

HYDROMETALLURGICAL PROCESSING OF SPENT PORTABLE LI-ION ACCUMULATORS

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Abstract

The work was focused on the leaching of the active materials from spent lithium accumulators, which consist of a cathode and an anode material together with the electrolyte. The active material was obtained by mechanical treatment, which included a two-stage crushing by double rotor crusher, followed by sieving for obtaining the finest fraction $-0.71 + 0$ mm. The oversize fraction was broken in a hammer crusher. Crushed material was sieved and also collected the finest fraction of active material with a particle $-0.71 + 0$ mm. The finest fractions were mixed together from both steps and the material was served as an input for further experiments. The chemical composition was determined by AAS method and the result was as follows: Co - 24.43%, Li -3.42%, Ni - 2.74%, Mn - 1.41 %. This material was further leached in H₂SO₄ at the concentration 0.5 - 2 M, at the temperature 20-80°C, l:s = 50, for 120 minutes. Leaching extraction of Co and Li was investigated. The highest Co extraction - 57.2% was achieved using 2 M H₂SO₄ at 80°C. In another set of experiments was added the concentrated H₂O₂ in various volumes to H₂SO₄. Hydrogen peroxide acts as a reducing agent in this case. The highest cobalt extraction (80%) was achieved at the following conditions: temperature 40°C, 1 M H₂SO₄ with addition of 20 ml H₂O₂, l:s = 50, 120 minutes.

Keywords: spent portable Li-ion accumulators, hydrometallurgy, leaching, cobalt, lithium

1 Introduction

Nowadays, the consumption of batteries and accumulators based on lithium is markedly growing because of the information technology expansion, increased application of new laptops and exchange of obsolete laptops, mobile phones etc., where a most commonly used source of electricity are lithium cells. According to available data, the annual rate of increase in world consumption of primary lithium cells is 3.7%, in consumption of secondary lithium cells 5.6% [1]. From point of view recycling, cobalt is one of the main metals, which is present in lithium accumulators. Another metal that can be obtained from spent lithium cells is lithium. About 25% of world lithium production is used for lithium cells production [2]. On the present time (April 2012), a cobalt price is 30.3 USD / kg [3,4] and a lithium price is 63 USD / kg [5].

According to the composition of lithium accumulators they can be divided into Li-ion and Li-ion polymer accumulators. Generally, electrochemical cells consist of cover, electrode (anode and cathode), electrolyte and separator. Anode and cathode powder material form together active material or "black mass". While in primary lithium cells metallic lithium is present, in lithium accumulators is lithium only in the compounds, which form the active cathode material. Components containing lithium, which can be used for the construction of lithium accumulator

cathode is LiCoO₂, LiNiO₂, LiMn₂O₄ and LiFePO₄. As the anode material, graphite, fine and hard carbon is used. In both types of cell electrolytes, organic solvents containing lithium salts, for example LiI, LiPF₆, LiBF₄, LiClO₄ are present. As a separator for separating the cathode and anode, micro porous polypropylene film is used, a good alternative are fluorocarbons or glass fibers [6, 7, 8].

Spent lithium cells can be processed by hydrometallurgical, pyrometallurgical or combined route. Before treatment, particularly hydrometallurgical treatment, a mechanical pre-treatment for separating the components and obtaining active material with interest metals in a single fraction is required. Mechanical treatment is carried out by crushing and grinding with various devices, followed by sorting using different mesh size sieves. The aim is to separate the active material from other parts and to prepare it for further processing by hydrometallurgical route. Other components that are concentrated in other fractions can be also recycled, especially steel container, aluminum and copper foil.

For the hydrometallurgical processing of the active material, mainly acid leaching agents such as H₂SO₄, HCl, HNO₃, or citric acid and oxalic acid are used. To increase the Co extraction, 30% H₂O₂ is added to H₂SO₄, which ensure nearly 100% Co recovery.

