



# Metal Bioleaching from Spent Lithium-Ion Batteries Using Acidophilic Bacterial Strains

Renáta MARCINČÁKOVÁ<sup>1)</sup>, Jana KADUKOVÁ<sup>2)</sup>, Anna MRAŽÍKOVÁ<sup>1)</sup>,  
Oksana VELGOSOVÁ<sup>1)</sup>, Alena LUPTÁKOVÁ<sup>3)</sup>, Stefano UBALDINI<sup>4)</sup>

<sup>1)</sup> Faculty of Metallurgy, Technical University in Košice, Park Komenskeho 11, 042 00 Kosice, Slovak Republic; email: renata@marcincakova.sk

<sup>2)</sup> Institute of Biology and Ecology, Faculty of Science, Pavol Jozef Safarik University, Srobarova 2, 04001 Kosice, Slovak Republic

<sup>3)</sup> Institute of Geotechnics, Slovak Academy of Sciences, Kosice, Slovak Republic

<sup>4)</sup> Institute of Environmental Geology and Geoengineering, CNR, Roma, Italy

## Abstract

In this present work lithium and cobalt recovery from spent lithium-ion batteries (27.5% LiCoO<sub>2</sub>) by bioleaching was investigated. The experiments were carried out using the consortia of acidophilic bacteria of *Acidithiobacillus ferrooxidans* and *Acidithiobacillus thiooxidans*. For the Li and Co bioleaching two different media were used. A rich nutrient medium was consisted of all minerals needed for bacterial growths, whereas a low nutrient medium contained only sulphuric acid and elemental sulphur as an energy source. In the rich nutrient medium the overall lithium and cobalt bioleaching efficiency was 80% and 67%, respectively, whereas in the low nutrient environment only 35% Li and 10.5% Co were released. The experimental results revealed that the presence of nutrients in the bioleaching medium influenced, to a large extent, lithium and cobalt dissolution from LIBs.

**Keywords:** bioleaching, spent lithium-ion batteries, *Acidithiobacillus ferrooxidans*, *Acidithiobacillus thiooxidans*, Li and Co recovery

## Introduction

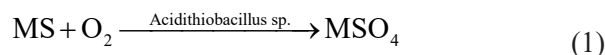
Lithium-ion batteries (LIBs) are ubiquitous in advanced economies, sensors, computers, electronic and medical devices. Due to their favourable properties such as a high energy density, high cell voltage, long store life, low self discharge rate and wide temperature range of use they have gradually replaced Ni-Cd and Ni-MH (nickel-metal-hydride) batteries (Swain et al., 2007). Worldwide, rechargeable lithium batteries power about 60% of cellular telephones and about 90% of laptop computers (Smith, 2010). Lithium batteries are and will also continue to be needed for powering all electric and hybrid vehicles. There is concern that demand for battery metals could increase, possibly to the point at which a shortage of these metals will occur (Goonan, 2012). Scarcity of primary resources of metals and awareness of environmental problems associated with a high amount of wastes containing heavy metals and other toxic matters forces us to seek economic and environmentally friendly processes on metal recovery from various materials.

The conventional techniques for treatment and recycling of metal-bearing wastes, mainly pyrometallurgy, hydrometallurgy or combination both of them, encompass several inherent constraints like, high energy and capital costs and serious second pollution as well (Xin et al., 2009). As environmental regulations become ever more stringent, particularly regarding the disposal of toxic wastes, the costs for ensuring environmental protection will continue to rise. Therefore there is a need to utilize

more efficient technologies to recover heavy metals from secondary sources in order to minimize capital outlay, environmental impact and to respond increased demand (Hoque and Philip, 2011, Zelena-kova and Zvijakova, 2011).

