

LITHIUM EXTRACTION FROM α -SPODUMENE BY HYDROALKALINE TREATMENT: RECENT PROGRESS AND OUTSTANDING CONSIDERATIONS

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ABSTRACT

Over the last five years, several hydrometallurgical processes have emerged to extract lithium from α -spodumene, by digesting this mineral with solutions of concentrated NaOH or KOH, 20 – 50 %, at temperatures between 250 and 300 °C, under pressure to contain the reacting systems, for residence time of 4 to 24 h, with or without a CaO dopant [1-5]. These processes aim to decarbonise the refining of lithium, by avoiding the decrepitation (phase inversion) of α -spodumene to β -spodumene. The decrepitation constitutes the most energy intensive step in processing of α -spodumene to lithium chemicals in the Chinese and the nascent Australian refineries. The application of CaO, either to induce a more effective decomposition of α -spodumene or to precipitate silicon-based impurities from the leachate, represents the key technological advancement of the new processes.

While the hydroalkaline digestion yields high Li recovery of ca 90 %, examination of literature indicates enlarged requirements for feedstock chemicals, increased by-product streams for disposal and more contaminated pregnant liquor solutions for downstream separation and purification. The processes comprise up to three pH swing operations, including the original hydroalkaline digestion step, acid dissolution of precipitated lithium species, followed by the removal of impurities that requires switching back to basic pH. Although analogies exist with the Bayer process for refining bauxite to alumina, there are also important differences, including slower kinetics and elevated silica to alumina ratios, which make Li refining more complicated and challenging than that of alumina. The hydroalkaline processes work by the dissolution-precipitation reactions, rather than by the ion exchange mechanism, which defines the leaching of β -spodumene with strong acids. Recycling streams cannot be avoided as they serve to recover the unreacted hydroxides and to intercept part of extracted Li, which departs to the aqueous phase in the digestion treatment. Thus, it appears that the hydroalkaline processes need to overcome important practical hurdles prior to being able to challenge the established position of the sulphuric acid digestion in the refining industry and the rising popularity of the analcime-type operations [6,7]; the latter involving the pressure leach of β -spodumene with solutions of Na₂CO₃ or NaCl, with straightforward purification to battery grade LiOH·H₂O or Li₂CO₃.

From these perspectives, this contribution examines the main aspects of the new processes, including

- (i) formation of aqueous and solid species arising in digestion reactions
- (ii) feedstock and by-product intensity
- (iii) digestion kinetics
- (iv) type and removal of impurities
- (v) effect of recycling of aqueous streams on energy demands, as well as
- (vi) Li recoveries in comparison with those of the sulfuric-acid and analcime operations.

- [1] Song Y, Zhao T, He L, Zhao Z, Liu X. 2019. A promising approach for directly extracting lithium from α -spodumene by alkaline digestion and precipitation of phosphate. *Hydrometallurgy* 189, 10514.
- [2] Qiu S, Liu C, Yu J. 2022. Conversion from α -spodumene to intermediate products Li₂SiO₃ by hydrothermal alkaline treatment in the lithium extraction process. *Minerals Engineering* 183, 107599.
- [3] Qiu S, Zhu Y, Jiang Y, Liu C, Yu J. 2022. Kinetics and mechanism of lithium extraction from α -spodumene in potassium hydroxide solution. *Industrial and Engineering Chemistry Research* 61, 15103-15113.
- [4] Napier A, Griffith C. 2021. Caustic Conversion Process, US Patent 20210180155A1.
- [5] Xing P, Wang C, Zeng L, Ma B, Wang L, Chen Y, Yang, C. 2019. Lithium extraction and hydroxysodalite zeolite synthesis by hydrothermal conversion of α -spodumene. *ACS Sustainable Chemistry & Engineering* 7, 9498-9505.
- [6] Tiihonen M, Haavanlammi L, Kinnunen S, Kolehmainen E. 2020. Outotec lithium hydroxide process – a progress update. ALTA 2020 Uranium-REE-Lithium Conference. Perth, Australia.
- [7] Alhadad M F, Oskierski H C, Chischi J, Senanayake G, Dlugogorski B Z. 2023. Lithium extraction from β -spodumene: A comparison of keatite and analcime processes. *Hydrometallurgy* 215, 105985.

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