Mechanochemical Leaching of Lithium from Battery Slags: Balancing Recovery and Processability

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Abstract. This work, conducted within the DFG Priority Program SPP 2315, investigates mechanochemical leaching as an approach for lithium recovery from engineered artificial minerals derived from synthetic battery slag. Different leaching strategies combining comminution and chemical treatment are evaluated, including stirred media milling, basket milling, and ultrasonic-assisted systems. Mechanical activation enhances lithium extraction by increasing surface area, inducing structural disorder, and improving mass transport. However, conditions that maximise lithium yield simultaneously promote the formation of gel-like structures, which severely impair processability by increasing viscosity and preventing solid–liquid separation. The influence of particle size, energy input, acid type, and chemical environment is systematically analysed. Sulfuric acid provides the highest lithium yields, particularly under combined mechanochemical activation and ultrasonication, but also induces pronounced gel formation. The addition of citric acid enables suppression of gel formation by maintaining pH < 2 and complexing dissolved gangue ions, resulting in both high lithium recovery (up to 91.6%) and stable slurry behaviour.

1. Introduction

The recovery of critical raw materials, particularly lithium, from secondary resources has gained increasing importance in recent years [1]. Engineered artificial minerals (EnAMs), derived from synthetic battery slags, represent a promising feedstock due to their defined composition and the presence of concentrated lithium-bearing mineral phases [2].

Mechanochemical leaching combines comminution and chemical dissolution in a single process step and has been shown to enhance reaction kinetics through increased surface area and structural activation [3]. However, the simultaneous dissolution of gangue phases introduces significant challenges with respect to processability. A major limitation is the formation of gel-like structures during leaching, which originate from the polymerisation of dissolved silica species. These gels lead to a significant increase in slurry viscosity and ultimately prevent solid–liquid separation, thereby limiting the applicability of the process [4].

2. Materials and methods

2.1. Leaching strategies

Different leaching strategies were investigated to assess the influence of mechanical and chemical process parameters on lithium recovery and slurry behaviour. Experiments were conducted under stirred conditions as a reference and under combined conditions including ultrasonication and mechanochemical activation.

Mechanochemical activation was carried out in a stirred media mill (SMM) (NETZSCH LabStar Alpha®Lab) at a stirrer tip speed of 9 m/s. A basket mill (BM) (TORUSMILL® TML) was used for simultaneous comminution and leaching under ultrasonic treatment at 3000 rpm. In both systems, the grinding media filling degree was 80% using 1 mm SiLibeads® Type ZY 6.0 yttria-stabilised zirconia beads. Ultrasonication (US) was applied with an ultrasonic probe.

Various leaching agents were evaluated, with focus on sulfuric acid (H_2SO_4) and citric acid. Temperature, ultrasonic intensity, milling duration, and additives were systematically varied.

The solid–liquid ratio was 10% and the acid concentration 1 mol/L for all experiments. All tests were performed using the same pre-comminuted battery slag (S6) with a median particle size of $x_{50,3} \approx 49$ µm. The phase composition is given in Table 1.

Table 1. Phase composition of battery slag (S6)

Mineral phase	Chemical formula	Mass fraction (wt%)
Lithium aluminate	$LiAlO_2$	8.4
Eucryptite	$LiAlSiO_4$	8.9
Gehlenite	$Ca_2Al_2SiO_7$	30.9
Lithium manganese silicate	Li_2MnSiO_4	14.9
Mn–Al spinel	–	35.8
Quartz	SiO_2	1.0

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2.2. Analytical methods

During the leaching experiments, samples were taken at defined time intervals. The particle size distribution was determined by laser diffraction using a Mastersizer 3000 (Malvern Panalytical). The pH value was monitored continuously throughout the experiments. Lithium concentrations in the filtrate were analysed by inductively coupled plasma optical emission spectroscopy (ICP-OES) using an iCAP 6000 series instrument (Thermo Fisher Scientific). This approach enables a direct correlation between particle properties, chemical conditions, and lithium recovery.

3. Results and discussion

3.1 Effect of Process Parameters on Lithium Recovery

The yield $Y(X)$ was calculated according to Eq. (1), where β represents the concentration of ion X in the volume of the liquid phase V_{Solvent}, while m_{Slag} and $w_{\text{Slag}}(X)$ denote the slag mass and the mass fraction of element X in the slag, respectively.

$$Y(X) = \frac{\beta(X) \cdot V_{\text{Solvent}}}{m_{\text{Slag}} \cdot w_{\text{Slag}}(X)} \quad (1)$$

Sulfuric acid provides significantly higher lithium recovery than other investigated acids. This behaviour can be attributed to its ability to maintain low pH values due to its two-proton donation, as well as to the precipitation of calcium sulfate, which reduces solution saturation and thereby enhances the dissolution of valuable ions. Accordingly, the following results focus on sulfuric acid as the primary leaching agent.