Biological techniques, which utilize microbiological activities to recover metal ions, are considered as one of the most promising and fast developing technologies (Ehrlich, 2004, Brandl and Faramarzi, 2006). Nowadays, microbial leaching plays a crucial role in recovery of metals from various sulphide minerals and low grade ores. The major microorganisms, which play a significant role in metal bioleaching from waste, belong to the acidophilic group. These acidophilic bacterial strains help in dissolution of metals from solid phase of waste into the aqueous phase (Luptakova et al., 2002, Mishra and Rhee, 2010, Willner and Fornalczyk, 2013). They generate the leaching agents and create a space in which the leaching reactions take place. In general, two types of major bioleaching mechanisms have been proposed (Sand, 2010, Brandl, 2008). In the direct mechanism the microbial cells have to be attached to the mineral surface and consequently can oxidize metal sulfides by obtaining electrons directly from the minerals (Eq. 1)

Direct bioleaching mechanism:

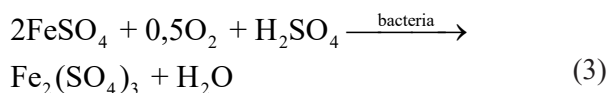
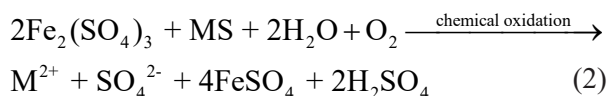


where: *M* – a bivalent metal

In the case of indirect mechanism the oxidation of reduced metals is mediated by ferric iron (Eq. 2)

formed during oxidation of ferrous iron present in the mineral. Consequently, ferric iron is converted into ferrous one which, in turn, is oxidized by bacteria again (Eq. 3). These reactions are expressed as follows:

Indirect bioleaching mechanism:



where: M – a bivalent metal

Apart from metal sulphides, the spent secondary batteries are characterized by metal oxides and metal hydroxides. Therefore the bioleaching mechanisms may differ from described above.

This present work is focused on lithium and cobalt recovery from spent lithium – ion batteries using the consortia of acidophilic bacteria of *Acidithiobacillus ferrooxidans* and *Acidithiobacillus thiooxidans*. The main aim of this study is to examine the influence of the environment on dissolution of both metals from LIBs.

## Material and methods

### *Characteristics of spent lithium-ion battery (LIBs)*

Spent Li-ion batteries used in laptops of different manufacturers were collected for this study. The LIBs were manually cut up into different portions; anode and cathode were uncurled manually, separated and dried for 24h at 60°C. Black material covering the cathode was separated from the copper foil, analysed and used for the bioleaching experiments. Based on the AAS results the content of Li and Co was 5% and 58%, respectively.

### *Microorganisms*

The acidophilic bacteria of *Acidithiobacillus ferrooxidans* and *Acidithiobacillus thiooxidans* were obtained from the Institute of Geotechnics of Slovak Academy of Science in Kosice, Slovakia and cultured in the 9K medium (Silverman and Lundgren, 1959) and the medium proposed by Waksman and Joffe (1922), respectively. The mixed bacterial strains were cultured in the rich nutrient medium composed of  $\text{K}_2\text{HPO}_4$  – 0.1 g,  $(\text{NH}_4)_2\text{SO}_4$  – 2.0 g, KCl – 0.1 g,  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  – 4.0 g,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  – 44.2 g, elemental sulphur – 4 g/l, and distilled water, 1000 ml at the initial pH = 1.5. Prior the bioleaching experiments the mixture of the bacteria were acclimated in presence of cathode powder for four weeks and consequently

used as bioleaching bacteria for lithium and cobalt extraction. The microbial activity was monitored by pH and ORP changes.

### *Bioleaching experiment*

The experiments were carried out in 250 ml Erlenmeyer flasks containing 200 ml of the bioleaching media. As the bioleaching medium two kinds of media were used, a rich and low nutrient medium. The rich nutrient medium, which chemical composition is described in the previous section, contained all minerals needed for bacterial growths. The low nutrient medium was composed only of sulphuric acid and elemental sulphur. The initial pH of both media was adjusted to 1.5. To the bioleaching media 10 ml of waste-adapted bacterial strains and 2 g cathode powder were added. Sterile abiotic controls were performed under the same conditions as those in bioleaching, however, in absence of bacteria. The samples for analysis were withdrawn on days: 1, 3, 7, 10, 14, 21, 28 and 35. All experiments were conducted in triplicates.

