PRELIMINARY RESEARCH OF LEACHING OF SPENT NIMH BATTERIES WITH CHOSEN ORGANIC ACIDS

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Abstract

Critical raw materials, such as rare earths (REEs), have a high economic importance for the EU, combined with a high risk associated with their supply depending on very limited sources. Therefore, the recovery of the RE elements is extremely important for both economic and environmental reasons. NiMH batteries contain nickel, cobalt, lanthanum and other REEs and can be used as a secondary source of those metals. One of possible methods of their recovery is a hydrometalurgicall process consisting of following steps: leaching of batteries, separation of metal ions from leach pregnant solution (LPS) and obtaining of final products (metals or their compounds). The presented paper deals with leaching of spent NiMH batteries in aqueous solutions of chosen organic acids (like acetic, lactic or tartaric). As a result, solutions containing nickel(II), cobalt(II), lanthanum(III), and cerium(III) ions with concentration up to 2.5, 0.4, 0.5, and 0.2 g/dm^3, respectively, were obtained.

Keywords: NiMH batteries, leaching, recovery, nickel, rare earths

1. INTRODUCTION

Rare earth elements of high purity play a significant role in many areas of contemporary techniques. They also have many scientific applications. For example, their compounds are used as catalysts in the production of petroleum and synthetic products, lanthanides are used in lamps, lasers, magnets, phosphors, motion picture projectors, X-ray intensifying screens and many others. The addition of the pyrophoric mixed rare-earth alloy called Mischmetal or lanthanide silicates improves the strength and workability of low alloy steels. Therefore, the preparation of high purity rare earth elements is very important for such technologies [1]. The rare earth elements (REE) are an unusual group of metallic elements with unique properties: chemical, catalytic, magnetic, metallurgical and phosphorescent which consists of seventeen elements belonging to lanthanides. The geochemical studies have revealed that rare earth elements are actually not rare at all. There are known abort 250 rare earth element minerals of which 10-20 are found to be useful and only 5 practically applicable. Over 90% of the world's economically recoverable rare earth elements are found in primary mineral deposits i.e. in bastnaesite ores which are located in China and at Mountain Pass in California (USA). Monazite deposits in Australia, South Africa, China, Brazil, Malaysia, India and Russia are the second largest concentrations of rare earth elements [1, 2]. Consumption of rare earth elements in individual countries all over the world is the measure of their technological level and modernity. This is evidenced by concurrence of intensive development of production of many new materials and possession of rare earth elements separation and purification technology. In recent few years China has contributed about 97% of the supply on the world market of rare earth elements, whereas according to the United States Geological Survey [3] in 2015 the total resources were about 130 million tons of rare earth. In that China had about 42%, however China's mine production was about 85% of total world production. The rare earth elements export reduction introduced by China in 2009 caused anxiety among many world economies including the largest ones as these in the USA or Japan. As follows from the market analysis for several years the exploitation of rare earth elements has been on the same level but the demand for rare earth element compounds has been growing. The total demand for rare earth elements is expected to grow from 128,000 tons in 2011 to 170,000 tons by 2015 and to 255,000 tons in 2020 and a growth rate of about 7-10%/yr is estimated.

Rare earth elements find application in many advanced materials such as high performance magnets ($Nd_2Fe_{14}B$ and $SmCo_5$, Sm_2Co_{17}) which revolutionized technology by miniaturization of hard disc drives, in fluorescent materials, chemical sensors, high temperature superconductors, magnetoptical discs and rechargeable nickel-metal hydride batteries (NiMH). The alloy used for the battery's positive pole consists of rare earth metals and this makes up 26% of the weight of the battery. Taking into account consumer products they are used in TVs, computer hard drives, plasma and LCD screens, laptop computers, cell phones, DVD players, cameras, electric motors and generators of hybrid cars (Nd-Fe-B magnets and La batteries). For example, in Toyota Prius, Chevy Volt, Nissan Leaf etc. motors and generators of hybrid auto use approximately 25-27 kilograms of rare earth elements. In cars, rare earth elements are also used in fuel injectors, airbags and seat belt sensors, anti-lock brakes, power steering and seat adjustment motors and even in the fuel and car catalytic converters. The next example, are new wind turbines that are 70% more efficient than the standard ones. Rare earth elements are also used in catalysts that can increase the capacity of refinery equipment up to 30% and gasoline production by 5%, commercial air conditioners, medical magnetic resonance imaging equipment, for peptide preparation as well as microfertilizers that can increase certain crop yields by 15% [4 - 6].

