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RECYCLING OF THE SLAG FROM LITHIUM BATTERY RECYCLING

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Abstract

This study investigates the recycling of lithium-ion batteries, focusing on combined pyrometallurgical and hydrometallurgical methods. Pyrometallurgical techniques are effective for processing large volumes of waste, while subsequent hydrometallurgical treatment of slags face challenges due to high silicon leaching. The introduction of the dry digestion method, combining powdery slags with concentrated sulphuric acid and water, addresses this issue by reducing silicon leaching from 50% to 1.25%. This approach improves the recovery efficiency of lithium and aluminium and enhances the practicality of hydrometallurgical recycling, supporting more effective material recovery and contributing to circular economy goals.

Keywords: *recycling; lithium ion batteries; pyrometallurgy; hydrometallurgy; leaching*

1. INTRODUCTION

The development of new technologies is transforming industries in the EU, with sustainability and sustainable development becoming increasingly important topics. One aspect of sustainability is the use of energy resources, where the consumption of oil and natural gas is gradually being replaced, and there is a push to increase the share of electricity usage and its production from renewable sources. The storage of electrical energy is essential, and various technologies are being considered, including battery storage, pumped hydro storage, thermal storage, mechanical storage, and hydrogen storage. While pumped hydro storage still holds the largest capacity, battery storage, particularly lithium-ion batteries, has become one of the most popular methods. This is due to its versatility, scalability, and rapid response to fluctuations in electricity demand.

2. LITIUM BATTERIES

Lithium-ion batteries (LIBs) operate on the principle of electrochemical cells, consisting of electrodes, most commonly from Cu and Al thin metal foil, electrolyte, active material layer on the surface of the cathode, graphite on the surface of the anode, and a separator. These cells are packaged into different shapes based on requirements, such as prismatic, pouch or cylindrical. When used in larger applications, such as electric vehicles, individual cells are connected parallel or in the series into modules, and multiple modules, along with a battery management system, form a battery pack [1].

The active material is produced by combining various compounds, with the most common being: LCO ($LiCoO_2$), LMO ($LiMn_2O_4$), NMC ($LiNiMnCoO_2$), LFP ($LiFePO_4$), NCA ($LiNiCoAlO_2$), LTO ($Li_4Ti_5O_{12}$), and others [1]. Currently, new alternative batteries are emerging such as solid-state batteries with higher energy density and sodium-ion batteries offering lower capacity but also lower cost [2], [3]. From a materials perspective, batteries are demanding in terms of production, and many of the mentioned materials are considered critically important for the economy and sustainable development of the EU [4].

The extraction of these materials from the primary sources in the EU may be insufficient, and their import poses a risk for the sustainable development in the event of supply disruptions. A sustainable approach to mitigating the risk of supply shortages is to integrate the recycling of end-of-life lithium batteries into a circular economy model [5].

3. LITHIUM BATTERY RECYCLING

The recycling of end-of-life lithium batteries is crucial both for recovering valuable secondary raw materials and from an environmental standpoint. The recycling technologies must meet criteria such as a minimum of 50 % material recovery from the spent batteries, best available recycling method and others. The first step in recycling involves manual disassembly in the case of large battery packs, discharging, in the case of fire risk, and mechanical pre-treatment aimed at separating the electrode materials and casings from the active material and graphite. The active material, being the most valuable component of spent lithium batteries, is recycled separately.

The options for recycling active materials include hydrometallurgical processing, pyrometallurgical processing, or combined methods. Hydrometallurgical processing offers good selectivity, high purity of the products, and also enables the recovery of graphite, thereby reducing the carbon footprint of the entire process. On the downside, these methods are sensitive to changes in the chemical composition of the input waste, consume large amounts of chemicals, and their overall capacity is insufficient to handle the growing waste stream of spent LIBs. Therefore, more robust pyrometallurgical recycling methods are better suited for the initial stages of LIBs recycling in the current state of technology. These processes include the thermal disintegration of cells, calcination, pyrolysis, smelting and others.