### *Analytical methods*

The pH value was measured periodically throughout the experimental period by a pH meter Gryf 208 L using a combine electrode. The leachant (6 ml) was periodically taken out, filtrated and consequently Li and Co concentrations were determined at 670 nm and 240.7 nm, respectively, by an Atomic Absorption Spectroscopy (AAS) (Perkin Elmer 3100). Chemical composition of the initial cathode material and the final leaching residues were determined by AAS and X – ray diffraction (XRD). XRD diffraction patterns were collected using the  $\text{Cu}, \text{K}\alpha$  wavelength of a D8 Advance diffractometer (Bruker, Germany). The generator was set-up at 40 kV and 40 mA. The divergence and receiving slits were  $0.3^\circ$  and 0.1 mm, respectively

## Results and discussion

The time-course for Li and Co dissolution from cathode powder during bioleaching in the rich and low nutrient medium is plotted in Fig. 1. As it can be seen, the presence of nutrients in the environment exhibited evident difference in dissolution behaviour and the bioleaching efficiency of lithium and cobalt. The metal bioleaching efficiency was the highest in the rich nutrient medium, where ferrous ions and elemental sulphur as well were present. The overall lithium and cobalt bioleaching efficiency was 80% and 67%, respectively, in the rich nutrient medium, whereas in the low nutrient environment only 35% Li and 10.5% Co were dissolved.

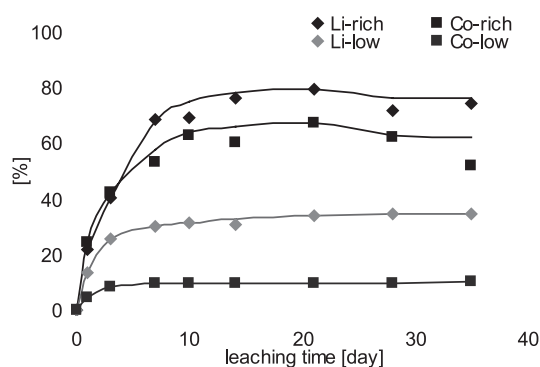


Fig. 1. Percentages of lithium and cobalt extraction in the rich and low nutrient medium

Rys. 1. Procent odzyskanego litu i kobaltu w ośrodkach o wysokiej i niskiej zawartości substancji odżywczych

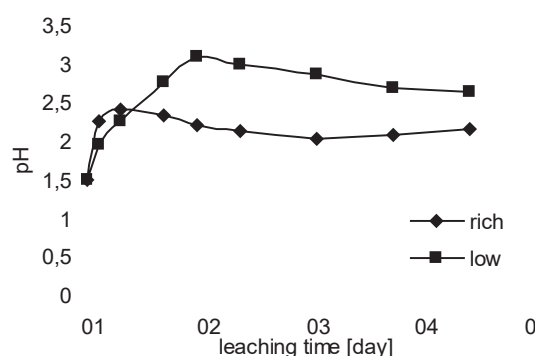


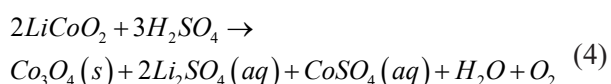
Fig. 2. The pH changes over the leaching time in the rich and low nutrient medium

Rys. 2. Zmiany pH w czasie ługowania w ośrodkach o wysokiej i niskiej zawartości substancji odżywczych

In the rich nutrient medium lithium and cobalt bioleaching rates were the fastest in the first seven and ten days, respectively, when majority of the metals released into the solution.

The pH changes over the leaching time during the metal bioleaching in the rich and low nutrient environment is plotted in Fig.2. During the metal bioleaching in the rich nutrient medium a rapid pH increase from the initial value of 1.5 up to 2.4 in the first three days was observed. After that it remained more or less stable. A higher pH increase was observed during the metal bioleaching in the low nutrient medium. The pH gradually increased in the first ten days up to 3.1 and afterwards it started decreasing up to value of 2.6 measured on the last day of the experimental period.

According to the literature ((Swain et al., 2007), a higher consumption of protons is related to faster  $\text{Li}^+$  a  $\text{Co}^{2+}$  dissolution from  $\text{LiCoO}_2$ . The reaction is presented as follows Eq (4):



Since in the rich nutrient medium not only elemental sulphur, but also ferrous ions were present it might be assumed that ferrous ions are responsible for dissolution of lithium and cobalt as well. Based on the results it is obvious that not only sulphuric acid is responsible for lithium dissolution since despite rather low pH during the metal bioleaching process in the low nutrient environment too low Li bioleaching efficiency was reached.

