CHEMICAL ENGINEERING TRANSACTIONS

VOL. 39, 2014

A publication of AIDIC
The Italian Association of Chemical Engineering
www.aidic.it/cet

Guest Editors: Petar Sabev Varbanov, Jiří Jaromír Klemeš, Peng Yen Liew, Jun Yow Yong

ISBN 978-88-95608-30-3; **ISSN** 2283-9216

DOI: 10.3303/CET1439269

Application of Innovative Processes for the Valorisation of Spent Alkaline Batteries

Stefano Ubaldini*[a], Jana Kadukova[b], Anna Mrazikova[b], Pietro Fornari[a], Alena Luptakova[c], Renata Marcincakova[b], Piersaverio Pizzichemi[a]

[a]Institute of Environmental Geology and Geoengineering, CNR, Area della Ricerca di Roma RM 1 – Montelibretti, Via Salaria Km 29 300, P.O. BOX 10 - 00015 Monterotondo Stazione, Roma, Italy
[b] Technical University in Kosice, Faculty of Metallurgy, Department of material science, Letná 9, 042 00 Košice, Slovak Republic;
[c] Department of Mineral Biotechnology, Institute of Geotechnics, Slovak Academy of Sciences, Watsonova 45, 04353 Kosice, Slovak republic
stefano.ubaldini@igag.cnr.it

Disposal of spent batteries constituted a serious environmental problem in terms of heavy metals content when these devices are disposed off in inadequate way.
Alkaline and zinc-carbon batteries represent about 80 % of the market. In particular, alkaline batteries have an average content of manganese dioxide (MnO_2) of 37 %, while zinc content is of 16 %. The high Mn and Zn content justifies the interest to recover the metals.
The present experimental work involves the application of innovative processes, such as the utilisation of the physical-chemical method (electrolysis) and biological-chemical (bioleaching) method for Mn–Zn recovery from spent alkaline batteries. Results have demonstrated the technical feasibility of the processes.

1. Introduction

One group of waste which amount continuously increases is the group of electrical and electro-technical waste including spent batteries. Battery is a collection of two or more electrochemical cells which represent a source of direct current. In an alkaline battery, the anode is made of zinc powder (which allows more surface area for increased rate of reaction therefore increased electron flow) and the cathode is composed of carbon and manganese dioxide (MnO_2). Acquisition of electric energy is based on chemical reaction between zinc and carbon in the presence of alkaline electrolyte (potassium hydroxide) (Xará et al., 2009). Electrochemical reactions are the following (Almeida et al., 2006):

Aanodic: $Zn + 2OH^- \rightarrow ZnO + H_2O + 2e^-$ (1)

Ccathodic: $2MnO_2 + H_2O + 2e^- \rightarrow Mn_2O_3 + 2\ OH^-$ (2)

Alkaline batteries are mostly used as energy source for clocks, portable car equipment, toys, cameras etc. After exhausting of chemical energy batteries become hazardous waste which contains many useful parts, including metals. The spent zinc-carbon batteries contain Zn, MnO_2, as well as ZnO and Mn_2O_3 produced from discharging reaction (Shin et al., 2009).
Alkaline and zinc-carbon batteries represent about 80 % of the market. They have an average content of manganese dioxide (MnO_2) of 37 %, while zinc content is of 16 % (EPBA, 2008). The high Mn and Zn content justifies the interest to recover the metals.
General ways of the alkaline batteries treatment can be divided into three groups: physical, pyrometallurgical and hydrometallurgical treatment. In physical treatment the same methods are used as are commonly used in mineral and ore processing with the aim to separate interesting metals or to create fractions rich in metals. Usually it is first step also in pyrometallurgical or electrolytic treatment. But

Please cite this article as: Ubaldini S., Kadukova J., Mrazikova A., Fornari P., Luptakova A., Marcincakova R., Pizzichemi P., 2014, Application of innovative processes for the valorisation of spent alkaline batteries, Chemical Engineering Transactions, 39, 1609-1614 DOI:10.3303/CET1439269

pyrometallurgical processes need a lot of energy because the temperature during treatment is often more than 800 – 1,000 °C (Sayilgan et al., 2009). When hydrometallurgical processes are used, metals are leached into solution and then recovered by precipitation or electrolysis. Zinc as amphoteric element may be leached in sulphuric acid but also in sodium hydroxide. The advantage of acidic leaching is relatively high efficiency; but part of the manganese is also leached. When hydroxide is used efficiency of Zn leaching is lower, only up to 40 %, but other metals stay insoluble. So it is possible to remove Zn selectively (Skoršepa et al., 1997). Very interesting possibility although not very studied in present time is the possibility offered by biohydrometallurgical processes using living bacteria to recover metals (Ubaldini et al., 1995).

