

## LITHIUM SLAG LEACH SOLUTION REFINING BY HYDROXIDE PRECIPITATION

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### Abstract

Lithium-ion batteries contain many of critically important metals and their effective recycling is key to the EU's sustainable development. In the past, only metals such as Co, Ni, and Cu were recycled by pyrometallurgy, while Li and Al were concentrated in the slags and not further processed. The novel approach of pyrometallurgical treatment of the black mass offers the possibility of further hydrometallurgical utilization of the slags. This paper examines the refining of the solution obtained by leaching the slag in sulfuric acid. The most valuable element in the leach solution is Li, but it also contains Al, Si, Co, Mn, Ni and Cu, which must be removed before high-purity Li recovery is possible. Purification is achieved by adjusting the pH by adding NaOH. The results confirm that Al and Mn can be removed by 100%, Si by 93.56%, Cu by 86.36% and Cu by 61.75%. The results also confirmed that solution refining by the adding NaOH causes lithium losses ranging from 10% at pH 7 to 28% at pH 12. Therefore, it is suggested that further solution refining methods should be combined before precipitating pure  $\text{Li}_2\text{CO}_3$  with minimal losses.

**Keywords:** Lithium-ion battery; Recycling; Hydrometallurgy; Precipitation; Hydroxide; Lithium hydroxide

### 1. Introduction

The use of new technologies requires variety of different materials, and countries in the European Union (EU) have a particularly high consumption. In order to ensure high demand, in addition to the extraction from primary raw sources by EU countries, it is necessary to import raw materials, which represents a significant risk for our supply chain and sustainable development. Reduction of the material shortage risk is possible through the production from secondary raw materials, which is the main goal of the circular economy implementation into strategic sectors of the EU [1].

Lithium-ion batteries (LIBs) are used in key sectors such as renewable energy, e-mobility, communications, and many others [2]. LIBs function as simple electrochemical rechargeable cells that can be used as a single cell or connected in series or parallel. This makes the batteries suitable for a wide range of applications. From a material point of view, the cells consist of an Al current collector with cathode material layer deposited on the surface (cathode), usually a Cu current collector with a graphite layer (anode), but some LIBs also have Al current collectors, a semi-permeable separator, electrolytes, binders and a casing cover, which is usually made of

Al and plastic composite films [3–5]. Battery packs consisting of several LIBs cells also contain cables, electronics for the battery management system and an additional cover made of plastic, Al or steel. Electrode active material of currently used LIBs are oxide mixtures such as LCO ( $\text{LiCoO}_2$ ), LMO ( $\text{LiMnO}_4$ ), NMC ( $\text{LiNiMnCoO}_2$ ), NCA ( $\text{LiNiAlO}_2$ ), LFP ( $\text{LiFePO}_4$ ) and LTO ( $\text{Li}_2\text{TiO}_3$ ).

Spent LIBs represent important secondary material suitable for recycling, since the EU does not have access to all primary raw material deposits to produce new LIBs and import is unreliable. The limit for recycling of spent LIBs is 50% of their weight, and it is assumed that this limit value will increase in the near future [6]. Success at implementation of circular economy in the EU can be evaluated by end-of-life recycling input rate (EOL-RIR), from which it is known, that recycling of LIBs is not sufficient. Only 10-22% of Cu, Co, Ni and Mn comes from secondary raw sources and EOL-RIR for Li was under 1% in 2020 [7].

LIBs recycling methods can be mechanical, where the focus is on crushing, milling, and sorting, pyrometallurgical, where temperature is evaluated to separate the different phases, and hydrometallurgical, where solvents are used to separate the LIBs materials by selective dissolution and selective recovery from solutions [8–13].

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Mechanical pre-treatment methods in LIBs recycling are used to recover Cu and Al current collectors and black mass, which is intermediate product of recycling containing both anode and cathode materials. Further recycling of black mass needs to use more sophisticated methods, since chemical reactions have to be implemented in order to selectively recover present elements.

