Ni-Cd batteries by bioleaching using the bacteria *Acidithiobacillus ferrooxidans* was examined. The possibility of the use of the bacteria for both the Ni and Cd recovery was analyzed. The anode of Ni-Cd batteries contains Ni^0, $Ni(OH)_2$, Cd^0 and $Cd(OH)_2$. The cathode is covered by nickel hydroxides and nickel oxy-hydroxides. The pH values and content of Ni and Cd in the solution were monitored throughout the experiment (the initial pH was 1.5, the experiment took 28 days). The bioleaching efficiency of Ni and Cd from anode powder reached 5.5% and 98%, respectively. During the cathode powder bioleaching Ni and Cd efficiency reached 45% and 100%, respectively. Throughout the bioleaching process mainly the dissolution of hydroxides occurred meanwhile Ni^0 leaching was not observed. The AAS analysis was used to analyze the amount of Ni and Cd in the solutions. The amount of Ni and Cd present in the solid samples before and after bioleaching was examined using X-ray analysis.

Keywords: Ni-Cd batteries, bioleaching, *Acidithiobacillus ferrooxidans*, heavy metals

1. Introduction

Since Ni-Cd batteries are still being used in various areas and the amount of spent Ni-Cd batteries increases, it is necessary to find eco-friendly way how to recycle and treat them and subsequently to recover valuable metals.

More than 55 % of the battery weight forms the material of electrodes. Nickel, cadmium and their hydroxides are main compounds of electrode material, which make Ni-Cd spent batteries an attractive material for heavy metals obtaining (NOGUEIRA and MARGARIDO, 2007).

Pyrometallurgical and hydrometallurgical processes or combination both of them are traditional techniques for the spent Ni-Cd batteries treatment (BARTOLOZZI *et al.* 1995; COX and FRAY, 1999; ESPINOSA *et al.* 2004; FREITAS and ROSALEM, 2005). Hydrometallurgical processes are more acceptable than pyrometallurgical ones due to the elimination of toxic air emissions and a high purity of the final metal product.

The hydrometallurgical processes of Ni-Cd batteries treatment deal with Ni and Cd solubilisation in the different solutions and under the different conditions. Hydrometallurgical processes offer many possibilities of changing the process conditions so that the required results may be achieved. Different leaching solutions, pH, temperature, treatment of solid stage (granularity, morphology, chemical treatment) or using bacteria are several variables that can influence the efficiency and duration of hydrometallurgical processes.

Nowadays, biohydrometallurgy comes to the forefront as an alternative method of metal obtaining. The bioleaching processes, in comparison to commonly used

DOI 10.2478/v10296-012-0013-0

processes, are less expensive and therefore they can be used as an option for the treatment of Ni-Cd batteries.

The acidophilic bacteria are the most widely used microorganisms. The bacteria *Acidithiobacillus ferrooxidans* gain energy from the oxidation of ferrous ions or elemental sulphur to meet their growth need and consequently produce sulfuric acid and ferric ions that play important role as leaching agents in the bioleaching process of sulfide ores. Many authors apply bioleaching mechanism of sulfide ores that have been described well for bioleaching of non-sulfidic material (e.g. spent secondary batteries) (CHAN *et al.* 2003; CHEN and LIN, 2004; ECCLES, 1999; MERUANE *et al.* 2003; RUDNIK and NIKIEL, 2007; ZHAO *et al.* 2008; ZHU *et al.* 2003), however, we should take into account the fact that they contain no sulfides but in the case of the spent batteries especially elemental metals, metal oxides and metal hydroxides are present therefore the bioleaching mechanisms might not be necessary the same. The bioleaching processes depend on many factors; therefore the explanation of their influences under certain conditions is necessary for the understanding of the bioleaching process. By the studying of the particular leaching factors we tried to shed light on the mechanisms involved and responsible for the waste bioleaching processes.

The purpose of this work was to study the bioleaching process of electrode powder from spent Ni-Cd batteries using *Acidithiobacillus ferrooxidans*, to analyze the possibility of using bacteria for Ni and Cd recovery, and to analyze the efficiency of Ni and Cd bioleaching processes.

2. Materials and methods

In this research spent rechargeable Ni-Cd batteries were used as the experimental material. The batteries were weighted and manually cut up into different portions. The electrode material forms about 55 % of the battery weight. The active electrode material, cathode and anode powders were physically removed from the metal grid, ground and sieved to obtain a mesh size of less than 40 μm. All remaining components of the battery were metal parts and separator with plastic parts. For the experiments cathode and anode electrode materials were used separately.