The present experimental work involves the utilisation of the physical-chemical and biological-chemical methods for Mn–Zn recovery from spent alkaline batteries. The main aims of the research were: - to develop the preliminary experimental work to recover selectively MnO_2 and Zn from bioleaching solutions containing Mn and Zn by electrolysis, with the scope to apply electrochemical technologies for Zn and Mn recovery from spent batteries; - to verify the possibility of spent batteries processing by bioleaching with *Acidithiobacillus ferrooxidans* together with the molasses coming, as waste materials, from agro-food industry.

2. Materials and methods

2.1 Physical preparation and characterization

Manual dismantling products of spent alkaline batteries, such as plastic films, ferrous scraps and paper pieces were discharged and mixture of the cathodic (manganese oxides) and the anodic (zinc oxides and electrolytic solution) materials in form of powder was extracted (Vegliò et al., 2003). The powder was dried ground, using a ball mill, sieved and analyzed by X-ray diffraction (XRD), utilizing an automatic diffractometer Bruker mod. D8 Advance (data not shown here). Quantitative chemical analysis was conducted by Inductively Coupled Plasma Mass Spectrometry (ICP-MS). Average content of Zn in alkaline batteries was 21.54 % and although we made it as homogenous as possible the zinc content was in the range 20.05 – 24.15 %. In the case of manganese, average Mn content was similar - 21.36 % but the content variance was bigger from 16.72 to 26.3 %. Average content in K was 4.9 %, while Ni 0.65 % and Fe 0.6 %.

Iron represents the major impurity when Zn and MnO_2 are deposited in the electrowinning step, so it has been precipitated by an alkaline reagent, while potassium has been removed by washing with distilled water.

2.2 Bioleaching

A pure bacterial culture of *A. ferrooxidans* originated from acid mine drainage coming from Smolník, Central Slovakia, has been utilised (Luptakova et al., 2012a). 30 mL of inoculum was filtered and added to 600 mL of growth medium. The acidithiobacilli were cultured at initial pH 1.5 in 9 K medium and incubated at t = 22 °C. Composition of 9 K medium was following (in g/L): KCl (0.1); $(NH_4)_2SO_4$ (3.0); K_2HPO_4 (0.5); $MgSO_4.7H_2O$ (0.5); $Ca(NO_3)_2.4H_2O$ (0.014); $FeSO_4.7H_2O$ (44.2); H_2SO_4 (1-5mL). Bacteria adaptation to the powder of alkaline batteries was done by adding 5 g powder per 1 L of 9 K medium. Adaptation process took one month at t = 30 °C. Before the start of the bioleaching experiments, the adapted bacteria were transferred into the fresh 9 K medium and cultivated for 3 days, after that 10 g/L powder of alkaline batteries was added. Then 5 g/L molasses were added as reducing agents (Vegliò et al., 1998). The bioleaching experiments were carried out at two different temperatures, 22 °C and 35 °C The pH values were measured throughout the experimental period. The samples for analysis were withdrawn after 1, 3, 7, 10, 21 and 29 days of bioleaching process (Luptakova et al., 2012b). The Zn and Mn concentration in each sample was determined by Atomic Absorption Spectrometry (Varian AA20+).

2.3 Electrowinning

With the aim to develop the electrowinning study, synthetic solutions, constituted from a manganese and zinc sulphate, together with the other dissolved metals presents in the real solutions from bioleaching, have been prepared, by reagents of high analytical degree of purity (Ubaldini et al., 2006).

A cylindrical glass laboratory cell of 200 mL in volume has been used. The cell was equipped by a thermostatic water jacket connected with thermostatic bath, magnetic system for stirring and three electrodes (Ubaldini et al., 2000).

The cell was connected to a potentiostat-galvanostat (AMEL mod. 555B), equipped with an instrument system to automatically control the process parameters at constant potential conditions. By analysing the residual solution with ICP-MS, the purity of the MnO_2 and Zn deposition was monitored, while the deposit was analysed by XRD.