Thermal decomposition involves heating the material, causing the disintegration of the cells structure, which facilitates easier processing in subsequent recycling steps. Calcination is used to remove volatile substances from the material at high temperatures, preparing metal oxides for further extraction. Combustion removes carbon and organic components from the batteries, reducing the waste volume. Pyrolysis is a thermal process that occurs in the absence of oxygen, breaking down organic compounds and facilitating the separation of active materials from the metal electrode parts. Sintering in the presence of salts converts the active material compounds into soluble salts, enhancing the efficiency of subsequent leaching processes. Smelting involves the reduction of metals at high temperatures, concentrating the metallic components in the melt, while the slag contains oxides such as lithium and aluminium.

While there are not sufficient capacities of pure hydrometallurgical treatment of spent LIBs, it is possible to use robust pyrometallurgical methods, followed by hydrometallurgical processing of the resulting slag. An example of a combined processing method is shown in the diagram in Figure 1.

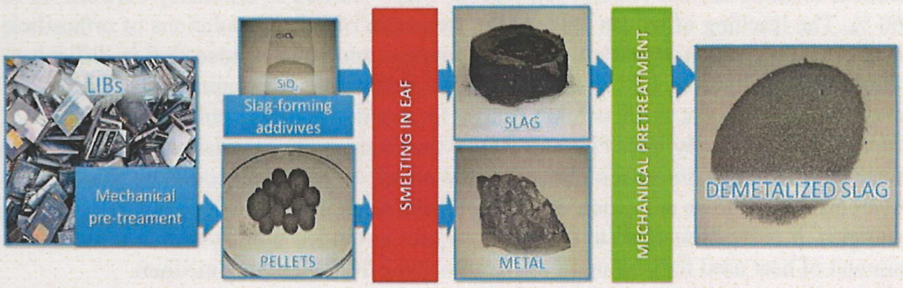

Figure 1. *Combined mechanical and pyrometallurgical method of end-of-life battery treatment with the aim to obtain the slag*

4. LITHIUM SLAG RECYCLING

The slag produced after pyrometallurgical processing is crushed for further hydrometallurgical treatment, with magnetic separation used to remove alloy remnants. The slag after magnetic separation is rich in Li, Al, and slag-forming additives, as confirmed by the chemical analysis shown in Table 1.

Table 1. *Chemical composition of the slag is shown in table 1*

[%]	Li	Co	Cu	Al	Fe	Si	Ca	Ni	Mn
Slag	6	1,17	1,53	14,32	0,51	48,62	1,16	0,15	0,65
Demetalized slag	6,08	0,18	0,33	13,86	0,18	50,38	1,22	0	0,74

The fine powdery demetalized slag material is suitable for leaching in standard inorganic acids, with sulfuric acid being able to achive a high leaching efficiency of the present metals. The leaching results of lithium, aluminum, and silicon are shown in Figure 2.

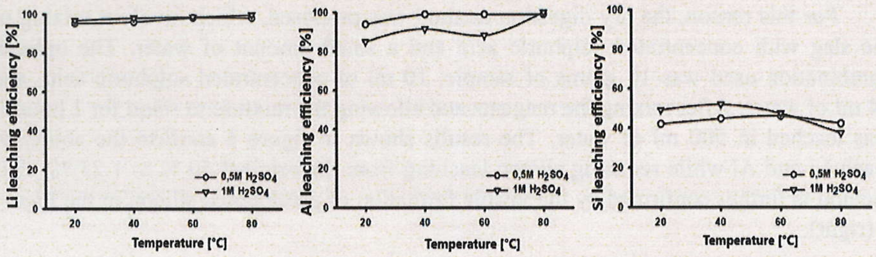

Figure 2. *Leaching efficiency of lithium, aluminium and silicon after 30 minutes of leaching in 0,5 and 1 molar H_2SO_4 at ambient temperature*

The analysis of the obtained leachates shows that 1M H_2SO_4 can leach out most of the lithium and aluminium into the solution, however, during the decomposition of lithium aluminosilicates ($LiAlSiO_4$), silicon is also leached at efficiency between 40 to 60 %. The leaching of silicon leads to the formation of gel-like solutions of orthosilicic acid (H_4SiO_4), which create a mixture of solution and solid residue that is difficult to filter, making hydrometallurgical processing impossible. Measurements of activation energies revealed that the activation energy for reactions during standard leaching is 25 kJ, which is relatively low. Figure 3 shows thermodynamic calculations to prevent the formation of orthosilicic acid by precipitation of SiO_2 which could be possible by overcoming unknown activation energies of these reactions. To achieve higher activation energies, it is recommended to supply more heat to the leaching system and reduce the amount of heat used for heating of the large volume of the leaching medium.