The use of REE alloys in rechargeable nickel metal hydride (NiMH) batteries is based on their hydrogen storage properties. As a representative of hydrogen storage materials $LaNi_5$ is capable of absorbing considerable amounts of hydrogen gas and forms a hydride $LaNi_5H_6$. The hydrogen density in $LaNi_5H_6$ is even higher than in liquid hydrogen [7]. A cubic meter of $LaNi_5H_6$ contains 88 kg of hydrogen, but the same volume of liquid hydrogen only weights 71 kg. The $LaNi_5$-related hydrogen storage alloys absorb hydrogen gas rapidly at ambient temperature and their hydrides can be easily dehydrided by heating to temperatures between 50 and 100 °C. $LaNi_5$ based alloys are ideal hydrogen storage materials, but their prices are high because pure lanthanum should be used as raw material. In order to reduce the price of the alloy, mischmetal is used to replace pure lanthanum, forming a family of mischmetal-Ni_5 based hydrogen storage alloys. Mischmetal (Mm) is a mixture of light rare earth elements (La, Ce, Pr, Nd) in the metallic state. The composition of mischmetal varies depending on the origin of the rare earth minerals and its processing. Its composition affects the characteristics of the hydrogen storage alloys. The higher content of cerium and neodymium in mischmetal, the higher dissociation pressure of the hydride will be. Nickel can be substituted by other elements (mainly Al, Mn, Cr, Fe, Co, Cu and Si). In the nickel metal hydride battery, the negative electrode is made of a hydrogen storage alloy, replacing the cadmium in the older Ni-Cd rechargeable battery. In current NiMH batteries, multicomponent alloys such as $La_{0.8}Nd_{0.2}Ni_{2.5}Co_{2.4}Si_{0.1}$, $La_{0.8}Nd_{0.2}Ni_{2.5}Co_{2.4}Al_{0.1}$, $MmNi_{3.55}Co_{0.75}Mn_{0.4}Al_{0.3}$ or $MmNi_{3.5}Co_{0.7}Al_{0.8}$ are used instead of LaNi5. Although the hydrogen storage capacity of these alloys is lower than that of $LaNi_5$, this disadvantage is outweighed by their much higher chemical stability in alkaline solution and lower tendency for pulverization. Hybrid electric cars represent more than half of the usage of NiMH batteries (57%). Spent nickel metal hydride batteries contain 36-42% nickel, 3-4% cobalt and 8-10% mischmetal consisting of lanthanum, cerium, praseodymium and neodymium [8].

Until recently, the state-of-the-art industrial recycling of NiMH batteries was their use in stainless steel production as a cheap nickel source, and the rare earths were lost in the smelter slags [9]. Several research groups have developed hydrometallurgical methods for the recovery of nickel, cobalt and rare earths from NiMH batteries [10-17]. An industrial scale pilot plant has been operational in Hoboken, near Antwerp (Belgium), since September 2011 and this pilot plant has an initial annual capacity of 7000 tons. Not only nickel metal hydride batteries, but also Li-ion batteries can be recycled in this facility. Most of mentioned technologies produce mixture of lanthanides in metallic form (as a mischmetall) or in form of their oxides. Lanthanides separation and preconcentration of high purity compounds is one of the most difficult problems in inorganic chemistry and technology as it makes use of the subtle differences between the physicochemical properties of these elements and their compounds like solubility, basicity, volatility and possibility of occurrence with different oxidation numbers. Most frequently used methods in the separation of rare earth elements are - fractional crystallization, selective precipitation, oxidation-reduction methods, ion exchange and liquid-liquid extraction [10-19]. The presented paper deals with leaching of spent NiMH batteries in aqueous solutions of chosen organic acids (acetic, lactic or tartaric) as a potential method can be applied for the recovery or REEs.

2. EXPERIMENTAL

NiMH rechargeable batteries are quite popular and widely used. Detailed description of their construction can be found elsewhere [7]. In our research batteries of AA size of different manufacturers were used. All batteries were not dismantled and cut into 6 - 8 pieces and crushed into small parts below 5 mm and used for leaching experiments. According to literature data, the most popular leaching media there are mineral acids at wide concentration range. In presented research three organic acids were chosen for experiments: acetic, lactic and tartaric. All of them can be obtained by natural methods so their use seems to be a „green” process.