## Conclusions

The results showed that the highest Li and Co bioleaching efficiency and bioleaching rates were achieved in the rich nutrient medium. This present fundamental study demonstrates that the extraction of both metals depends not only on sulphuric acid but also ferrous ions are responsible for dissolution of lithium and cobalt from LIBs.

## Acknowledgements

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## Literatura – References

1. BRANDL, H., FARAMARZI, M. "Microbe-metal interactions for the biotechnological treatment of metal containing solid waste." *China Particuology* 2(2006): 93–97.
2. BRANDL H., *Microbial leaching of metals, Biotechnology Set*, Wiley-VCH Verlag GmbH, Weinheim, Germany, 2008.
3. EHRLICH, H.L., *Beginnings of rational bioleaching and highlights in the development of biohydrometallurgy: a brief history*. *EJMP&EP* 4(2004): 102–112.
4. GOONAN, T. *Lithium use in batteries*, U.S. Geological Survey [online]. Reston, Virginia, 2012, Circular 1371, [cit.2013-04-20]. available on www. <http://pubs.usgs.gov/circ/1371/>.
5. HOQUE MD. E., PHILIP O.J. "Biotechnological recovery of heavy metals from secondary sources." *Materials Science of Engineering C/31*(2011): 57–66.
6. LUPTÁKOVÁ, A., KUŠNIEROVÁ, M., FEČKO P. *Minerálne biotechnológie II, Sulfuretum v prírode a v priemysle*, VŠB Technická univerzita v Ostrave, 2002.
7. MISHRA, D. AND RHEE, J-H. *Current research trends of microbial leaching for metal recovery from industrial wastes*, Formatex, 2010.
8. SAND W., GEHRKE T., JOZSA P-G., SCHIPPERS A., "(Bio)chemistry of bacterial leaching – direct vs. indirect bioleaching." *Hydrometallurgy* 59(2001): 159–175.
9. SMITH L., "Demand not to be taken lightly: While future lithium markets appear promising." *Industrial Minerals* 2010: 45-46.
10. Swain, B. et al., "Hydrometallurgical process for recovery of cobalt from waste cathode active material generated during manufacturing of lithium ion batteries." *Journal of Power Sources* 167(2007): 536–544.
11. WILLNER, J., FORNALCZYK, A. "Extraction of metals from electronic waste by bacterial leaching." *Environmet Protection Engineering* 2013: 197–208.
12. XIN, B. et al., "Bioleaching mechanisms of Co and Li from spent lithium-ion battery by the mixed culture of acidophilic sulphur-oxidizing and iron-oxidizing bacteria." *Bioresource Technology* 100(2009): 6163–6169.
13. ZELEŇÁKOVÁ, M., ZVIJÁKOVÁ, L. "Selection of impact indicators and their evaluation for environmental assessment of water construction." *Pollack Periodica* 6/3(2011): 83–92.

### *Bioługowanie metali z baterii litowo-jonowych za pomocą bakterii kwasolubnych*

W prezentowanym artykule zbadano odzysk litu i kobaltu ze zużytych baterii litowo-jonowych (27.5% LiCoO<sub>2</sub>) za pomocą bioługowania. Eksperymenty zostały przeprowadzone za pomocą kultur bakterii kwasolubnych *Acidithiobacillus ferrooxidans* oraz *Acidithiobacillus thiooxidans*. Dla bioługowania Li i Co zastosowano dwa różne ośrodki: ośrodek bogaty we wszystkie minerały potrzebne do wzrostu bakterii oraz ośrodek o niskiej zawartości substancji odżywczych, którym był ośrodek zawierający jedynie kwas siarkowy oraz siarkę pierwiastkową jako źródło energii. W pierwszym ośrodku ogólna efektywność bioługowania litu i kobaltu wyniosła, odpowiednio, 80% i 67%. Dla drugiego ośrodka wyniki te były, odpowiednio, 35% Li oraz 10.5% Co. Wyniki eksperymentalne ukazały, że obecność substancji odżywczych w bioługowaniu wpływa znacząco na odzyskanie litu i kobaltu z baterii litowo-jonowych.

Słowa klucze: bioługowanie, zużyte baterie litowo-jonowe, *Acidithiobacillus ferrooxidans*, *Acidithiobacillus thiooxidans*, odzysk Li i Co