The aim of this work was leaching of active material from spent Li-ion accumulators, in the first series of experiments in H₂SO₄ without reducing agent for the study of the leaching reagent concentration and temperature influence on the recovery of Co and Li. In the second series of experiments, leaching in H₂SO₄ with the addition of H₂O₂ was carried out. The goal was to determine the optimal amount of hydrogen peroxide that was added to increase the extraction of cobalt and lithium from the active material.

2 Experimental

2.1 Material

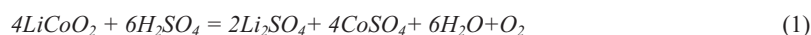
Spent portable Li-ion accumulators were subjected to mechanical treatment using a double rotor and hammer crusher. By sieving was obtained a finest fraction with a particle size $-0,71 +0 mm$ which is called active material and that fraction contains metals like Co, Li, Ni, etc. By quartering the active material sample was taken and the chemical composition was determined by AAS on a Varian AA-240. Chemical composition is shown in the Tab. 1.

Tab. 1 Chemical composition of active material sample from spent Li-ion accumulators

Sample	Metal content [%]						
	Co	Li	Ni	Cu	Al	Mn	Fe
$-0,71 +0 mm$	24.43	3.42	0.88	2.74	1.06	0.72	1.41

2.2 Thermodynamical study

Thermodynamical study was carried out in order to predict leaching conditions before the leaching. As the leaching agent was used H₂SO₄, where during leaching of active material are expected following reactions [9, 10]:



E – pH diagrams (Fig. 1, 2) for the system Co - S - H₂O and Li - S - H₂O at 20°C and 80°C was calculated by HSC Chemistry 6.1.

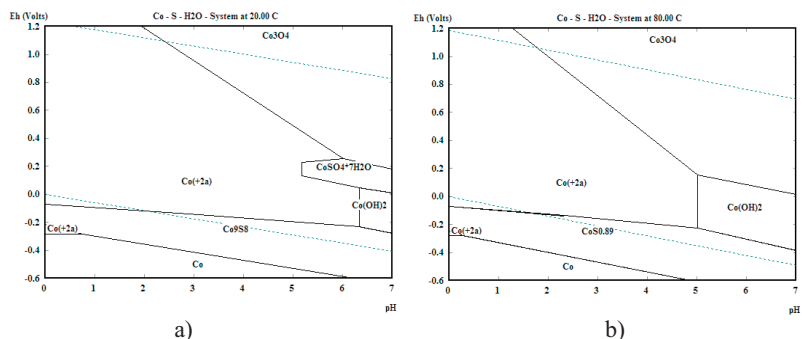


Fig. 1 E-pH diagrams of the system Co-S-H₂O a) 20°C b) 80°C

As Fig. 1a) shows, Co²⁺ is in the solution to pH~6, while from pH~5 it may crystallize out of the solution as CoSO₄*7H₂O. At 80°C (Fig. 1b) Co²⁺ is stable in the solution to pH ~ 5. By increasing the pH it is possible to precipitate Co(OH)₂ according to the reaction (3),

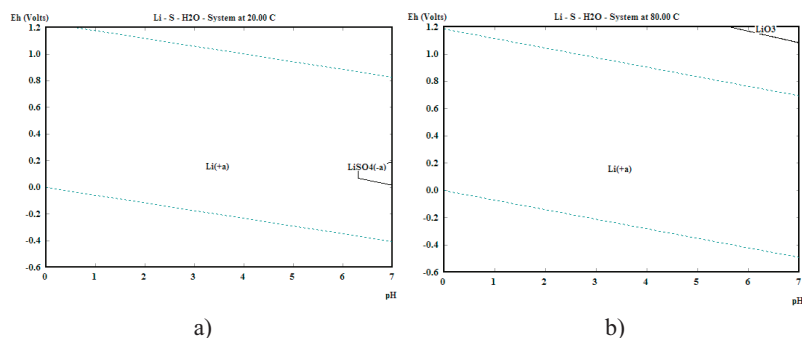


Fig. 2 E-pH diagrams of the system Li-S-H₂O a) 20°C b) 80°C

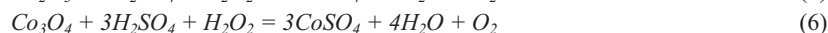
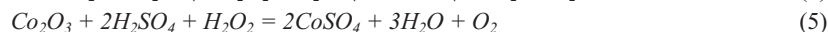
Lithium ion is stable in the whole water stability area in the water solution throughout the whole acid pH range at 20°C, as well as at 80°C.

