# Innovative approach to lithium extraction: Integrating COOL+ process with sustainable solid waste management

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Lithium is a strategic and indispensable material for future technologies where the demand for Li-ion batteries is constantly increasing (Martin et al. 2017), (Pavón et al. 2021b). Extracting Li from primary sources is challenging since it does not occur in an elementary state but either as a trace element in a firmly bound structure in the form of $\alpha$-spodumene, $LiAlSi_2O_6$, which is the most economically exploitable lithium-bearing mineral and is widely used for the extraction of such key metal (Abdullah et al. 2019), (Nazir et al. 2022). While most processes deal with lithium extraction from primary sources using environmentally inconceivable chemicals, such as $H_2SO_4$, HF, HCl, and NaOH (Dessemond et al. 2020), (Gao et al. 2022), the COOL+ process (**$CO_2$ l**eaching process) uses water and $CO_2$ to selective leach Li from any silicate mineral. This approach is an environmentally friendly route to battery-grade $Li_2CO_3$ with a zero-waste principle because the silicate residue can be used for geopolymer production (Kaiser et al. 2021). The entire process is shown in *Figure 1*. Furthermore, the advantage of this process is that battery grade $Li_2CO_3$ can be obtained regardless of the feedstock used (primary or secondary - black mass). For instance, > 96 % of Li recovery was reached from black mass according to (Mende et al. 2023).

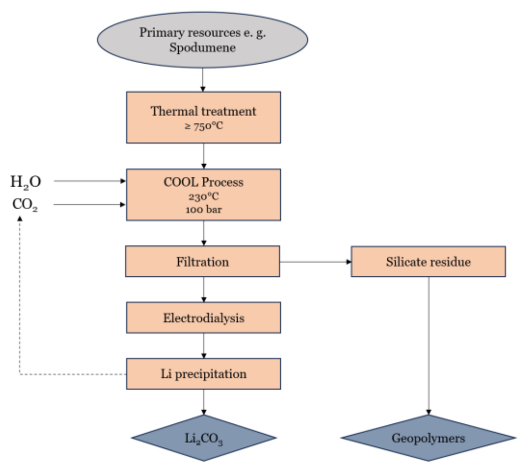


***Figure 1.*** Process flow of the COOL+ process. (Mende et al. 2023; Kaiser et al. 2021; Martin et al. 2017; Pavón et al. 2021a)

METALLICO project aims to extract critical battery metals from primary and tailing materials through the development of cost-efficient processes. Hence, the COOL+ process provides a possible solution for the lithium production from local minerals and, considering the geographical boundaries, contributing to secure the material base in Europe by reducing the import dependency.

In this work, spodumene was mixed with different concentrations of $Na_2CO_3$ to improve Li leaching. In calcination process, $Na_2CO_3$ enhances lithium extraction by forming water soluble compounds to improve leaching of Li during COOL+ process, enhancing $Li_2CO_3$ precipitation in the process. It also increases kinetics of reaction lading to faster and more efficient extraction of Li. The homogeneous mixture with a particle size ≤ 250 µm was calcinated at 750 °C for 2 hours. The leaching using supercritical $CO_2$ was conducted in a high-pressure reactor for 3 hours at 100 bar and 230 °C. The solid residue was dried after filtration step and used for geopolymer production. Further processing consists of concentrating the lithium species by electrodialysis and final precipitation of $Li_2CO_3$ in battery grade. The calcinated solid mixture and solid residue after COOL+ process was analyzed by XRD to investigate the phase transformation and quantitative analysis. The leaching solution was analyzed by ICP-OES and AAS to determine Li and other element' recovery rate.

During the calcination process, a new phase occurred, nepheline, whose concentration increases with the increase of $Na_2CO_3$ concentration in the mixture, making the silicate residue that contains nepheline and albite a valid resource for geopolymer production. The use of geopolymers as construction materials, high-performance binders, waste stabilization and immobilization, 3D printing, insulating materials, and glass and ceramics production, makes them a very important product in the entire process cycle. The results show an increase in Li recovery proportionally to the amount of $Na_2CO_3$ with a maximum Li yield of 60 % using 30 wt.% of $Na_2CO_3$. However, further increase of $Na_2CO_3$ in the mixture leads to a Li recovery decrease. With further optimization of the process (decreasing the particle size, l/s ratio and time of the reaction), it is possible to achieve more than 80 % of Li recovery. Regarding the solid residue obtained after the $CO_2$ leaching, it can be confirmed that it is a valuable resource for the geopolymer production since, during the calcination process, a new phase, nepheline, occurred whose concentration increases proportionally with the increase in $Na_2CO_3$ concentration of the mixture.

It is evident that the COOL+ process enables the Li extraction from spodumene and similar minerals, such as lepidolite, petalite and zinnwaldite, and can be included in the circular economy due to the zero-waste principle (Bertau und Martin 2019). Solid residue as a generated waste, which is rich in aluminosilicates (albite and nepheline), can be used for geopolymer production.

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