In each test a sample of about 3.0 g of the crushed battery was leached in appropriate volume of chosen acid solutions of suitable concentrations in a thermostatic beaker under mechanical stirring at the rate of 600 rpm. Preliminary tests have shown that the rates above 500 rpm do not influenced the rate of leaching. During and at the end of the experiments, samples of the pulp were taken and separated by filtration. The concentration of metal ions in the leach aqueous solutions was determined by atomic emission spectrometry method (spectrometer MP-AES 4200, made by Agilent).

3. RESULTS

The rechargeable nickel-metal hydride battery is a relatively new technology with characteristics similar to those of the previously applied nickel-cadmium battery. The principal difference is that the nickel-metal hydride battery uses hydrogen, absorbed in a metal alloy, for the active negative material in place of the toxic cadmium used in the nickel-cadmium battery. The active metal of the positive electrode of the nickel-metal hydride battery in the charged state is nickel oxyhydroxide. The negative active material in the charged state is hydrogen in the form of a metal hydride. This metal alloy is capable of undergoing a reversible hydrogen absorbing-desorbing reaction as the battery is charged and discharged. The overall reaction on discharge/charge can be written as:

$$MH + NiOOH = M + Ni(OH)_2 \qquad (1)$$

where MH denotes the hydride of metal M.

In presented preliminary studies the influence of reaction time on concentration of metal ions in aqueous solutions was investigated. The results are shown in **Figures 1 - 3**. During experiments there was found out that in the solutions there were present ions of nickel, cobalt, iron, lanthanum, cerium, zinc, manganese, aluminium and potassium. The findings are shown in three groups of battery components:

- Nickel, cobalt and iron - from this group nickel and cobalt can be taken into account as the elements possible to recovery and iron is a disturbing element and is present in comparable concentration,
- Lanthanum and cerium as representatives of lanthanides - recovery of these elements is particularly interesting,
- Other elements (zinc, manganese, aluminium and potassium) - their recovery is not profitable, but they are presented in the leach solution and can interfere with other metal ions.

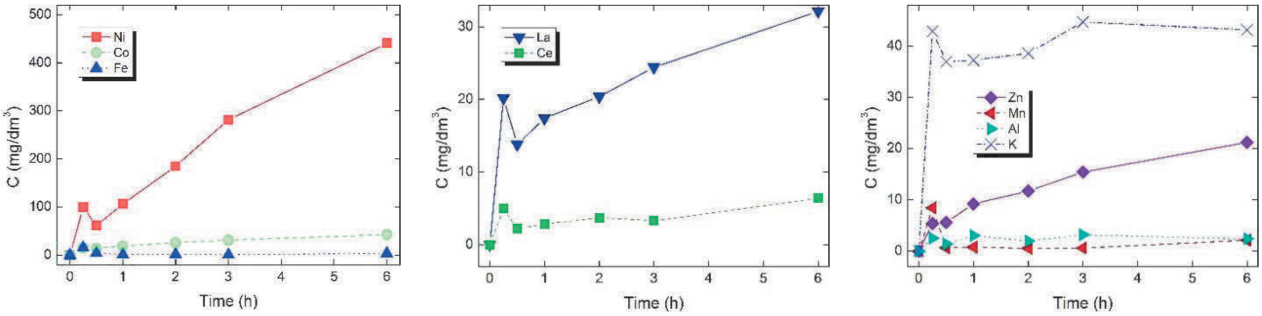

Figure 1 Kinetics of leaching NiMH battery in 1M acetic acid solution
(solid:liquid ratio = 1:100, temperature 20 °C)

For all applied acids, the highest concentration of metal ions was observed in the case of nickel. It changed from 430 to above 2200 mg/dm^3 for acetic and tartaric acids, respectively. Concentration of cobalt ions was in the range from about 50 to 300 mg/dm^3. In the group of lanthanides always higher concentrations of lanthanum than cerium were observed. It is easy to see that concentrations of all metal ions in acetic acid solutions were lower than in other acids. What is interesting, in acetic acid solutions there wasn't observed leaching of iron (**Figure 1**).