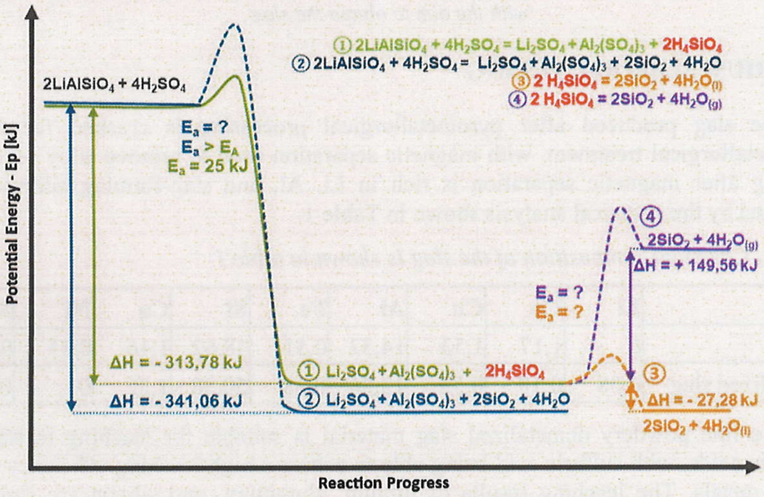

Figure 3. *Theory of gel formation prevention by precipitation of* SiO_2

For this reason, the dry digestion method was proposed, which involves mixing of the slag with concentrated sulphuric acid and a small amount of water. The optimal combination used was 10 grams of sample, 10 ml of concentrated sulphuric acid, and 24 ml of water. After mixing the reagents and allowing the mixture to stand for 1 hour, it was leached in 500 ml of water. The results shown in figure 4 confirm the ability to leach Li and Al while reducing silicon leaching from the original 50 % to 1.25 %. This method is further confirmed by the visible formation of precipitated silicon in the Figure 4 (right).

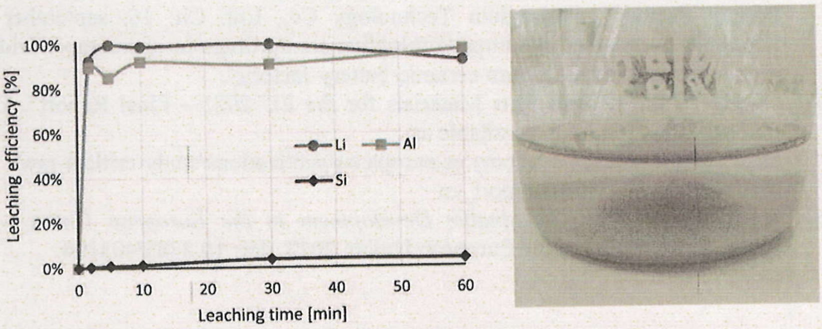

Figure 4. *Results of dry digestion leaching (left) and precipitation of SiO_2 (right)*

5. CONCLUSION

The recycling of lithium-ion batteries is critical for recovering valuable raw materials and reducing environmental impact. Both hydrometallurgical and pyrometallurgical methods offer viable options for processing, with pyrometallurgical techniques proving more robust for handling larger waste volumes, followed by hydrometallurgical treatment of slag. A significant challenge lies in the leaching of silicon, which forms difficult-to-filter gel-like mixtures. To address this, the dry digestion method has been developed, effectively reducing silicon leaching from 50% to 1.25% by promoting the precipitation of amorphous silicon. This approach not only improves the efficiency of lithium and aluminium recovery but also enhances the feasibility of hydrometallurgical processes by minimizing silicon-related complications. The results published in this paper are part of the scientific publication Klimko J. et al.: A Combined Pyro- and Hydrometallurgical Approach to Recycle Pyrolyzed Lithium-Ion Battery Black Mass Part 2: Lithium Recovery from Li Enriched Slag—Thermodynamic Study, Kinetic Study, and Dry Digestion, *Metals* 2020, *10*(11), 1558.

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