

Recycling of lithium accumulators

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Abstract — More than 200,000 tons of portable batteries and accumulators are placed on the market annually in the EU countries and more than 20 wt. % of them are lithium ones. In addition to lithium, they contain metals such as cobalt, nickel, manganese, copper aluminum and others. High share of lithium battery and a limited lifespan results to a large quantities of waste. Pyrometallurgical recycling methods, which are currently more widely used, have a lower selectivity and consist only in the recovery of selected metals. The remaining substances are concentrated in slag, which is deposited in landfills. Lithium slag composition and leaching behavior of lithium and cobalt in Sulfuric acid was studied in this paper. The leaching was carried out in 0.1, 0.5, 1 and 2M H₂SO₄ with and without 30 ml of H₂O₂ at temperatures of 20, 40, 60 and 80°C. All slag samples were leached for 90 minutes with constant stirring of 300rpm at liquid to solid ratio of 50. The obtained results showed that 66.85% of Co and 99% of Li was leached at 1M H₂SO₄ with addition of H₂O₂ at temperature of 80°C.

I. INTRODUCTION

The production of metals from primary raw materials already faces several problems, such as the high costs of mining, the loss of raw materials, low content of metals in the primary raw materials, their problematic processing, the production of large quantities of waste and others. These problems can be partially or completely eliminated in the case of the recovery of metals from secondary raw materials. In 2017, 61 materials (or groups of materials) were judged by the European Commission, resulting in a list of 27 Critical Raw Materials (CRMs). The results show that there is a risk of supplying EU with lithium, but economic importance is not significant to the EU. However, in the case of cobalt, its economic importance and supply risk are above threshold values and is therefore classified as CRM. These 2 metals are also represent in waste of portable lithium batteries. Their recycling can partially secure the needs of these metals in the EU and reduce the risk of supply [1].

The average annual quantities of lithium mined from primary raw materials ranged from 30000 to 35000 tons per year between 2010 and 2016 [2]. The consumption of lithium in the form of LiCO₃ increased from 100,000 metric tons per year in 2010 to 212,000 metric tons per year in 2016 [3]. Converted into lithium, consumption is 20,000 tons per year. Global lithium reserves are estimated at 14 million tons, while the largest reserves of countries have Chile, China, Argentina and Australia. EU countries do not have significant stocks or deposits and therefore it is necessary to rely on import and recycling.

Approximately 35% of the world's lithium production is consumed to produce lithium batteries. Lithium also used for the production of Ceramics and Glass (32%), lubricating greases (9%), continuous casting (5%), air pollution treatment (5%) polymers (4%) and other (11%) [4]. Lithium price is currently at 16,500.00 \$/t [5]. Despite the fact that lithium is not CRM, the content in Li batteries is the same as in the primary raw material (2-5%), the recycling of this element is still economically and environmentally appropriate.

Cobalt is an important part of lithium accumulators. In 2016 approximately 60% of cobalt mined was as a by-product of copper, 38% as a by-product of nickel, and the remaining 2% from primary cobalt mines [6]. Approximately 51% of annual world cobalt production is consumed for the production of lithium batteries. Cobalt is also used to make super alloys (20%), hard materials (8%), ceramics and pigments (8%) and others [6]. The price of cobalt stabilized again at \$ 37,000 per ton after its price increase in 2016 [7]. While the content of cobalt in ores is very low, 0.06 - 0.7%, its content in Li-ion accumulators is up to 20%. The increasing demand for cobalt and the limited supply, which is also confirmed by its rising price, are the reasons for obtaining these resources from secondary raw materials. Such appropriate secondary source are also waste of portable Li batteries not just because of the cobalt content, but also other present metals like copper aluminum, nickel and lithium. Lithium battery recycling helps to save primary resources of many metals used for their production, creates new jobs, protects the environment and promotes the sustainable development of EU countries by reducing the risk of supplying of these metals [8]. They can be processed mechanically, pyrometallurgically, hydrometallurgically or by combining some of these methods. Mechanical processing is often the first of the processing steps. This includes crushing, milling and sizing and is carried out in order to separate individual components. In the case of mechanical pre-treatment, the battery should be discharged in order to avoid short-circuiting and subsequent fire of the material. Pyrometallurgical methods are a processes of obtaining metals at high melting temperatures or methods for thermal pre-treatment of inputs for leaching processes. Mechanical pre-treatment is not necessary, and careful battery sorting is not always required but it may negatively affect product quality and purity of products. The smelting product is an alloy of interest metals, and a slag, which may also contain metals suitable for further recovery. Hydrometallurgy is a series of metal-recovery