Electrowinning experiments were carried out in potentiostatic operations at constant anodic potential and stirring conditions. The kinetics of MnO_2 and Zn deposition were studied by selected voltages (Luptakova et al., 2012).
In this way, the voltage between working and reference electrodes was automatically monitored. The corresponding voltages (V) between working and counter electrodes (cell voltages) was measured with differential electrometer.
Average experimental cell voltages were utilised to calculate the energy consumption during the tests. The current flowing through the electrolytic cell was automatically integrated. To calculate the current efficiency and the average energy consumption, experimental data were utilised (Ubaldini et al., 1994).

3. Results and discussion

3.1 Bioleaching

The bioleaching experiment was carried out to study the influence of temperature and molasses on Mn and Zn dissolution (Vegliò et al., 1998). Zinc concentration in the solution increased in the first 14 days of bioleaching when the highest amount of Zn was dissolved. In general, a higher metal leaching efficiency by *A. ferrooxidans* is reached in the 35 – 38 °C temperature range (Barrett et al., 1993). However, based on our results (Figures 1-2, Table1) a higher Zn bioleaching efficiency was reached at a lower temperature (room temperature). Similar results were observed by Turocziova (2009) in zinc bioleaching from computer motherboards. The addition of molasses as a reducing agent did not enhance Zn dissolution.

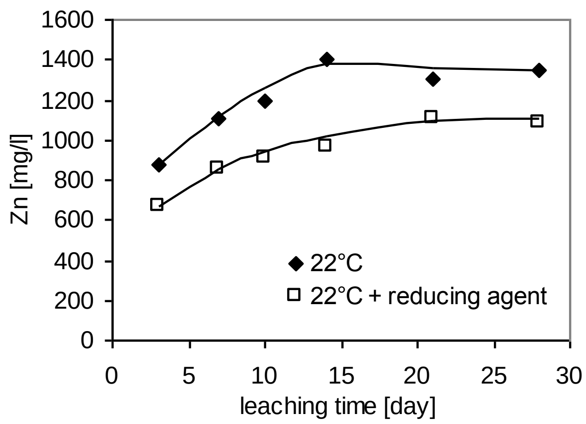

Figure 1: Influence of reducing agent on Zn bioleaching by Acidithiobacillus ferrooxidans at temperature of 22 °C

The Mn bioleaching process rates were the similar to those in Zn bioleaching. Manganese dissolution was the highest during the first 14 days of bioleaching. Mn bioleaching efficiency at a low temperature (22 °C, room temperature) and in the absence of molasses was found to be 30 %. The addition of molasses did not increased Mn bioleaching efficiency significantly (Figure 3, Table 1).
Based on the results (Figure 4, Table 1) it may be assumed that a higher temperature can slightly enhance Mn dissolution from spent alkaline batteries.

Table 1: Efficiency of alkaline batteries bioleaching on day 14

Conditions	Zn [%]	Mn [%]
22 °C	63	45
22 °C + reducing agent	45	41
35 °C	53	51.5
35 °C + reducing agent	45	41

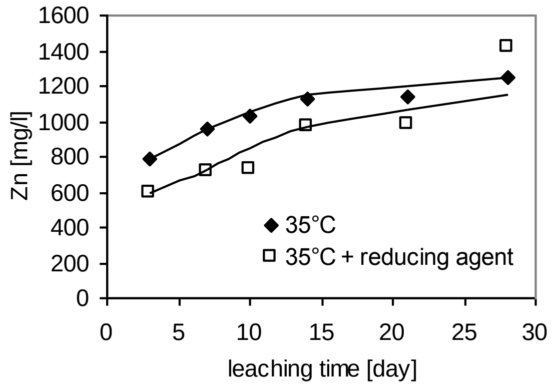

Figure 2: Influence of reducing agent on Zn bioleaching by Acidithiobacillus ferrooxidans at temperature of 35 °C