Hydrometallurgical treatment offers good selectivity, high purity of the products obtained and also enables the recovery of graphite [14–18], reducing the carbon footprint of the whole process. On the other hand, these methods are sensitive to changes in the chemical composition of the waste input, consume large amounts of chemicals and the total capacity is not sufficient for the amount of LIBs waste generated. Therefore, the more robust pyrometallurgical recycling methods are more suitable for the first stages of LIBs recycling at the current state of the art [19, 20].

Pyrometallurgical methods, such as the direct smelting process, do not require cell level disassembly or intensive mechanical pretreatment, no discharge of the cells and the risk of fire is partially neglected. On the other hand, the carbon present as active anode material cannot be recovered as this material is oxidized to  $\text{CO}_2$ . Careful control of the addition of slag-forming additives causes selective oxidation of the present elements and up to 98.7% of Li, 100% of Al and 98.5% of Mg and 40% of Mn are transferred to the slag and up to 100% of Co, Ni, Cu and 99.8% of Fe are reduced and form the alloy [21]. Further recycling of the metal alloy is possible, but the recycling of slag is currently complicated because the slag-forming additives in hydrometallurgical leaching steps form dense gels in the case of  $\text{SiO}_2$  additive and gypsum in the case of CaO additive, which adsorb metal ions [22]. To prevent gel formation, the dry digestion method is used, which enables the subsequent recovery of lithium from the solutions. Leach solution refining is an essential process to prevent the co-precipitation of impurities with the lithium. During the refining process, lithium losses can occur, which can be up to 30%, depending on the initial concentration of lithium and the concentration of impurities in the solution [23].

The aim of this paper is to study conditions for impurities removal from the leach solution. Hydroxide precipitation is used as refining method and the effect of pH change on impurity removal efficiency and lithium losses is investigated.

## 2. Materials and Methods

### 2.1. Sample preparation

This scientific article builds on the results of the authors' previous research in the processing of black mass using the combined mechanical, pyrometallurgical and hydrometallurgical method. Pellets of lithium-ion battery black mass generated from Accurec Recycling GmbH black mass were processed in the electric arc furnace at the Metallurgical Process Engineering and Metal Recycling – Institute of RWTH Aachen University, Germany with the addition of  $\text{SiO}_2$  used as flux and CuO used to react with excess graphite from pyrolyzed battery black mass [24]. Output of electric arc furnace smelting were Co, Cu alloy and Li-Al slag. Obtained slag was then crushed, sieved and metal particles impurities were separated by magnetic separation. The chemical and phase analysis of slag confirmed high content of Li (6.8%), Al (16.52%), Si (48.62%) and minor content of Co, Cu, Ni and Fe. Phase analysis confirmed  $\text{LiAlSiO}_4$  and  $\text{Li}_2\text{SiO}_3$ . Results of chemical composition before and after pre-treatment of the lithium slag are shown in Table 1.

Obtained Li slag powder was leached in sulfuric acid achieving high Li and Al leaching efficiency, but also high Si leaching efficiency, which caused gelation of solution by oligomerization of orthosilicic acid. Therefore, novel approach of leaching was studied, in which Li slag powder was firstly mixed with concentrated sulfuric acid and small amount of water, which resulted in exothermic reaction and caused silicon from  $\text{LiAlSiO}_4$  and  $\text{Li}_2\text{SiO}_4$  phases to precipitate as insoluble  $\text{SiO}_2$ . After reaction of this dry digestion experiment ended, mixture was dissolved in water. This process maintained high Li and Al leaching efficiency and significantly reduced Si leaching from 50% to 1.25% at optimal conditions [25]. Overall lithium-ion battery process by proposed combined pyrometallurgical and hydrometallurgical method with the aim to recover pure lithium from slags is shown in Figure 1.