processes where the principle is to transfer the metal to the leachate and then selectively recover it from the leachate. Leaching, metal transfer to the leachate, may be acidic or basic, oxidative or non-oxidative, pressure or atmospheric. The leaching is most often carried out at temperatures of 25-100°C or in the cases of high pressure leaching up to 250°C. A large part of the research focuses on the hydrometallurgical methods processing because of their high selectivity and the possibility of recovering reusable compounds for the production of new lithium batteries. Metals present in the active mass of lithium batteries can be leached in sulfuric acid [9,10,11,12,13], hydrochloric acid [14,15,16], ammonium sulfate with sodium sulfate, phosphoric acid [17], acetic acid [18], malic acid [19] and citric acid [20,21]. The leaching is followed by processes such as precipitation, cementation, ion exchange, liquid extraction, electrolysis and its combinations to obtain metals, their salts or other chemical compounds.

Despite the advantages of hydrometallurgical methods, the use of pyrometallurgical processing methods still dominates the industry due to their bigger capacities. The slag that is produced in this process is currently being landfilled.

The aim of this work is to analyze the metal content in the slag and to study the possibilities of hydrometallurgical processing.

II. EXPERIMENTAL PART

A. Analytical methods

The chemical composition of input material, intermediates and products was determined by the AAS method on a Varian Spectrometer AA20+, XRF analysis on a Shimadzu EDX-7000/8000 and SEM-EDX analysis were performed at Mira3 TESCAN.

B. Input material

Sample of lithium batteries slag was obtained by smelting of battery active mass containing Li and Co with a slag-forming additives such as Fe₂O₃, CaO and SiO₂. Melting products were metal with high cobalt content and mentioned slag. Separated slag was mechanically treated by grinding and milling and 5 representative samples were taken and analyzed by AAS method (Table I) and XRF (Table II). Optical microscope observations of sludge is shown in Fig 1. and SEM-EDX in Fig 2.

C. Leaching conditions

The aim of the leaching experiments was to determine the

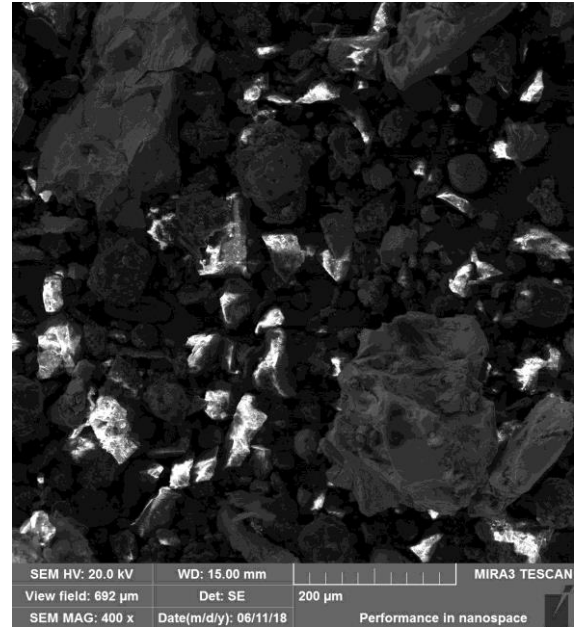


Figure 1 Slag morphology at 400X magnification observed by SEM-EDX Mira3 TESCAN

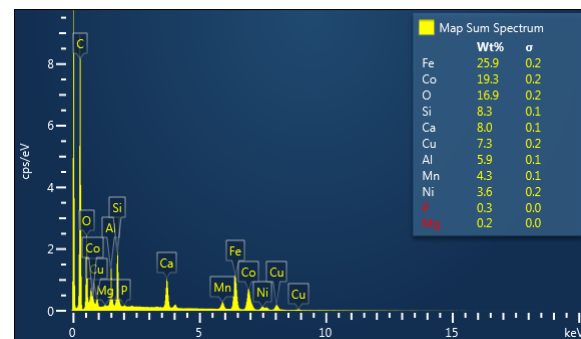


Figure 2 SEM-EDX analysis of spectrum from Fig 1 by SEM-EDX Mira3 TESCAN.

leaching efficiency of lithium and cobalt at different H₂SO₄ concentrations and temperatures. Leaching experiments were carried out in a glass reactor placed in a heated water bath stirred at 300 rpm. The ratio of liquid to solid phase was set to 50. The duration of all experiment was set to 90 minutes with sampling time at 10, 30, 60 and 90 minute. In the first step, the effect of concentration at 80°C using 0.1M, 0.5M, 1M and 2M acid was studied. The second series of experiments was carried out with 1M H₂SO₄ at 20, 40, 60, 80°C. All experiments were carried out in parallel with and without the addition of H₂O₂ used as oxidizing agent.