For the bioleaching the adapted bacteria *Acidithiobacillus ferrooxidans* for the electrode powder material were used. The pure culture of *Acidithiobacillus ferrooxidans* was obtained from the Institute of Geotechnics of Slovak Academy of Science, Košice. The microorganisms were cultured in Erlenmeyer flasks containing 200 ml of 9 K medium at the initial pH of 1.5 in the incubator at 30°C. Then 2 g of cathode or anode powder was added to these cultured bacteria**.** After 3 weeks, 5 ml of adapted bacteria were poured into the Erlenmeyer flask containing 295 ml of basic 9K medium and were cultivated for another 4 days. After that 3 g of electrode powder was added.

The experiments were carried out in the incubator at 30°C, the solid / liquid (w/v) ratio was 1/100 in all experiments. The samples were withdrawn at these days: 1, 3, 7, 10, 13, 21, and 28. All experiments were conducted in triplicates. The leachate (5 ml) was periodically taken and filtrated.

Atomic Absorption Spectrometry (AAS) (SpectrAA 20 PLUS VARIAN) was used to determine the Ni and Cd concentrations in the solutions. The pH of each experiment was measured throughout the experimental period by the pH meter GRYF 208 L using a combine electrode. X-ray analysis was used to analyze the input of the solid samples and the solid residues.

3. Results and discussion

The chemical composition of the electrode powder obtained from the Ni-Cd spent batteries was determined by X-ray analyses. The anode consists of cadmium and cadmium hydroxide in combination with a small amount of nickel and nickel hydroxide (Fig. 1). The cathode is covered by nickel hydroxide and nickel oxy-hydroxide, (Fig. 2). The small amount of cobalt was present in both samples. It is apparent that the anode contains a high amount of Cd and a small amount of Ni. This fact was also confirmed by the AAS analysis. The results of AAS analysis of cathode and anode input samples showed that Ni content in the battery was 47.1 % and 22.2 % for cathode and anode, respectively. Cd content was 6.3 % and 37.5 % for cathode and anode, respectively

In the electrode powder bioleaching process the solution pH did not change significantly (Fig. 3). The pH increased from the value of 1.5 to 2.8 up to 21th day of the experiment, after that the pH value remained constant. The pH increase was probably caused by the neutralization when, at least part, cadmium and nickel hydroxides dissolved.

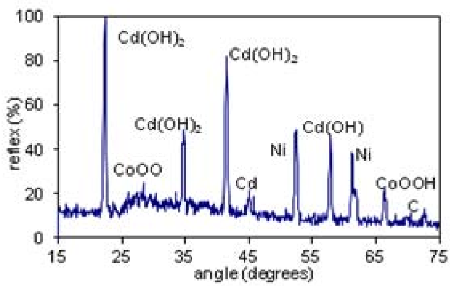

Fig. 1. X-ray of the initial anode material of spent Ni-Cd battery.

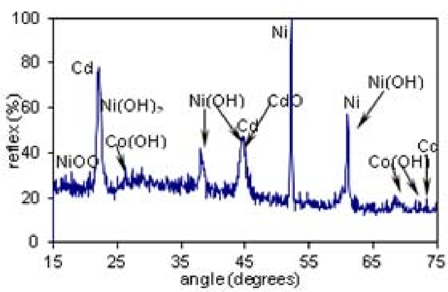

Fig. 2. X-ray of the initial cathode material of spent Ni-Cd battery.

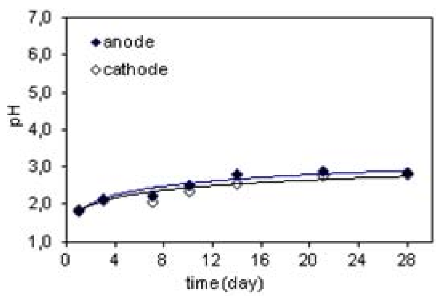

Fig. 3. Dependence of pH on leaching time.

Ni and Cd bioleaching efficiency of the anode powder was 5% and 98%, respectively (Fig. 4) and the bioleaching efficiency of Ni and Cd from the cathode powder reached 45% and 100% respectively (Fig. 5). The results exhibited evident difference in Cd and Ni dissolution behavior during the bioleaching process. These findings can be explained by the fact that cadmium as a less noble element is oxidized easier than metallic nickel and Cd hydroxides are dissolved faster than hydroxides of nickel, too.

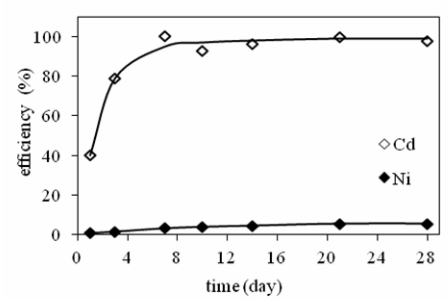

Fig. 4. The efficiency of Ni and Cd bioleaching from anode powder.