Lithium leach solution was obtained by dry digestion and leaching of lithium slag from EAF smelting of black mass pellets with the addition of  $\text{SiO}_2$  and CuO according to process shown in Figure 1. In dry digestion experiment with the duration of 1 hour, 50 g of lithium slag was mixed with 50 ml of concentrated  $\text{H}_2\text{SO}_4$  and 120 ml of deionized  $\text{H}_2\text{O}$ . Another 500 ml of deionized  $\text{H}_2\text{O}$  was added to the mixture and dry digestion and solution was stirred for

**Table 1.** Chemical composition of lithium slag before and after magnetic separation

Sample	Li	Co	Cu	Al	Fe	Si	Ca	Ni	Mn
Li slag [%]	6.80	1.17	1.53	16.52	0.51	48.62	1.16	0.15	0.65
Demetallized Li slag [%]	6.96	0.00	0.11	16.40	0.20	51.10	1.26	0.01	0.88



next 15 minutes at room temperature. Leach solution used for this study was obtained by filtration of solid residues by vacuum filtration.

### 2.2. Analytical Method

The chemical composition of the solutions before and after refining was analyzed by atomic absorption spectrometry using spectrAA20+ spectrometer (Varian, Australia). The pH of the solutions was measured with pH-meter (Inolab, WTW 3710, Germany).

### 2.3. Solution Refining Methodology

Thermodynamic calculations used as background for solution refining were performed by MEDUSA software (Make Equilibrium Diagrams Using Sophisticated Algorithms, 32-bit version 2010, Royal Institute of Technology, Stockholm, Sweden).

Three parallel refining experiments were carried out simultaneously in 200 ml glass beaker with continuous pH measurement and magnetic stirring of 200 rpm. Input material for the experiments was 100 ml of leach solution. 10 ml liquid samples were taken at the beginning of the experiment and after each pH adjustment. The pH value was adjusted from initial 0.48 to 1, 1.5, 2, 2.5, 3, 3.5, 4, 4.5, 5, 6, 7, 8, 9, 11 and 12. For each 10 ml of sample taken, specific amount of 2M NaOH solution was added until next pH value was reached. Remaining volume (until 100 ml mark of glass beaker) was filled with deionized water.

Each sampling and filling up to volume 100 ml resulted in dilution of solution by 10%, which was

taken into account and concentration values in the results were corrected by number of dilutions.

## 3. Results and Discussion

### 3.1. Input Leach Solution Analysis

The results of atomic absorption spectrometry of the input solution obtained by slag leaching are shown in Table 2. Leach solution contains Al and Li in relatively high concentration and Si, Mn, Co, Cu and Ni in minor concentration. Although Al has the highest concentration, the highest value in solution is represented by Li (2367 \$/m<sup>3</sup>). Apart from Al, all other metals in the solution have a negligible value due to their low concentration and therefore we consider them as impurities. Impurities reduce the quality of the obtained Li, and for that reason, they have to be removed from the solution before obtaining Li itself.

### 3.2. Theoretical Study of Precipitation

The aim of this study is to verify solution refining by precipitation of the impurities. Precipitation can be defined as a process where metal ions react with other compounds to form a low solubility product and metal hydroxide precipitation (by addition of NaOH) is the most common example of this process [26].

Reactions 1 – 6 show potential reactions of metal sulfates present in leach solution with NaOH and Table 3 shows the ΔG° values between 20 °C and 80 °C.