TABLE I
CHEMICAL COMPOSITION OF LITHIUM BATTERIES SLAG DETERMINED BY AAS METHOD

Element	Co	Li	Mn	Ni	Fe	Ca	Al	Cu	Ti	Si
Percentage [%]	13.10	2.75	1.96	1.96	9.09	3.99	7.91	2.24	0	14.14

TABLE II
CHEMICAL COMPOSITION OF LITHIUM BATTERY SLAG DETERMINED BY SEMI-QUANTITATIVE XRF METHOD (MEASUREMENT RANGE: ¹¹Na - ⁹²U)

Element	Ca	Si	Al	Fe	Co	Mn	Cu	Ni	S	La	K	Ce	Zr	Pr
Percentage [%]	27.79	21.99	17.22	13.66	9.74	3.83	2.28	1.58	0.71	0.25	0.20	0.18	0.17	0.13

III. RESULTS AND DISCUSSION

A. Sulfuric acid concentration dependance

The first step of the leaching study was to analyze the effect of concentration on leaching efficiency at 80°C. As can be seen in Fig. 3, as the concentration increases, the yield of lithium and cobalt also increases. Lithium leaching efficiency ranges from 58.14% using 0.1M H₂SO₄ to 100% using 2M H₂SO₄. The cobalt leaching efficiency ranges from 4.46% using 0.1M H₂SO₄ to 65.85% using 1M H₂SO₄. A further increase in concentration to 2M H₂SO₄ resulted in a decrease in cobalt leaching efficiency. The addition of H₂O₂ has a positive effect on the leaching efficiency of cobalt, but negative on lithium. The lithium leaching efficiency reaches a maximum in 10 minutes and cobalt leaching efficiency reaches a maximum in 30 minutes. Figure 4 shows the leaching efficiency of lithium (a) and cobalt (b) in the 30th minute of leaching, with the X-axis showing different concentrations. Due to the higher cobalt content in the slag, it is appropriate for further study to focus on the conditions of better cobalt leaching. Therefore, 1M H₂SO₄ was chosen as sufficient for further study.

B. Leaching temperature dependance

The heating of the leaching solutions is an energy demanding process and, therefore, in the next experimental study, the lowest possible temperatures at which the slag metals are leached were searched. Figure 5 shows slag leaching efficiency in 1M H₂SO₄ at 20, 40, 60 and 80°C. Lithium leaching efficiency in 10 minutes reaches from 55.62% at 20°C to 92.27% at 80°C. The maximum leaching efficiency of 99.91% was achieved in a 30 minute leaching at 60°C without using of H₂O₂. The concentration of lithium in the solution decreases with longer leaching durations. The cobalt leaching efficiency at 30 minutes and 80°C was 61.51%. At 60°C, the leaching efficiency drop to 54.49%. Further lowering of the temperature to 20°C slows down the cobalt leaching process, but the overall efficiency of the process is not significantly reduced. 50.26% leaching efficiency was archived after 60 minute of leaching, which significantly reduces process costs by eliminating solution heating step. Input sample and solid residues after leaching were weighed and analyzed by semi-quantitative XRF. Absolute amounts of metals in the samples before and after leaching (Fig. 6) were calculated from sample weight and XRF analysis. The addition of H₂O₂ and temperature increase have a positive effect on leaching of metals such as nickel, manganese, iron, aluminum. In addition to metals, slag-forming additives are leached to the solution, which can negatively affect the process of recovering the metals from the solution. Silicon ions increases the density of the solution and the calcium recrystallizes after leaching and may act as an adsorbent for other elements, which may be undesirable. These experiments confirmed that all lithium present in the slag can be leached, but in the case of cobalt, only 66.85% leaching efficiency was achieved. Further study is necessary to increase cobalt leaching efficiency.