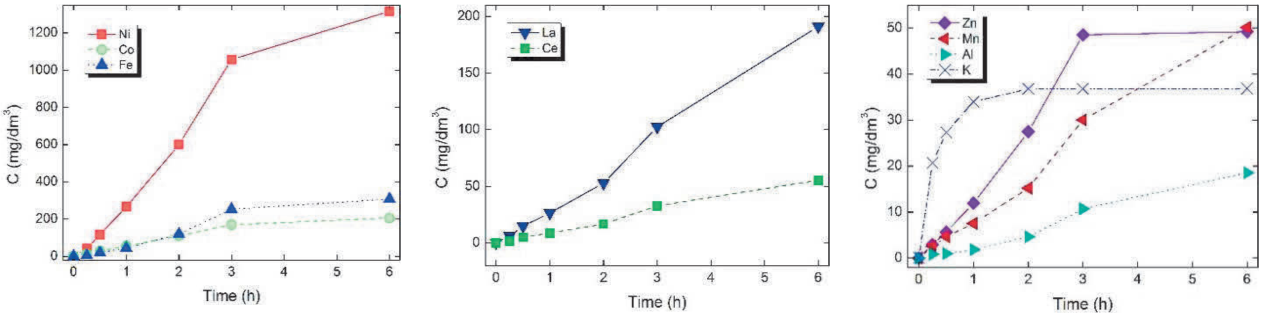

Figure 2 Kinetics of leaching NiMH battery in 1M lactic acid solution
(solid:liquid ratio = 1:100, temperature 20 °C)

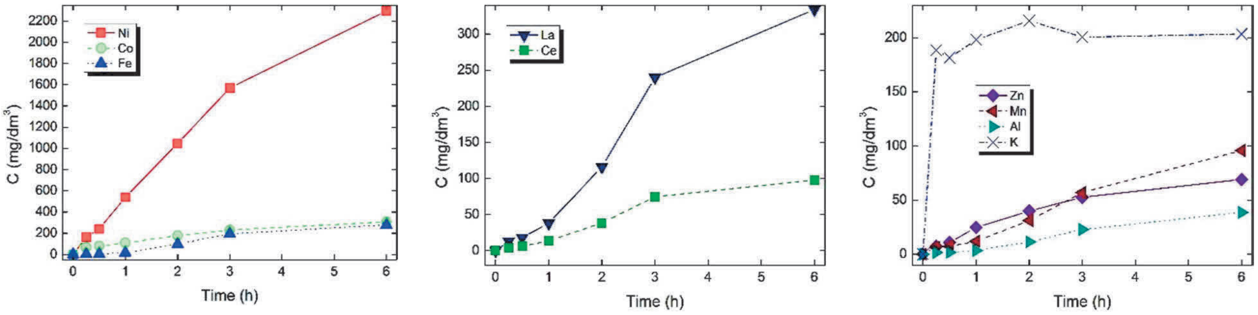

Figure 3 Kinetics of leaching NiMH battery in 1M tartaric acid solution
(solid:liquid ratio = 1:100, temperature 20 °C)

Leaching in solutions of lactic and tartaric acids (**Figures 2** and **3**) gave the better results for all analysed metals than in solutions of acetic acid. The obtained concentrations of all ions were from 3 to 5 times higher. Unfortunately, both mentioned acids dissolved steal can of battery, what resulted in the presence of iron ions In the leach solution. The oxidation state of iron ions was not analysed because it is not imported at this step of research. Their presence in the solution will be taken into account in the future, when the process of metal ions separation will be investigated. The results from **Figures 2** and **3** show that concentration of lanthanide ions is about ten times lower than nickel and cobalt and on the similar level as Zn, Mn and Al ions. Recovery of these metals is unprofitable due to their prices, as it was said before. Their presence in leach solution may interfere with separation and recovery process of valuable metals. On the other hand, in an industrial process of metal recovery, the leach solution should be recycled. In that case concentration of interfering metals will increase in each step. On that reasons, the problem of their presence must be solved in the future.

4. CONCLUSION

Due to a large amount of NiMH batteries selling every year they are a promising secondary source of such metals like nickel, cobalt and light lanthanides. This paper discusses and demonstrates the alternative use of leaching with chosen organic acids as the first step of those metals recovery process from spent batteries. The results of the examinations indicate that the method of leaching with tartaric acid gave the best results (i.e. the highest concentration of metal ions in obtained solution). There is possible to put used acids in the following order of growing concentration of metal ions: acetic < lactic < tartaric. The observations correspond to increasing strength of acids as well as their complexation properties. The further studies will concern with the use of different concentration of acids and solid/liquid ratio as well as to investigate of temperature influence on the efficiency of the process.

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