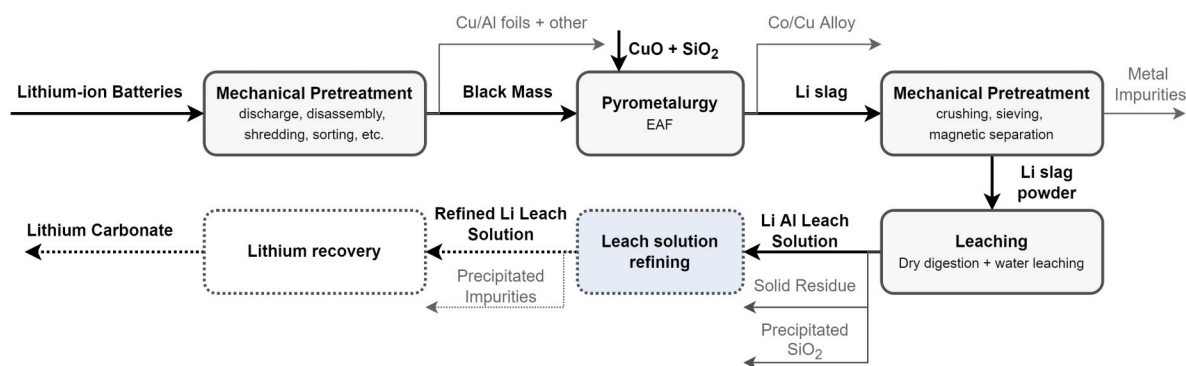
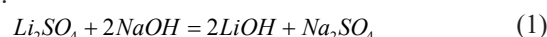
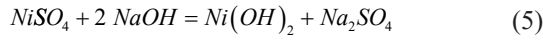
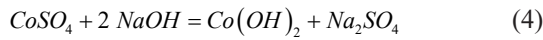
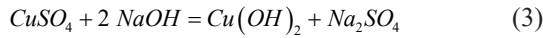
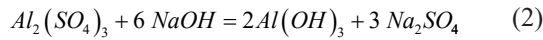


Figure 1. Proposed combined mechanical, pyrometallurgical and hydrometallurgical lithium-ion battery recycling process with the aim of extracting lithium

Table 2. The chemical analysis of the input leach solution and specific material value of individual metal ions in solution

Input Leach Solution	Li	Al	Si	Co	Ni	Cu	Mn
Concentration [µg/ml]	5 606	11 870	244.3	56.0	4.8	17.3	136.2
Molarity [mol/dm <sup>3</sup> ]	0.81	0.44	0.01	0	0	0	0
Molarity [mmol/dm <sup>3</sup> ]	808	439.96	8.7	4.15	0.09	0.31	2.48
Me Theoretical Value [\$/m <sup>3</sup> ]	2 367	27.25	-	2.91	0.10	0.13	4.32





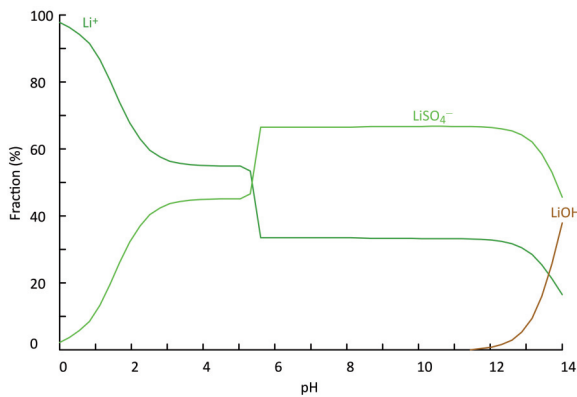
Figures 2-7 shows fraction diagrams of Li, Al, Co, Ni, Cu and Mn respectively. The fraction diagram for Li (Figure 2) shows presence of  $\text{Li}^+$  and  $\text{LiSO}_4^-$  ions in solution at calculated molarity in all pH under 12. According to the diagram, small portion of LiOH should start to precipitate at pH 12. Solubility of

LiOH is 12.8 grams per 100 ml which represents Li concentration of 3699  $\mu\text{g}/\text{mL}$ . Hydroxide precipitation method is not suitable for recovery of Li from solution since Li concentration is only slightly greater than the Li solubility and precipitation occur only at high pH, but removal of impurities from the leach solution should be possible at pH below 12 without loss of Li. Losses of Li may occur due to adsorption on the surface of the precipitated phases, which needs to be verified experimentally.