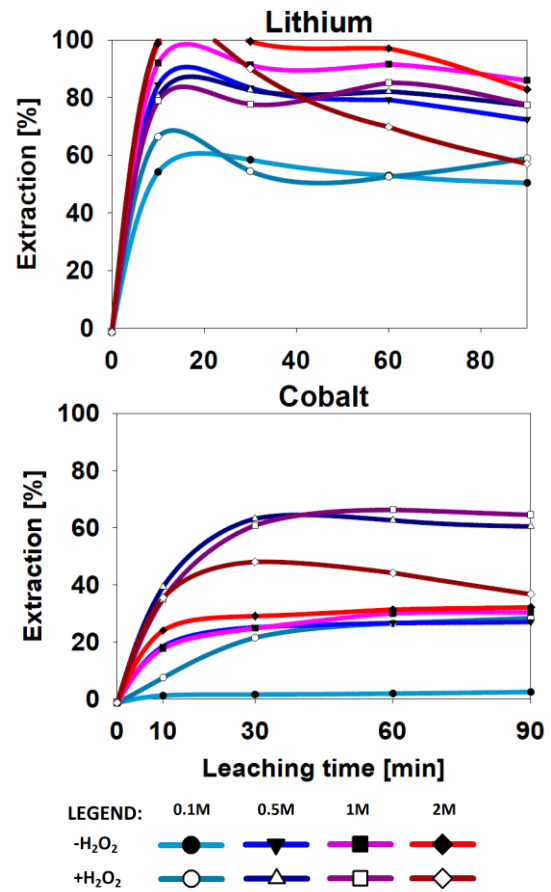


Figure 3 Leaching efficiency of lithium (top) and cobalt (bottom) in time at 80°C with 4 different concentrations of H₂SO₄

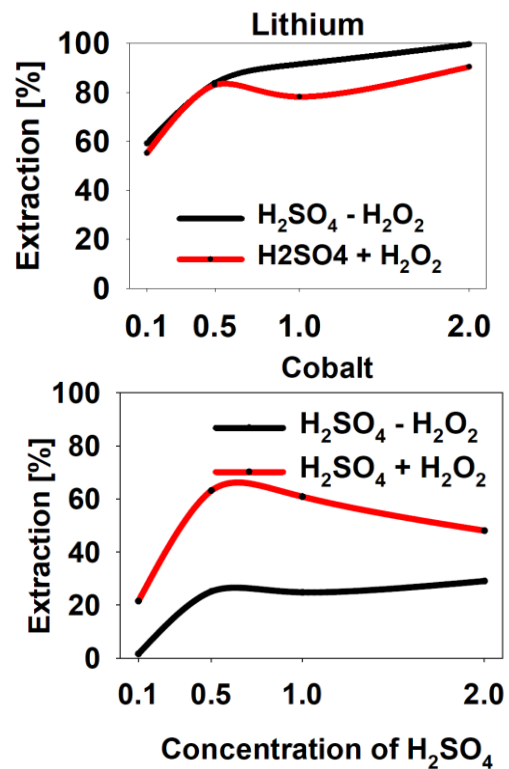


Figure 4 Sulfuric acid concentration dependence on the leaching efficiency of lithium (top) and cobalt (bottom) at 80°C after 30 minutes of leaching

IV. CONCLUSION

Lithium battery slag from pyrometallurgical recycling of lithium batteries can be also an interesting secondary raw material. Sample used in this study contains up to 13.1% cobalt and other valuable metals such as nickel, copper aluminum, lithium manganese and others. The possibilities of slag leaching in sulfuric acid were investigated in this study. Experiments showed the following:

- Increasing the temperature and concentration of H_2SO_4 increases the leaching efficiency of lithium and cobalt,
- In the leaching experiments at a constant temperature of $80^\circ C$ but with different H_2SO_4 concentrations of 0.1, 0.5, 1 and 2, it was found that a sufficient concentration for cobalt leaching was in the range of 0.5 to 1,
- Furthermore, experiments were performed with 1M H_2SO_4 but at leaching temperatures of 20, 40, 60 and $80^\circ C$.
- Leaching at $80^\circ C$ for 60 minutes with the addition of H_2O_2 gave the highest leaching efficiency of 66.85%.
- The addition of H_2O_2 as an oxidizing agent has a positive effect on the leaching efficiency of cobalt, but lowers the leaching efficiency of the lithium,
- Lithium leaches more rapidly, often reaching a maximum concentration in solution within 10 minutes. In the case of cobalt, this time is 30 minutes and after that the cobalt concentration in the solution increases insignificantly. The exception is leaching at $20^\circ C$ with the addition of H_2O_2 , in which the maximum cobalt in solution is reached after 60 minutes of leaching.
- These facts of different leaching rates and the effect of H_2O_2 allow leaching to take place in 2 stages. In the first stage, the slag would be leached at $40^\circ C$ without H_2O_2 for 10 minutes. Under these conditions, 76.05% lithium but only 6.36% cobalt should be leached.
- The second leaching step would take place at $20^\circ C$ with the addition of H_2O_2 . In this step, cobalt and the remaining lithium should be leached.
- To increase the cobalt leaching efficiency from 60% to 100%, it is necessary to verify repeated leaching of the solid residue in the same medium or to analyze the remaining cobalt phase in the slag and use a more suitable leaching solution.
- In the following study, it is necessary to verify the possibilities of selective leaching of cobalt and lithium, to determine the effect of silicon and calcium in solution on the subsequent recovery of metals in solution and to compare the results with classical hydrometallurgical methods using direct leaching of the active matter.