2.3 Leaching experiments

Leaching experiments were carried out in leaching apparatus consisting of the glass reactor with stirrer, which was inserted into the thermostat-controlled water bath. Leaching sample consisted from the active material of Li-ion accumulators, the finest fraction after mechanical pre-treatment (particle size $-0.71 + 0$ mm). Leaching conditions were the following: leaching agent 0.5, 1, 1.5 and 2 M H₂SO₄, temperature 20, 40, 60, 80°C, l:s = 50, leaching time 120 minutes, 300 rpm, analyzed metals Co and Li. Collected samples were analyzed by AAS.

The second series of experiments was focused on to the intensification of leaching process using 30% H₂O₂ as an addition to the leaching agent in various volumes. H₂O₂ is generally considered as a strong oxidizing agent. However, in the case of cobalt, H₂O₂ acts as a reducing agent, because there is the reduction of Co³⁺ to Co²⁺ and also the oxidation of the oxygen atoms

in the peroxide group (oxidation stage -I) of gaseous oxygen (oxidation number 0), according to reaction (4), (5), (6),



Experiments were conducted like in the previous case with the difference that just before adding the solid sample, the exact volume of 30% H₂O₂ - 5, 10, 15 or 20 ml was added to the solution. The conditions of the experiment, which were constant are following: 1 M H₂SO₄, temperature 40°C, l:s = 50, leaching time 120 min., 300 rpm, analyzed metals Co and Li.

3 Results and discussion

3.1 Effect of leaching agent concentration on the extraction of cobalt and lithium

Extraction of Co achieved by leaching of active material using 0.5, 1.5, 1 and 2 M H₂SO₄ at temperatures from 20 to 80°C are graphically illustrated in Fig. 3a-d.

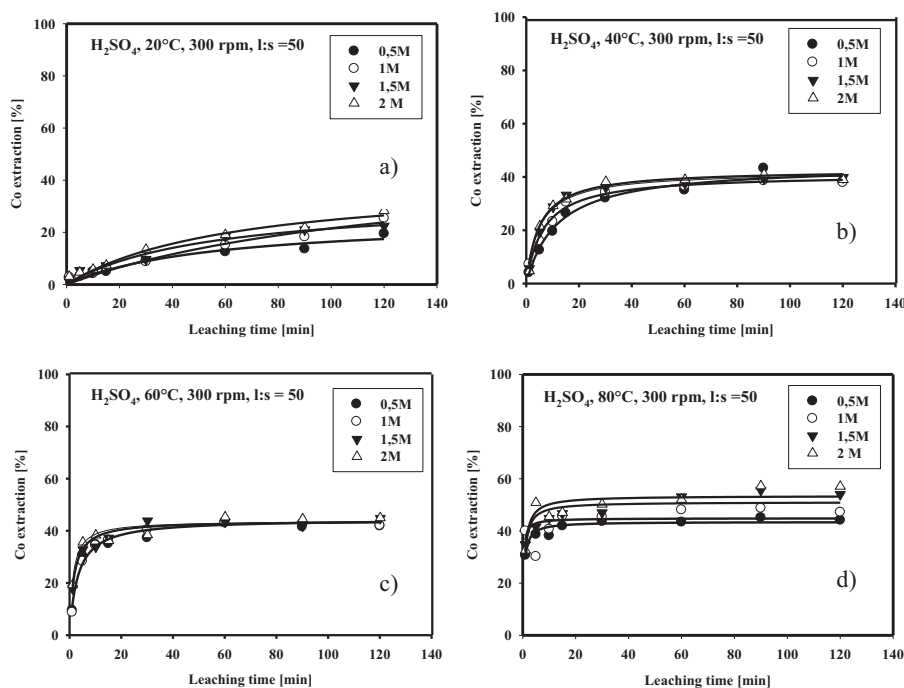


Fig. 3a-d Kinetic curves of Co extraction depending on the leaching agent concentration

Extraction of Li achieved by leaching of active material using 0.5, 1.5, 1 and 2 M H₂SO₄ at temperatures from 20 to 80°C are graphically illustrated in Fig. 4a-d.