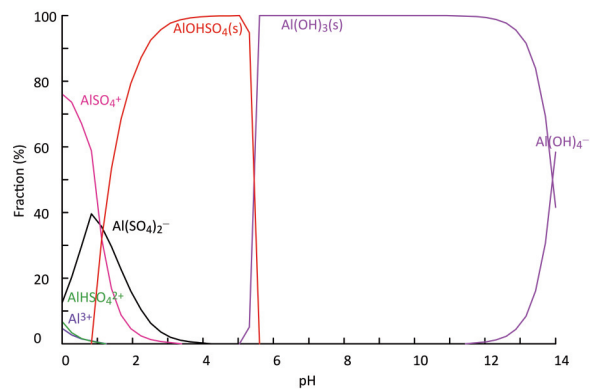
According to the fraction diagrams of Al (Figure 3),  $\text{AlOHSO}_4$  complex, which solubility is unknown, should start to precipitate at pH 1. From pH 5 to 5.5, insoluble  $\text{Al}(\text{OH})_3$  should precipitate. Cu hydroxide should start to precipitate from solution at pH 6 (Figure 4), Co and Ni hydroxides at pH from 8 to 9

**Table 3.**  $\Delta G^\circ$  Values of Hydroxide Precipitation Reactions 1 – 6

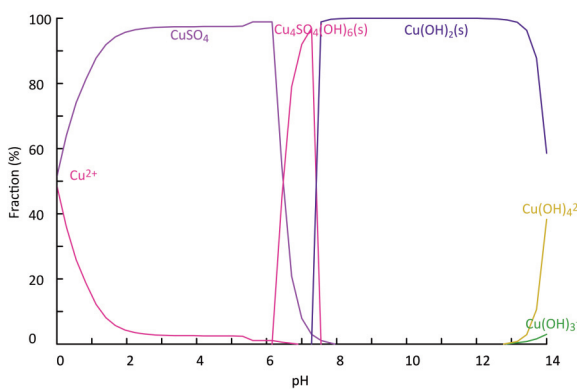
Temp.	$\Delta G^\circ$ [kJ/mol]					
	-1	-2	-3	-4	-5	-6
20 °C	-55.40	-595.81	-201.68	-167.05	-164.97	-147.65
40 °C	-56.33	-610.73	-205.58	-170.72	-169.05	-150.66
60 °C	-57.17	-625.09	-209.32	-174.24	-172.97	-153.52
80 °C	-57.93	-638.91	-212.89	-177.60	-176.73	-156.23



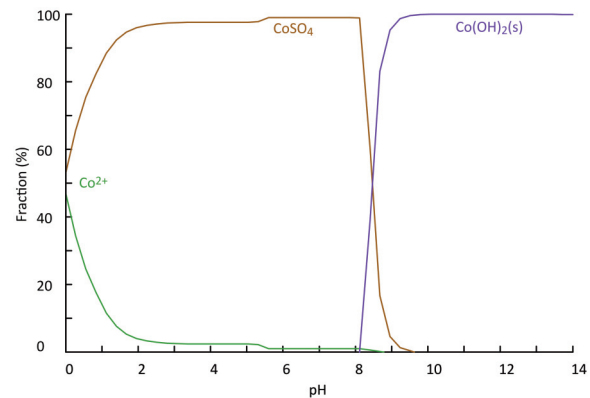
**Figure 2.** Predicted fraction diagram of lithium:  $[\text{Li}] = 808 \text{ mM}$