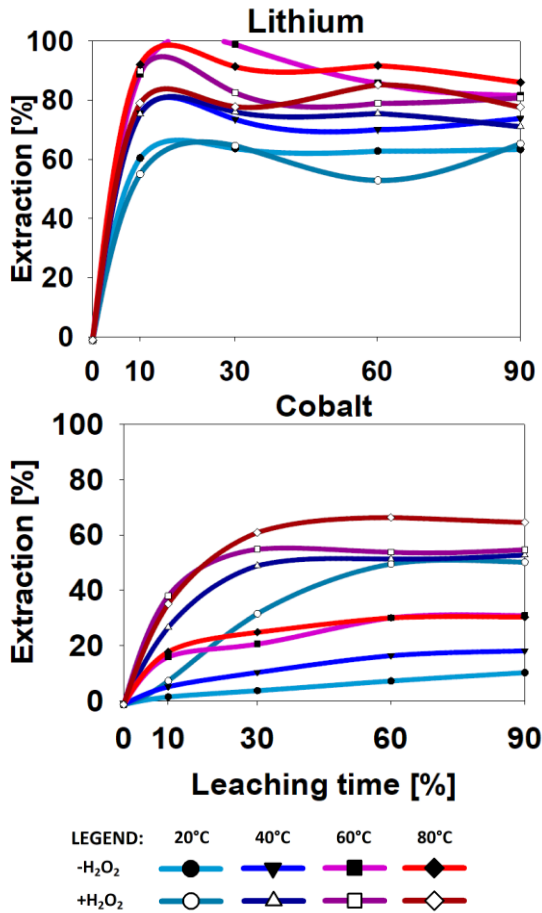


Figure 5 Leaching efficiency of lithium (top) and cobalt (bottom) in 1M H_2SO_4 at different temperatures with and without H_2O_2 .

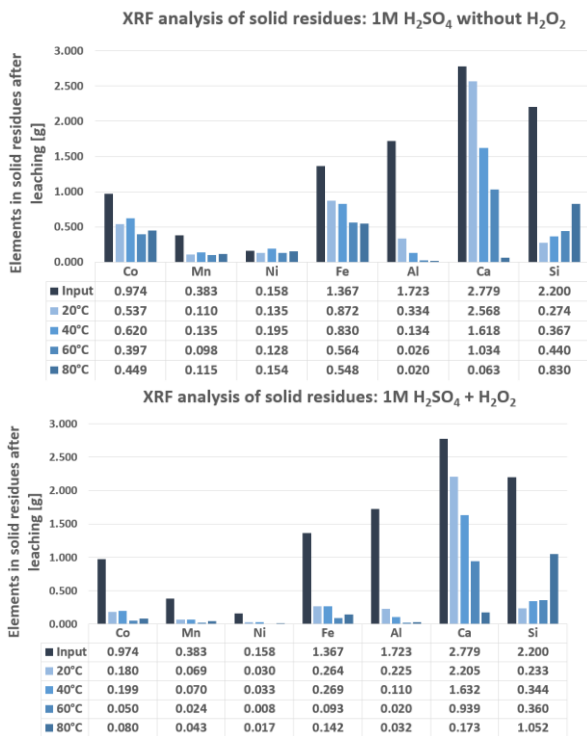


Figure 6 XRF analysis of input sample and solid residues after leaching in 1M H_2SO_4 at different temperatures without H_2O_2 (top) and with addition of H_2O_2 (bottom)

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