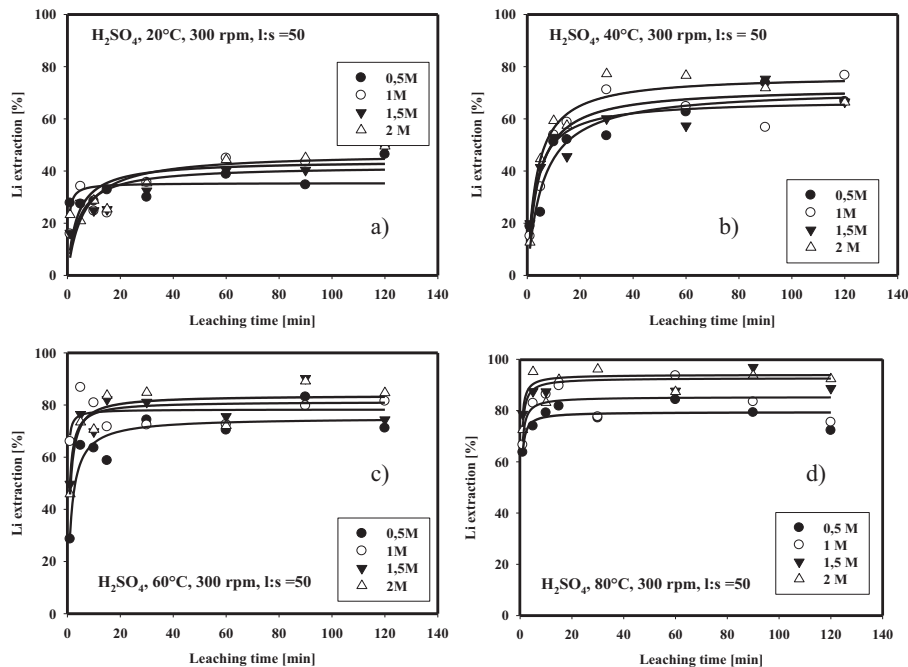


Fig. 4a-d Kinetic curves of Co extraction depending on the leaching agent concentration

As it results from the kinetic curves, acid concentration has no significant effect on the extraction of Co and Li, which means sufficient amount of free acid also at lowest acid concentration. The difference in extraction of cobalt by leaching in 0.5 M H₂SO₄ and 2 M H₂SO₄ is less than 10%. The Co extraction was most effective in 2 M H₂SO₄ at 80°C. Under these conditions, the Co extraction was reached 57% (Fig. 3d) in 90th leaching minute. The reason for achieving a relatively low maximum Co extraction is that Co in the active material is in several phases, for example CoO, LiCoO₂, Co₃O₄ [11], some of which are probably resistant to leaching in H₂SO₄. Phases in which Co is in the trivalent form are probably no leachable without the presence of complex-forming agent. As the kinetic curves show, in the first minutes leachable Co phases are leached and then the process is stopped. For the leaching of Co from other phases is therefore necessary to use a complex-forming agent and/or reducing agent, e.g. H₂O₂, which reduces Co³⁺ to Co²⁺.

The highest Li extraction was achieved in 1.5 M H₂SO₄ at 80°C. Under these conditions the Li extraction nearly 100% was achieved (Fig. 4c). The reason is the high reactivity of Li.

3.2 Effect of temperature on the extraction of cobalt and lithium

Effect of temperature on the leaching of Co from spent lithium accumulators at 20 to 80°C at different concentrations of H₂SO₄ is shown in Fig. 5a-d.