**Figure 3.** Predicted fraction diagram of aluminum:  $[\text{Al}] = 439.96 \text{ mM}$



**Figure 4.** Predicted fraction diagram of copper:  $[\text{Cu}] = 0.31 \text{ mM}$



**Figure 5.** Predicted fraction diagram of cobalt:  $[\text{Co}] = 4.15 \text{ mM}$



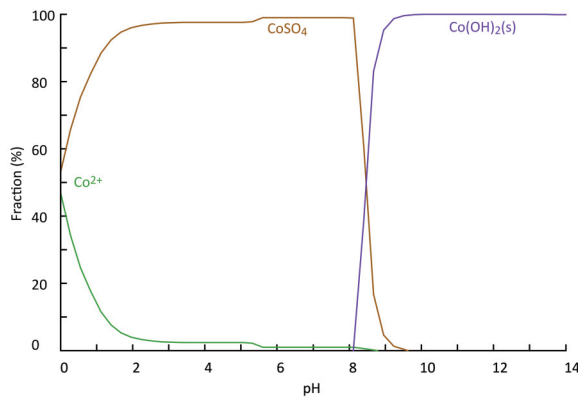


Figure 6. Predicted fraction diagram of nickel:  $[Ni] = 0.09 \text{ mM}$

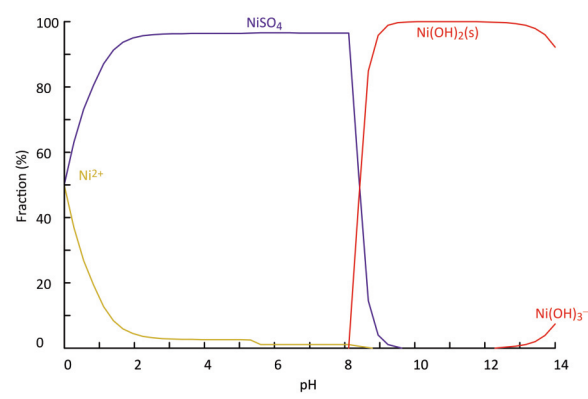


Figure 7. Predicted fraction diagram of manganese:  $[Mn] = 2.48 \text{ mM}$

(Figure 5 and 6) and Mn from pH 10 to 11 (Figure 7).

Figure 8 was constructed from the outputs of the fractional diagrams and the concentration of individual components in the thermodynamic system. Straight lines represent pH range, where metal should be soluble and curves represent pH ranges, where metal solubility is lower than concentration in solution and therefore - precipitation should occur.

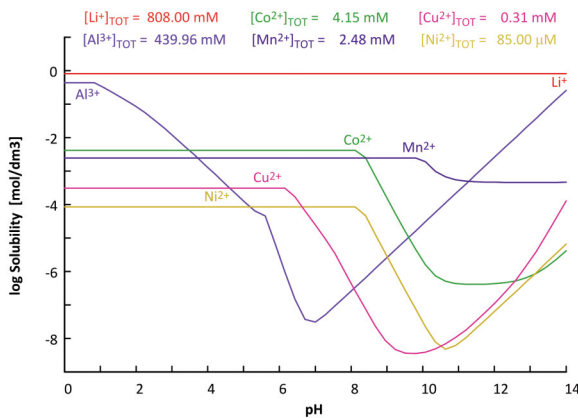


Figure 8. Molar solubility of elements present in lithium slag leach solution as function of pH

### 3.3. Solution Refining Experiment

In this section of the scientific publication, the results of an experiment conducted according to the methodology outlined in Chapter 2.3 are presented. The aim of the experiment was to verify thermodynamic calculations and identify the possibilities of selectively obtaining individual components from solutions by changing the pH through the addition of NaOH. Metals concentration change as function of pH is shown in Figure 9 and changes of concentrations in percentage are shown in Figure 10.

No significant concentration changes of ions were measured between initial pH 0.48 of input Li leach solution and 3.5. The first changes appeared between pH 3.5 and 6, where 99.37% of Al and 85.91% of Si precipitated out of solution. More than 80% of Cu was precipitated out at pH 6. Further increase to pH 7 resulted in precipitation of Co with the 60% efficiency. The concentration of Ni was not changed during the experiments since input concentration was only 15 μg/mL. Mn precipitation was observed above pH 8 and 95.06% efficiency was achieved at pH 9. Precipitated Al, Si and Co phases started to dissolve again at pH above 11.