Figure 1 shows the lithium and aluminium recovery obtained under different leaching conditions. The investigated process configurations include stirred conditions (Stirring), stirred media milling (SMM), basket milling (BM), and ultrasonication (US). All experiments were conducted using sulfuric acid, with selected experiments including citric acid as an additive.

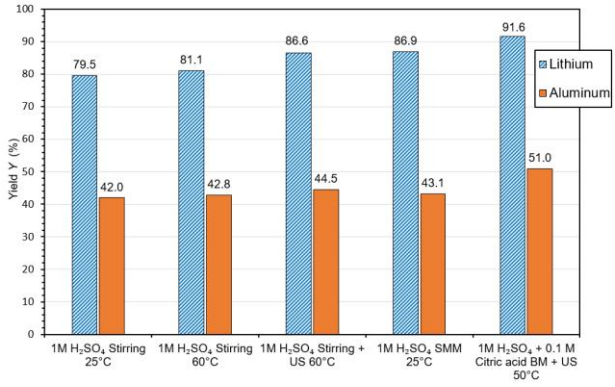

Figure 1. Lithium and aluminium recovery for different leaching conditions using sulfuric acid. Citric acid was added in selected experiments.

As shown in Figure 1, temperature has only a minor influence on lithium recovery. Increasing the temperature from 25 °C to 60 °C under stirred conditions results in only a slight increase in yield from 79.5% to 81.1%, indicating a negligible effect on extraction performance.

In contrast, the application of ultrasonication leads to a noticeable increase in lithium recovery, from 81.1% to 86.6%, which can be attributed to cavitation effects enhancing mass transport and promoting mineral dissolution through localised pressure and temperature fluctuations [5].

Mechanochemical activation in the stirred media mill further increases lithium recovery to 86.9%, due to continuous particle size reduction, increased specific surface area, and the generation of structural defects.

The highest lithium recovery of 91.6% is achieved in the basket mill, where comminution and ultrasonication are combined, highlighting the strong synergistic effect of mechanical and ultrasonic activation. The addition of citric acid in this system enables stable operation and is discussed in detail in the following section.

3.2 Gel Formation and its Impact on Processability

A critical process limitation was identified in the form of gel formation, which occurs during extended milling and leaching. As shown in Figure 2, particle size measurements reveal a drastic increase in apparent particle size after approximately one hour of processing, indicating the onset of gelation. This phenomenon is irreversible and leads to the formation of highly viscous, gel-like suspensions that prevent further processing, including filtration, and require termination of the experiment. The physical appearance and rheological behaviour of this resulting gel are illustrated in Figure 3.

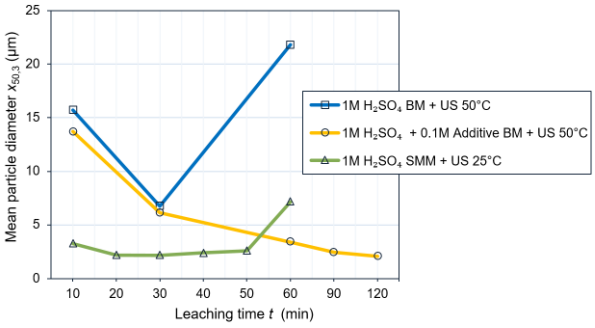

Figure 2. Evolution of mean particle diameter $x_{50,3}$ during leaching under different process conditions. Gel formation is indicated by a sharp increase in particle size, while stable particle size reduction reflects good processability.

Gelation is particularly pronounced for the BM + US system using H_2SO_4, where a sharp increase in particle size is observed after approximately 60 min. This behaviour can be attributed to the elevated temperature of 50 °C, which accelerates gel formation [6]. A similar trend is observed for the SMM + US system, where a gradual increase in particle size begins after about 30 min and becomes more pronounced after 60 min, indicating progressive gel formation.

In contrast, no increase in particle size is observed when citric acid is added to the sulfuric acid system. Instead, the particle size continuously decreases over the

entire leaching period of 120 min, demonstrating the complete suppression of gel formation under these conditions.

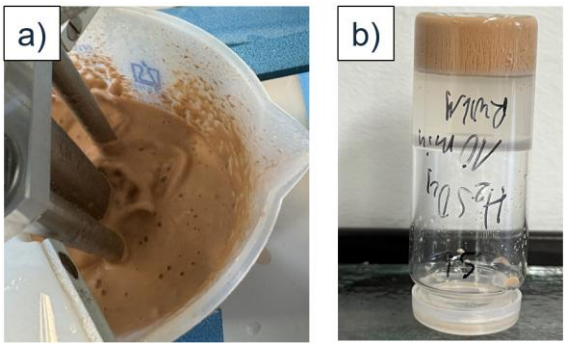

Figure 3. Visual appearance of gel formation during leaching. (a) Highly viscous suspension in the basket mill, resulting in impaired fluid motion and transport within the grinding chamber. (b) Formation of a stable gel network after leaching, preventing flow even when the container is inverted.

