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Lithium extraction from natural brines and salars – thermodynamic modeling of electrolytic systems and the evaporative sequences

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The recovery of minerals from saline waters has been practiced since the antiquity and salt is still of great value for man needs and technological developments. Seawater contains large quantities of valuable minerals, some of them being very scarce and expensive in their land-based form. Brines from salted lakes, salars, oil and geothermal reservoirs contain high concentrations of valuable metals (i.e., Li, Zn, Cu, Zn, Mg, K, Br, B, REE, etc.). Brine mining is becoming an attractive option mainly because of the depletion of high-grade ores exploited by land-based mining industries. However, up to now, only few minerals are mined from natural brines. Among the numerous valuable elements issued from natural brines, the lithium is one of the most attractive. Indeed, large amounts of lithium are found in the salars of the Altiplanos in South America, mostly in Chile, Argentina and Bolivia. Many other sources of lithium exist in saline lakes, geothermal and oil brines in other countries.

Regardless of the sources and geochemical cycle of lithium in hydrogeological systems, an understanding of its thermodynamic properties and its geochemical behavior is a prerequisite for its exploration, extraction and exploitation. Indeed, it can reach abnormally high concentrations in aqueous solutions due to the very high solubility of the lithium salts. Comprehensive and consistent thermodynamic models are then needed to accurately predict lithium aqueous chemistry (like speciation) and associated lithium mineral solubilities in highly saline waters. The development of such approach is a prerequisite for developing and optimizing extraction processes.

Numerical simulations of the thermodynamic properties of the brines and salt solubilities allow establishing the specific evaporation sequence and estimating the amounts of valuable precipitated solids (LiCl, Li₂CO₃, etc.) to be recovered from the exploited brines taking into account the salinity of the brine, the exploitation conditions (temperature, evaporation rate, etc.). This allows identifying the family of minerals and their maximal precipitable amounts depending on the rate of its precipitation and the reaction paths constrained by some internal loops. A global overview of the state of the art will be presented with some challenges for Lithium extraction from salars.