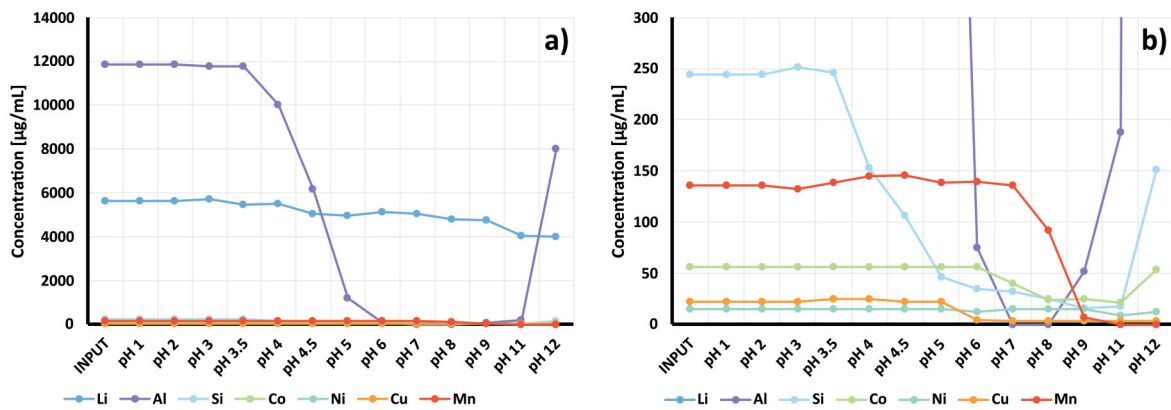


Figure 9. Results of lithium slag leach solution refining by pH adjustment: a) High concentration elements b) low concentration elements



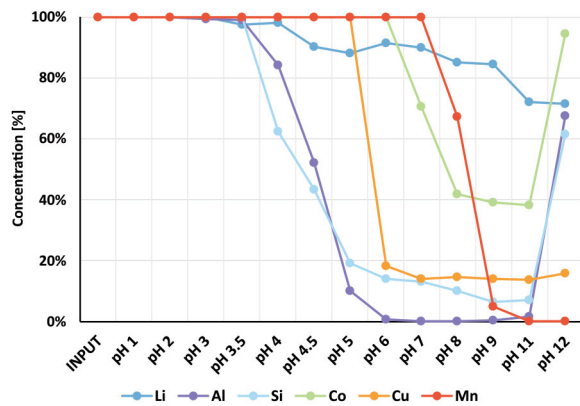


Figure 10. Results of lithium slag leach solution refining expressed in percentages

Figure 11 shows comparison of lithium concentrations and concentrations of all other present impurities and ratio between Li and impurities, and lithium losses. Li losses at pH 6 were between 8-12% at pH 8 and 9 were around 15% and at pH 11 and 12 around 28%. Ratio between Li and impurities increased from 3 to 16 between pH 5 and 6. The maximum ratio of 41 was achieved at pH 9 with concentration of Li 4741  $\mu\text{g/mL}$ , lithium losses 15% and concentration of impurities 116  $\mu\text{g/mL}$ .

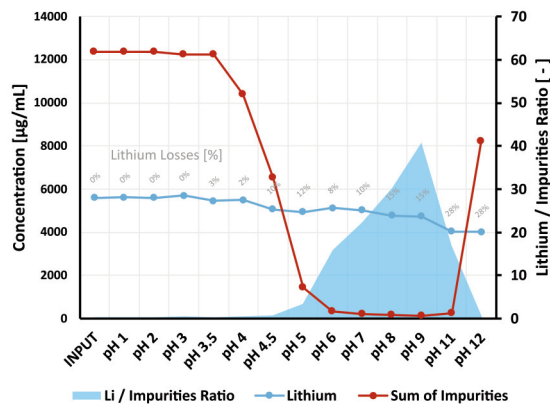


Figure 11. Concentration of lithium compared to the sum of concentration of other present elements (right axis), ratio between lithium and impurities (left axis), and lithium losses at specific pH values

#### 4. Conclusions

Hydroxide precipitation is a simple and effective method for removal of some partially soluble ions from solutions. In this study, hydroxide precipitation was used on LiBs leach solution with the high concentrations of Al (11870  $\mu\text{g/mL}$ ), Li (5606  $\mu\text{g/mL}$ ) and with other elements such as Si, Mn, Co, Cu and Ni in concentrations below 250  $\mu\text{g/mL}$ . The aim was to conduct thermodynamical study of hydroxide precipitation and compare conclusions with the results

of experiments.

Theoretical order of hydroxide precipitation was Al at pH 5-5.5, Cu at pH 6-7, Co and Ni at pH 8-9 and Mn at pH 10-11. The results of the experiments partially coincided with the thermodynamic study, but in some cases, it was possible to observe different intervals of elements precipitation.