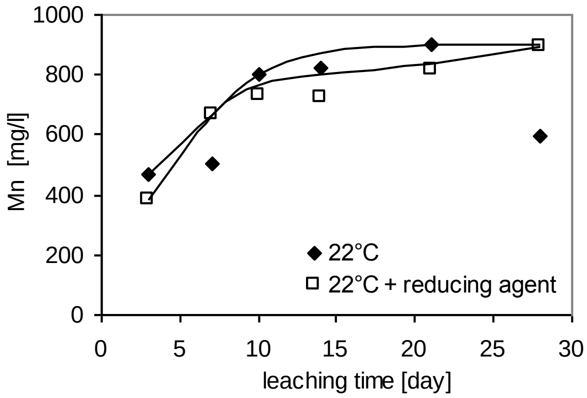

Figure 3: Influence of reducing agent on Mn bioleaching by Acidithiobacillus ferrooxidans at temperature of 22 °C

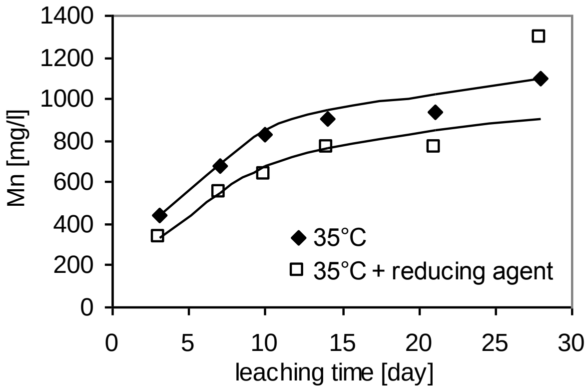

Figure 4: Influence of the reducing agent on Mn bioleaching by Acidithiobacillus ferrooxidans at temperature of 35 °C

3.2 Electrowinning

Main observations consequent to the experimental texts for electrolytic selective recovery of MnO_2 from synthetic solution containing Zn, have been the following:

- On the basis of data achieved during the preliminary electrodeposition texts, the experiments should be conducted at temperature of 95 °C, at constant potential, at fixed value of 1.8 V (Anode - SCE) and corresponding cell potential (anode - cathode) of 2.6-2.8 V.
- After 120 min of electrolysis 97.55 % of MnO_2 has been recovered, with average faradic yield of about 49 %, while the energetic consumption was of 3.48 kWh/kg of MnO_2 recovered.
- Zinc remains quantitatively in solution, after MnO_2 anodic deposition.
- By Zn electrolysis of a solution containing only Zn sulphate, conducted at temperature of 40 °C, constant potential, fixed value of 1.4 V (cathode - SCE) and corresponding cell potential (anode - cathode) of 3.6 V, about 99 % of metallic cathodic deposition of Zn was achieved, with a faradic current efficiency of 72.89 %, in 2 hours of electrolysis and an energetic consumption 4.08 kWh/kg of Zn recovered.
- Selective recovery of MnO_2 and Zn from synthetic solution containing Mn e Zn, both in concentration of 10 g dm^{-3} has been achieved. Best electrowinning results of the experiments have been shown in Table 2. MnO_2 and Zn deposit at high grade of purity has been attained; this fact was demonstrated from the results of the analyses conducted by diffractometric techniques.

Table 2: Main electrowinning results of the solution containing Mn and Zn

Species	Recovery (%)	η (%)	E (kWh/kg)
Zn	98.90	72.89	4.08
MnO_2	97.55	48.98	3.48

η = faradic current yield - E= energetic consumption

4. Conclusions

Results have demonstrated the technical feasibility of the application of bio-hydrometallurgical processes – integrated by electrochemical technologies - for Zn and Mn recovery from exhaust batteries.
Bioleaching of spent batteries is one of the possibilities how in economical and environmentally friendly way recover metals from batteries. As there is only very little knowledge about alkaline batteries bioleaching our aim was to verify the possibility to use bacteria in this process. In according to our results, bioleaching - integrated by electrochemical technologies - can be successfully used in the process of spent alkaline batteries treatment. Influence of temperature on Zn and Mn bioleaching can help in selective recovery of mentioned metals from batteries.
A quantitative recovery (about 98 %) of purified manganese (MnO_2) and zinc dissolved in solution has been achieved at the end of the electrodeposition step.
These results are very encouraging, considering that it is an innovative process. The further work, including the optimization of parameters and operating conditions and the subsequent scale-up in continuous applications, will permit to increase the process yields and to determine the economical sustainability of the application.

Acknowledgements

This work was supported by Joint Project of the CNR/SAV (2013/2015), Project CNR RSTL n. 0042.0005 and Slovak grant agency VEGA during the projects with the number 1/0134/09 and 2/0166/11.