Effect of temperature on the leaching of lithium from spent lithium accumulators at 20 to 80°C, at different concentrations of H₂SO₄ is shown in Fig. 6a-d.

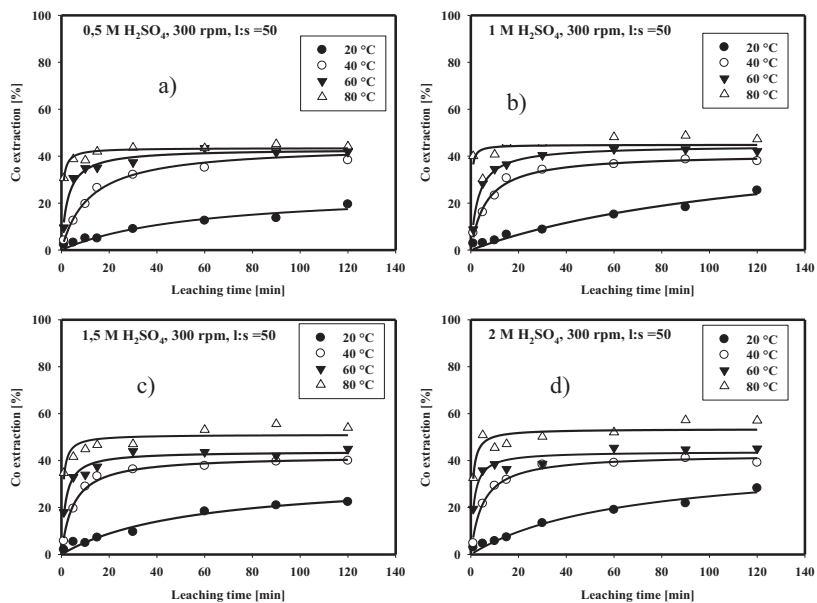


Fig. 5a-d Kinetic curves of Co extraction depending on temperature

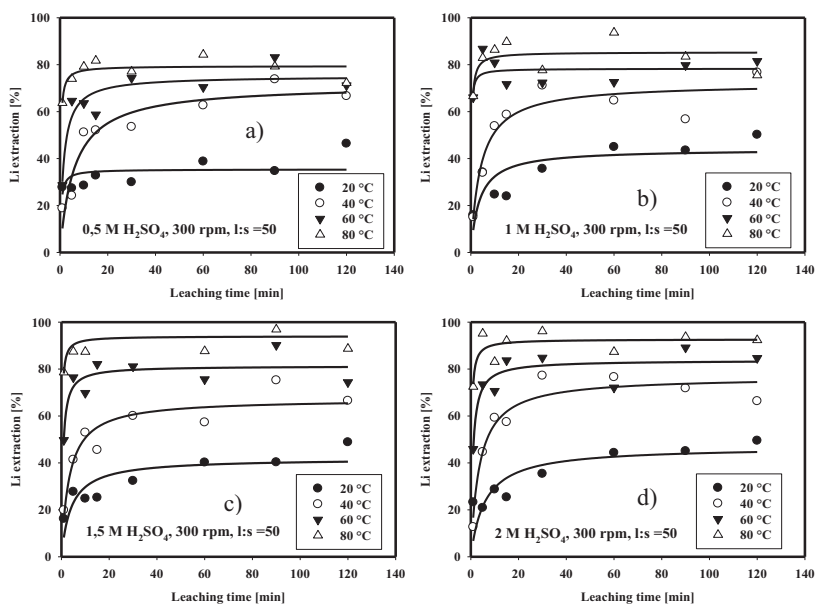


Fig. 6a-d Kinetic curves of Li extraction depending on temperature

As it is shown in Fig. 5 and 6, in contrast to the acid concentration, the temperature has the significant effect on extraction of metals, particularly cobalt. The highest extraction of Co (about

30%) was achieved at 20°C using 2 M H₂SO₄, whilst using the same acid at 80°C led to almost 60% Co extraction (Fig. 5d). Increasing temperature has a positive effect on the Li extraction too. Li extraction in 2 M H₂SO₄ at 20°C was about 50%; whilst at 80°C was almost 100%.