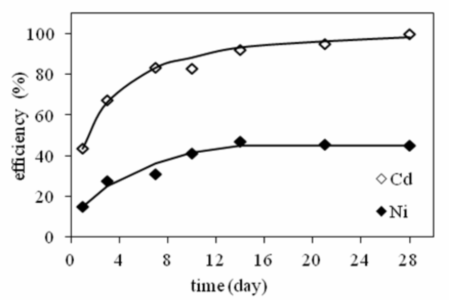

Fig. 5. The efficiency of Ni and Cd bioleaching from cathode powder.

The solubility of metal Ni is significantly affected by its resistance to corrosion, from thermodynamic point of view the dissolution of Ni is possible at pH bellow 6.3. Many authors studied the passivation of nickel in different acidic solutions. It was reported that the passive film formed on nickel surface in low concentrations of sulfuric acid is formed by NiOOH or NiO and Ni_2O_3. On the other hand, β-$NiSO_4.6H_2O$ was suggested as the passive compound formed in very high concentrations of sulfuric acid (ABDALLAH *et al.* 2003; OHTSUKA *et al.* 1979; KOVTUN *et al.* 2005). But Ni solubilization can be reached by modification of leaching conditions e.g. by increasing of the leaching potential or temperature (NOGUEIRA *et al.* 2004; PIETRELLI *et al.* 2005; GOYAL *et al.* 2003).

During the bioleaching process the microbial oxidation of ferrous to ferric ions occurs as follows:

$$2FeSO_4 + \tfrac{1}{2}O_2 + H_2SO_4 \xrightarrow{A.\ ferroox.} Fe_2(SO_4)_3 + H_2O \qquad (1)$$

The consumption of protons also occurs and this is together with the dissolution of Ni and Cd hydroxides probably responsible for the increase of the leaching solution pH value up to 2.8 (Fig. 3). But despite the total dissolution of hydroxides just a very small increase of the solution pH was observed. It might be due to jarosite formation. This process is expressed as follows:

$$Fe_2(SO_4)_3 + 6H_2O \rightarrow 6H^+ + 3SO_4^{2-} + 2Fe(OH)_3 \qquad (2)$$

The dissolution of ferric sulphate and its subsequent hydrolysis causes the release of protons to the solution. It is supposed that ferric hydroxides and parts of the sulphate ions formed during this reaction (2) participate in the jarosite formation. Potassium, which is a part of the jarosite molecule, is getting to the process from an electrolyte. This process can be described as follows:

$$K^{+} + 5OH^{-} + 3Fe^{3+} + 2SO_4^{2-} + H_2O \rightarrow KFe_3(SO_4)_2(OH)_6 + H^{+} \quad (3)$$

Consequently, during this reaction equilibrium shifts to the right, and the release of protons results in the decrease of pH values. This process helps to maintain the low leaching solution pH values which lead to the further dissolution of hydroxides up to their total elimination. X-ray analysis confirmed jarosite formation and the removal of hydroxides from the solution (Fig.6 and Fig.7).

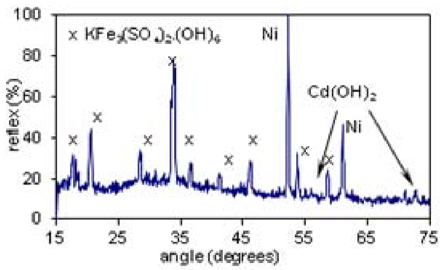

Fig. 6. X-ray of bioleached anode material.

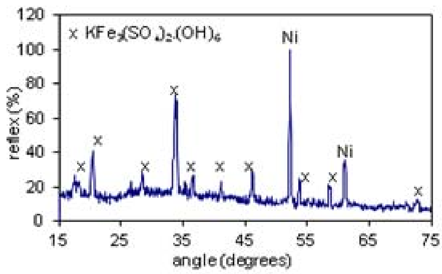

Fig. 7. X-ray of bioleached cathode material.

The X-ray analysis of solid residuum obtained after the anode powder bioleaching showed the negligible amount of Cd hydroxides, metallic Ni and jarosite. After the cathode powder bioleaching only metallic Ni remained. The large majority of jarosite was present in the solid residuum in the both samples.

One of the factors that can influence the process rate inhibition and causes lower efficiency of Ni leaching is the presence of cadmium, which is to a certain extent toxic to bacteria. However *Acidithiobacillus ferrooxidans* have good resistibility to toxic elements their high concentration can kill the bacteria. According to CABRERA *et al*. 2005, it is possible to establish the order of metal toxicity to *Acidithiobacillus ferrooxidans* bacteria: Cr(III)>Cu(II)>Cd(II)>Ni(II)>Zn(II). For nickel, the tolerance up to 40 g Ni/l was found.