References

Almeida M.F., Xarà S., Delgado J., Costa C., 2006, Characterization of spent AA household alkaline batteries, Waste Management, 26, 466–476.

Barret J., Hughes M.N., Karavaiko G.I., Spencer P.A, 1993, Metal extraction by bacterial oxidation of minerals, Ellis Horwood, London.

European Portable Battery Association (EPBA), 2008, <www.epbaeurope.net/ pub_technicalSupport.html> accessed on 27.06.2014.

Luptakova A., Ubaldini S., Macingova E., Fornari P., Giuliano V., 2012a, Application of Physical-chemical and Biological-chemical Methods for Heavy Metals Removal from Acid Mine Drainage, Process Biochemistry, 47, 1633–1639, ISSN: 13595113, doi:10.1016/j.procbio.2012.02.025.

Luptakova A., Ubaldini S., Fornari P., Mačingova E., 2012b, Physical-chemical and biological-chemical methods for treatment of acid mine drainage, Chemical Engineering Transactions, 28, 115-120. DOI: 10.3303/CET1228020.

Sayilgan E., Kukrer T., Civelekoglu G., Ferella F., Akcil A., Vegliò F., Kitis M., 2009, A review of technologies for the recovery of metals from spent alkaline and zinc–carbon batteries, Hydrometallurgy, 97(3-4), 158-166.

Shin S.M., Senanayake G., Sohn J-S., Kang J-G., 2009, Separation of zinc from spent zinc-carbon batteries by selective leaching with sodium hydroxide, Hydrometallurgy, 96, 349–353.

Skoršepa M., Šebek P., Imriš I., 1997, Possibilities of zinc recovery from spent household batteries (in Slovak), Metallurgy, Refractories and Environment, Proceeding from 25th Anniversary of Foundation of the Institute of Metallurgy and Materials, Košice, 1997, 135-142.

Turocziova E., 2009, Bioleaching of mother boards (PhD Thesis), Technical University in Kosice.

Ubaldini S., Massidda R., Abbruzzese C., Veglió F., Centofanti M., Toro L., 1994, Factorial experiments in the study of a biooxidative pretreatment for a conventional cyanidation of a Turkey arsenical gold ore, Progress in Mineral Processing Technology, Balkema, Eds Hamil Demirel & Salih Ersayin, ISBN 9054105135, Cappadocia, Turkey, 6-8 September 1994, 403-409.

Ubaldini S., Vegliò F., Toro L., Abbruzzese C., 1995, Gold recovery from Pyrrhotite by Bioleaching and Cyanidation: a preliminary study using statistical methods, JOM-Journal of The Minerals, Metals and Materials Society, Mineral bioprocessing II, 1, 145-155.

Ubaldini S., Veglio' F., Toro L., Abbruzzese C., 2000, Combined bio-hydrometallurgical process for gold recovery from refractory stibnite, Minerals Engineering, 13(14-15), 1641-1646, ISSN: 08926875, Doi:10.1016/S0892-6875(00)00148-5.

Ubaldini S., Massidda R., Veglio' F., Beolchini F., 2006, Gold stripping by hydro-alcoholic solutions from activated carbon: Experimental results and data analysis by a semi-empirical model, Hydrometallurgy, 81, 40-44, ISSN: 0304386X, DOI: 10.1016/j.hydromet.2005.10.004.

Veglio' F., Centofanti M., Beolchini F., Ubaldini S., Toro L., 1998, Manganese dioxide reductive leaching by sulphuric acid solutions containing carbohydrates, Innovations in Mineral and Coal Processing, Balkema, Eds Di Suna Atak, Güven Önal, Mehmet Sabri Çelik, Proceedings of the 7th Int. Mineral Processing Symposium, ISBN 9058090132, Istanbul, Turkey, 15-17 September 1998, 457-462.

Veglio' F., Quaresima R., Fornari P., Ubaldini S., 2003, Recovery of Valuable Metals from Electronic and Galvanic Industrial Wastes by Leaching and Electrowinning, Waste Management, 23(3), 245-252, ISSN: 0956053X, DOI: 10.1016/S0956-053X(02)00157-5.

Xarà S.M., Delgado J.N., Almeida M.F., Costa C.A., 2009, Laboratory study on the leaching potential of spent alkaline batteries, Waste Management, 29 (7), 2121-31, DOI: 10.1016/j.wasman.2009.03.010.