

Lithium Recovery from Spodumene via Calcium Chloride-Assisted Roasting

J. Almeida¹, F. Pedrosa¹, M.J. Plancha¹, A. Gonçalves¹, C. Nogueira¹

¹Laboratório Nacional de Energia e Geologia, I. P. (LNEG), Campus do Lumiar, 1649-038 Lisboa, Portugal

Keywords: Critical Raw Material, Decarbonization, Recovery Process, Thermal Treatment.

Presenting author email: joana.almeida@lneg.pt

In 2024, total energy-related CO₂ emissions increased by 0.8% compared with the previous year, reaching a record of 37.8 Gt CO₂. The transportation sector accounts for approximately one-third of global greenhouse gas emissions, where electrification is expected to play a crucial role in mitigation. Electric vehicles (EV) alone avoided 80 Mt of CO₂ emissions during the past year, highlighting the environmental benefits of transitioning to electric mobility (International Energy Agency, 2025). In this context, lithium (Li) is a key element in the global energy transition, primarily due to its use in EV battery components. However, Li is classified as critical raw material in the EU list due to its economic relevance and supply risk (European Commission, 2024). Ensuring that Li production is reliable and sufficient to meet the growing demand for modern technologies is essential for achieving long-term reductions in global CO₂ emissions.

Conventional Li recovery from Li-bearing ores relies on metallurgical methods that consume high amounts of energy, with processing temperatures reaching up to 1100 °C, contributing to CO₂ emissions increase. These processes also generate co-products and solid waste, such as silicates and metal sulphates, which require additional purification steps, increasing both complexity and cost. The use of sulfuric acid (H₂SO₄) for ore digestion introduces further challenges, including corrosiveness, the need for frequent equipment maintenance and the release of harmful gases. From an environmental perspective, these operations may contribute to air pollution, acidification and wastewater generation.

These concerns have leveraged the development of more sustainable Li recovery techniques. Recent studies have identified calcium chloride (CaCl₂) as a promising alternative pathway. CaCl₂-assisted thermal treatment has demonstrated high Li extraction efficiencies across diverse Li-bearing resources, including α - and β -spodumene, spent Li-ion batteries and clay-rich materials, with reported yields ranging from 90% to 99% under temperatures between 700 °C and 1000 °C and reaction times of 60–120 minutes (Barbosa et al., 2015; Braga et al., 2020; Fosu et al., 2022). For battery waste, Li recovery up to 99% has been reported under 700 °C for 60 min, combining CaCl₂ and carbon black (González et al., 2022). Subsequent leaching (Li solubilization in aqueous media) typically employs water at low solid-to-liquid ratios and temperatures below 100°C, corroborating the simplicity and effectiveness of this approach (Dang et al., 2020; Ran et al., 2024).

Regarding spodumene, the use of CaCl₂ in the roasting step decreases the α - to β -spodumene transformation temperature, reducing energy consumption while breaking the mineral's crystalline structure to turn Li more available for leaching steps. This method achieves Li recovery rates comparable to conventional calcination, without generating SO_x emissions, minimizing the need for gas-treatment systems. CaCl₂ preferentially reacts with spodumene, limiting the dissolution of impurities (e.g., Fe, Mg, Al) and, due to its lower corrosiveness compared to H₂SO₄, reduces equipment maintenance and associated costs.

Despite these advantages, CaCl₂-assisted roasting faces challenges due to operating temperatures (that remain above the desired range), and the large salt-to-concentrate ratio often required. Combining mechanical activation (high-energy milling) with CaCl₂ roasting has been proposed to lower the phase-transition temperature, resulting in Li extraction up to 90%. However, although a mechanical activation duration of approximately 3 hours yields the highest extraction efficiency, such prolonged milling also involves high energy demand (Ni et al., 2024).

The present study aimed to optimize Li extraction from spodumene using CaCl₂ roasting alone and combined with mechanical activation. Experimental tests were conducted on spodumene concentrate (3.2% Li) to evaluate processing parameters including concentrate/CaCl₂ stoichiometry, temperature, reaction time, and hydration conditions. The solid samples were also characterized by X-ray diffraction, particle size analysis and specific surface area measurements, to further investigate the behavior and potential changes in the crystal structure in response to variations in the operating conditions. The results demonstrated that up to 90% of Li could be extracted from spodumene, highlighting CaCl₂ roasting and mechanical activation potential as an environmentally friendly alternative to conventional methods.

Acknowledgments: This paper is a result of the Innovation Pact “NGS – New Generation Storage” (C644936001-00000045) by the “NGS” consortium, cofinanced by NextGeneration EU, through the Incentive System – “Agendas for Business Innovation”, within the Recovery and Resilience Plan (PRR).

References

- Barbosa, L.I., González, J.A., Del Carmen Ruiz, M., 2015. Extraction of lithium from β -spodumene using chlorination roasting with calcium chloride. *Thermochim Acta* 605, 63–67. <https://doi.org/10.1016/J.TCA.2015.02.009>
- Braga, P.F.A., França, S.C.A., Pinto, C.P., Rosales, G.D., 2020. Recovery of lithium from spodumene by chlorination roasting. IMPC 2020: XXX International Mineral Processing Congress, Cape Town, South Africa, 18-22 October 2020 18–22.
- Dang, H., Li, N., Chang, Z., Wang, B., Zhan, Y., Wu, X., Liu, W., Ali, S., Li, H., Guo, J., Li, W., Zhou, H., Sun, C., 2020. Lithium leaching via calcium chloride roasting from simulated pyrometallurgical slag of spent lithium-ion battery. *Sep Purif Technol* 233, 116025. <https://doi.org/10.1016/J.SEPPUR.2019.116025>
- European Commission, 2024. Regulation (EU) 2024/1252 of the European Parliament and of the Council of 11 April 2024 establishing a framework for ensuring a secure and sustainable supply of critical raw materials and amending Regulations (EU) No 168/2013, (EU) 2018/858, (EU) 2018/1724 and (EU) 2019/1020. Brussels.
- Fosu, A.Y., Kanari, N., Bartier, D., Vaughan, J., Chagnes, A., 2022. Novel extraction route of lithium from α -spodumene by dry chlorination. *RSC Adv* 12, 21468–21481. <https://doi.org/10.1039/D2RA03233C>
- González, Y.C., Alcaraz, L., Alguacil, F.J., González, J., Barbosa, L., López, F.A., 2022. Study of the Carbochlorination Process with CaCl_2 and Water Leaching for the Extraction of Lithium from Spent Lithium-Ion Batteries. *Batteries* 2023 9, 12. <https://doi.org/10.3390/BATTERIES9010012>
- International Energy Agency, 2025. Global Energy Review 2025.
- Ni, C., Liu, C., Liu, J., Wang, J., Liang, Y., Sun, W., Zhong, H., He, Z., 2024. Thermochemically driven crystal phase transfer via mechanical activation-assisted chlorination roasting toward the selective extraction of lithium from spodumene. *J Indust Eng Chem* 138, 632–640. <https://doi.org/10.1016/J.JIEC.2024.05.022>
- Ran, Y., Qu, G., Yang, J., Zhou, S., Li, B., Wang, H., Wei, Y., 2024. Efficient separation and extraction of lithium from low-grade claystone by chloride salt-enhanced roasting process. *J Clean Prod* 434, 140156. <https://doi.org/10.1016/J.JCLEPRO.2023.140156>