4. Conclusions

Series of experiments were carried out to contribute to understanding of the mechanisms of non-sulfidic material bioleaching processes. The results of the bioleaching experiments can be summarized as follows:

1. Under the studied conditions, all Ni hydroxides are leached to the solution but the leaching of metallic Ni is negligible.
2. The better leachability was observed in the case of Cd bioleaching. The efficiency of Cd bioleaching from anode and cathode powders reached almost 100%.
3. The jarosite formation was confirmed by X-ray analysis.

It would be of value to carry out these bioleaching experiments under other conditions to extract Ni, for example, to change the chemical composition of the bioleaching media since not only the presence of iron ions but also its amount in the media can significantly influence the bioleaching process rate, to use mixed acidophilic bacteria, two-step leaching system or to use continuous bioleaching and bioleaching with retention time in bioreactors.

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

References

ABDALLAH, M., EL-ETRE, A.Y.: Corrosion Inhibition of Nickel in Sulfuric Acid Using Tween Surfactants, Portug. Electrochimica Acta, 21, 2003, 315-326.

BARTOLOZZI, M., BRACCINI, G., BONVINI, S., Marconi, P.F.: Hydrometallurgical recovery process for nickel–cadmium spent batteries. J. Power Sources, 55, 1995, 247–250.

CABRERA, G., GÓMEZ, J.M., CANTERO, D.: Influence of heavy metals on growth and ferrous sulphate oxidation by *Acidithiobacillus ferrooxidans* in pure and mixed cultures, Process Biochem., 40, 2005, 2683-2687.

CHAN, L.C., GU, X.Y., WONG, J.W.C.: Comparison of bioleaching of heavy metals from sewage sludge using iron- and sulfur-oxidizing bacteria. Adv. in Environ. Res. 7, 2003, 603–607.

CHEN, S.Y., LIN, J-G..: Bioleaching of heavy metals from livestock sludge by indigenous sulfur-oxidizing bacteria: effects of sludge solids concentration. Chemosphere, 54, 2004, 283–289.

COX, A., FRAY, D.J.: Recycling of cadmium from domestic sealed NiCd battery waste by use of chlorination. Trans. Instn. Min. Metall. – C: Mineral Process. Extr. Metall. 108, 1999, 153–158.

ECCLES, H.: Treatment of metal-contaminated wastes: why select a biological process? Trends in Biotechnology, 17, 1999, 462-465.

ESPINOSA, D.C.R., BERNANDES, A.M., TENORIO, J.A.S.: An overview on the current processes for the recycling of batteries. J. Power Sources, 135, 2004, 311-319.

FREITAS, M.B.J.G., ROSALÉM, S.F.: Electrochemical recovery of cadmium from spent Ni–Cd batteries. J. Power Sources, 139, 2005, 366–370.

GOYAL, N., JAIN, S.C., BANERJEE, U.C.: Comparative studies on the microbial adsorption of heavy metals. Adv. Environ. Res., 7, 2003, 311-319.

KOVTUN, V.N., BOLOTIN, A.V.: Dynamic behavior of Ni-H_2SO_4 system at high anodic potentials and different electrolysis conditions, Russ. J. Electrochem., 41, 2005, 111-115.

MERUANE, G., VARGAS, T.: Bacterial oxidation of ferrous iron by Acidithiobacillus ferrooxidans in the pH range 2.5-7.0. Hydrometallurgy, 71, 2003, 149-158.

NOGUEIRA, C.A., MARGARIDO, F.: Leaching behaviour of electrode materials of spent nickel-cadmium batteries in sulphuric acid media. Hydrometallurgy, 72, 2004, 111-118.

NOGUEIRA, C.A., MARGARIDO, F.: Chemical and physical characterization of electrode materials of spent sealed Ni–Cd batteries. Waste Manage., 27, 2007, 1570–1579.

OHTSUKA, T., HEUSLER, K.E.: Potential-dependent properties of the passivating film on nickel in sulphuric *acid solution from multiple-angle-of-incidence refle*ctivity measurements, J. Electroanal. Chem., 102, 1979, 175-187.

PIETRELLI, L., BELLOMO, B., FONTANA, D., MONTEREALI, M.: Characterization and leaching of NiCd and NiMH spent batteries for the recovery of metals, Waste Managem., 25, 2005, 221-226

RUDNIK, E., NIKIEL, M.: Hydrometallurgical recovery of cadmium and nickel from spent Ni–Cd batteries. Hydrometallurgy, 89, 2007. 61–71.

ZHAO, L., YANG, D., ZHU, N-W.: Bioleaching of spent Ni–Cd batteries by continuous flow system: Effect of hydraulic retention time and process load. J. Hazard. Mater., 160, 2008, 648–654.

ZHU, N., ZHANG, L., LI, C., CAI, C.: Recycling of spent nickel–cadmium batteries based on bioleaching process. Waste Manage., 23, 2003, 703–708.

Presented at the 2nd International Conference "Biotechnology and Metals - 2011", September 22–23, 2011, Košice, Slovak Republic.