3.3 Effect of addition of hydrogen peroxide on the extraction of cobalt and lithium

The effect of addition of H₂O₂ in a volume of 0-20 ml on the extraction of Co and Li during the leaching of lithium accumulators in 1 M H₂SO₄ for 120 min. at 40°C are shown in Fig. 7a-b.

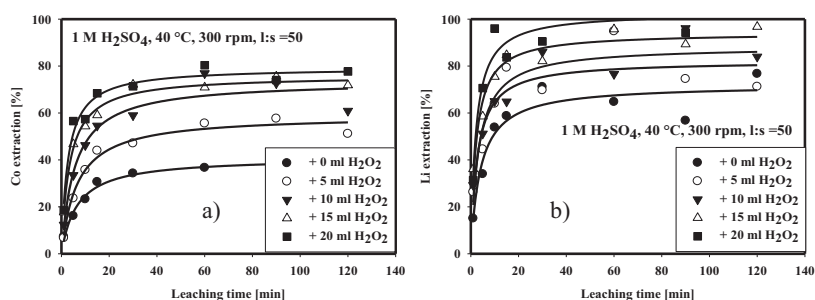


Fig. 7 Kinetic curves of extraction depending on hydrogen peroxide addition
a) cobalt, b) lithium

H₂O₂ is added to the process mainly in order to increase extraction of Co. Li as a highly reactive light metal is well leached without the additional agent use, particularly at higher temperatures (in some cases the extraction of Li achieves almost 100%).

H₂O₂ acts on phases of trivalent cobalt, like LiCoO₂ and trivalent Co is reduced to divalent, which can be leached under these conditions. It is evident from Fig. 7a), where Co extraction achieved 38% without a reducing agent. When 20 ml concentrated H₂O₂ was used, at the same condition, 80% Co extraction was achieved. The addition of H₂O₂ has a positive effect on the Li extraction, which was increased from 77% to 100%. Since Li is only in the univalent form, H₂O₂ can not act as reducing or oxidizing agent in this case. The higher extraction of Li with increasing addition of H₂O₂ could be related to increasing Co extraction, since the structure of Li and Co phases could prevent Li leaching. Therefore, after Co was leached out more substantial, leaching of Li could occur.

4 Conclusion

In the work hydrometallurgical processing of spent portable lithium accumulators for recovery of cobalt and lithium was investigated. Before leaching of lithium cells, their pre-treatment was required, so they were repeatedly crushed, thus the release of all components and the concentration of active material in one fraction were ensured. The particle size fraction -0.71 +0 mm containing 24.43% Co and 3.42% Li was subjected to leaching with sulfuric acid under the following conditions: 0.5, 1, 1.5 and 2 M H₂SO₄, temperature 20, 40, 60 and 80°C, l:s = 50, time 120 min. Maximum extraction of lithium almost 100% of lithium and less than 60% of cobalt in 2 M H₂SO₄ at 80°C and l:s = 50 was achieved.

This extraction of cobalt is not sufficient from economic reasons, so next experiments were realized, when 30% H₂O₂ - 5, 10, 15, 20 ml under constant conditions: 1 M H₂SO₄, 40°C, l:s = 50, 120 minutes was added to H₂SO₄. Addition of H₂O₂ had a positive effect on the cobalt

extraction; with increasing volume recovery of cobalt was rising. The highest extraction of cobalt (80%) was obtained at 40°C, 1 M H₂SO₄, l:s = 50.

All experiments were performed for 120 minutes, but the kinetic curves showed that 90 min. of leaching time is sufficient.

The subject of further study will be achieving higher metal extraction, particularly cobalt, by using higher temperatures and higher volume of hydrogen peroxide during the leaching with sulfuric acid, or using other leaching agent which is complex-forming, e.g. hydrochloric acid or the high pressure leaching. The leach-liquor obtained after the leaching of the lithium accumulators will be processed for obtaining cobalt and lithium from a solution by precipitation, solvent extraction or crystallization.

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