Precipitation is suitable for removing the most concentrated Al by adjusting the pH to 7. Si and Cu also precipitate together with Al, at pH 7. Li is partially adsorbed on the surface of the precipitated Al phases, which caused a loss around 10%. At this point, it was proposed to filter the solution and, according to the analysis, the residual leach solution should contain 5034.9  $\mu\text{g/mL}$  of Li, Al, and Cu should be below level of detection, 31.9  $\mu\text{g/mL}$  of Si, 39.5  $\mu\text{g/mL}$  of Co, 14.8  $\mu\text{g/mL}$  of Ni and 136.1  $\mu\text{g/mL}$  of Mn. Ratio between concentration of Li and impurities at current pH 7 was 22.

By further increase of pH from pH 7 above would remove other impurities, but also cause higher Li loss up to 15% at pH 8 and 9 and 27.81% at pH 11 and 12.

Recovery of Li from solution by LiOH precipitation was not suitable for this specific leach solution, since large volume of NaOH solution was required to reach pH above 14. Therefore, it is proposed to combine pH 7 hydroxide precipitation with other more suitable selective solution refining methods to remove other impurities with small concentration below 100  $\mu\text{g/mL}$ .

Recovery of pure Li from refined Li leach solution after hydroxide precipitation followed by second refining method should be possible by precipitation of  $\text{Li}_2\text{CO}_3$ , which is commonly used marketable product for production of new LIBs. This  $\text{Li}_2\text{CO}_3$  precipitation occurs at lower pH values compared to precipitation of LiOH and therefore is considered to be advantageous.

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#### Author Contributions

Conceptualization, J.K., V.M. and D.O.; methodology, J.K., V.M., J.P., T.V., P.L., Z.T. and D.O.; investigation, J.K., V.M., Z.T., T.V., P.L., and D.O.; resources, J.P., T.V., P.L.; writing—original draft preparation, J.K., V.M., Z.T. and D.O.; writing—review and editing, Z.T., P.L. and J.P.; project administration, J.K., D.O. and Z.T. All authors have



read and agreed to the published version of the manuscript.

### Data availability Statement

The data that we used in this study can be requested by contacting the corresponding author.

### Declarations of interest

The authors declare that they have no conflict of interest.

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## RAFINISANJE LITIJUMSKE ŠLJAKE U RASTVORU ZA LUŽENJE POSTUPKOM TALOŽENJA HIDROKSIDA

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### Apstrakt

*Litijum-jonske baterije sadrže mnogo važnih metala, a njihovo efikasno recikliranje ključno je za održivi razvoj EU. U prošlosti su se metali poput Co, Ni i Cu reciklirali pirometalurškim postupcima, dok su Li i Al ostajali koncentrisani u šljaci i nisu dalje obrađivani. Novi pristup pirometalurškom tretmanu crne mase pruža mogućnost dalje hidrometalurške upotrebe šljake. Ovaj rad ispituje prečišćavanje rastvora dobijenog luženjem šljake sumpornom kiselinom. Najvredniji element u rastvoru za luženje je Li, ali on sadrži i Al, Si, Co, Mn, Ni i Cu, koji moraju biti uklonjeni pre mogućeg izdvajanja Li visoke čistoće. Pročišćavanje se postiže podešavanjem pH vrednosti dodavanjem NaOH. Rezultati potvrđuju da se Al i Mn mogu ukloniti 100%, Si 93.56%, Cu 86.36% i Cu 61.75%. Rezultati takođe potvrđuju da prečišćavanje rastvora dodavanjem NaOH uzrokuje gubitke litijuma od 10% pri pH vrednosti 7 do 28% pri pH vrednosti 12. Stoga se predlaže da se dalji metodi prečišćavanja rastvora kombinuju pre taloženja čistog  $\text{Li}_2\text{CO}_3$  s minimalnim gubicima.*

**Ključne reči:** Litijum-jonska baterija; Recikliranje; Hidrometalurgija; Taloženje; Hidroksid; Litijum hidroksid