The formation of gel-like structures during leaching can be attributed to the polymerisation of dissolved silicic acid species. During acid leaching, silicate phases dissolve and release monomeric silicic acid ($Si(OH)_4$), which subsequently undergoes condensation reactions to form oligomeric and polymeric silica species [6]. These species further aggregate into a three-dimensional network, entrapping liquid and solid particles and ultimately forming a highly viscous gel [6, 7].

This process is strongly influenced by the pH value. Silica exhibits an isoelectric point at approximately pH ≈ 2, where the surface charge of particles approaches zero, minimising electrostatic repulsion and promoting particle aggregation [8]. Consequently, gel formation is favoured when the pH approaches this value.

Mechanochemical activation enhances this effect, as overgrinding increases the dissolution of silicate phases, leading to higher silicic acid concentrations. At the same time, the increased consumption of acid can result in a rise in pH towards the isoelectric point, further promoting aggregation and gel formation.

In addition, dissolved gangue ions such as Al^{3+} and Ca^{2+} promote flocculation and enhance silica polymerisation, further accelerating gel formation [8].

The addition of citric acid effectively suppresses gel formation by maintaining the pH below the isoelectric point and by complexing dissolved metal ions. Citric acid is known to chelate a wide range of divalent and trivalent metal ions, thereby reducing their reactivity and interaction with silica species [9]. This reduces flocculation and stabilises the suspension, preventing gel formation even during extended processing.

The evolution of pH during leaching confirms the importance of maintaining sufficiently low pH values. As shown in Figure 4, significant differences in pH behaviour are observed depending on the applied process conditions.

In the stirred H_2SO_4 system, the pH increases gradually but remains below the critical value of pH ≈ 2 over extended leaching times, indicating limited acid consumption due to the absence of intensive comminution. This explains the absence of gelation in stirred beaker conditions.

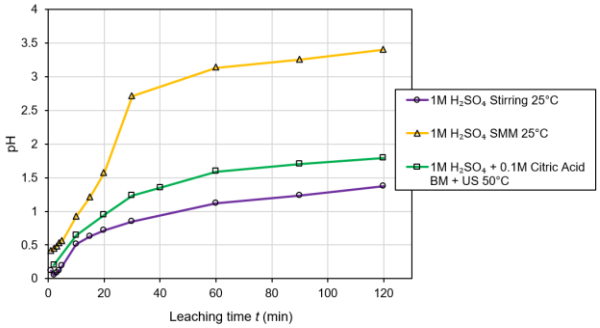

Figure 4. Evolution of pH during leaching under different process conditions. Mechanochemical activation leads to a rapid increase in pH, while the addition of citric acid stabilises the pH below the isoelectric point of silica.

In contrast, mechanochemical activation in the stirred media mill results in a rapid increase in pH. The pH exceeds a value of 2 within the first 30 minutes and reaches values above 3 after 60 minutes, indicating strong acid consumption caused by enhanced dissolution of mineral phases. This behaviour directly correlates with the onset of gel formation observed in Figure 2.

When citric acid is added, the pH remains below 2 throughout the entire leaching period. This stabilisation can be attributed to the buffering capacity of citric acid as well as the complexation of dissolved metal ions, which together suppress silica polymerisation and prevent gel formation.

These observations are in excellent agreement with the proposed gelation mechanism, highlighting the critical role of pH control in maintaining processability.

4. Conclusions

The results demonstrate that mechanochemical activation significantly enhances lithium recovery, particularly when combined with ultrasonication. However, it should be noted that the feed material was already relatively fine ($x_{50,3} \approx 49$ µm), and lithium-bearing phases were largely liberated. As a result, the overall improvement potential was limited, while more pronounced effects can be expected for coarser feed materials, where liberation is progressively achieved during comminution.

Processability is strongly limited by gel formation, which is induced by the dissolution of silicate phases and subsequent silica polymerisation. The experiments show that gel formation is governed by the interplay of pH, mechanical energy input, and temperature. Overgrinding increases acid consumption, thereby shifting the pH towards or above the isoelectric point of silica, which in turn promotes aggregation and gel formation. In addition, elevated temperatures further accelerate these processes and should therefore be avoided.

The addition of citric acid proved to be an effective strategy to suppress gel formation by stabilising the pH below the isoelectric point and by complexing dissolved

metal ions, thus maintaining processability even under intensive processing conditions.

Overall, the results highlight that efficient lithium recovery from engineered battery slags requires a careful balance between mechanical activation and controlled chemical conditions.

Acknowledgement

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