

Removal of calcium and magnesium from lithium brine concentrate via continuous counter-current solvent extraction



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ABSTRACT

In this research project, a process for purifying Li brine concentrate with a typical composition of Li 30 g/L, Ca 1.36 g/L, Mg 0.049 g/L via solvent extraction was studied. The goal was to remove Ca to below 20 mg/L and Mg to the ppm level while keeping the co-extraction of Li below 10%. Laboratory-scale batch experiments showed that conventional cation-exchange reagents D2EHPA and Versatic 10 could be used for the task in pH ranges of 3.5–4.0 and 6.5–8.0, respectively. Of these reagents, Versatic 10 had better selectivity for the target metals and better phase disengagement properties, while D2EHPA had a higher capacity. However, with either of these reagents, the organic phase cannot be loaded to a very high extent, because Ca, which has the highest affinity, then replaces Mg.

The effect of the operating parameters (pH, temperature, phase ratio, and residence time) were studied in a bench-scale two-stage continuous counter-current setup with both reagents. The overall performance was good, yielding ppm impurity levels in terms of Ca and Mg and, typically, 3–5% Li co-extraction. While the Mg extraction could be increased by increasing the pH in the mixers and decreasing the A/O phase ratio, the Li co-extraction would also be increased. A compromise must be made between purity and Li yield. Decreasing the temperature or residence time did not have a significant effect on performance. It was demonstrated that a high throughput can be achieved because a mixer residence time of 2 min or even less can be used.

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1. Introduction

The demand for lithium is expected to increase almost 4-fold from 2011 to 2025, mainly due to its use in batteries, especially those used in electric vehicles (Cabeza et al., 2015). According to a Mineral Commodity Summaries report (United States Geological Survey, 2015) 31% of Li is used in batteries, with other uses including, for example, glass and ceramics, greases, rubbers, and the pharmaceutical industry (Meshram et al., 2014).

Brines are the most important Li source, and most of the worldwide reserves are located in brines (21.6 Mt). Pegmatite ores contain 3.9 Mt of Li and other types of primary raw materials 5.4 Mt. Also, the recovery of Li from the brines is easier and more economical than recovery from other sources (Kesler et al., 2012; Meshram et al., 2014). The recycling rate for Li was reported to be only 3% in 2011 (Talens Peiro et al., 2013).

An et al. (2012) have listed the most important Li-containing brines and their compositions. The brine deposits are located in South America,

China, the USA, Israel, and India. The main component is NaCl (Na content 4.7–11 wt.%), Li content is 0.001–0.16 wt.%, and the minor elements and compounds of varying concentrations include K (0.2–2.4 wt.%), B (0.003–0.071 wt.%), Mg (0.003–3.09 wt.%), Ca (0.002–3.9 wt.%), and SO_4^{2-} (0.061–50 wt.%). The most significant of these impurities is Mg because Mg and Li are not easily separated due to their similar chemical natures. Thus, only those brines with low Mg/Li ratios are used industrially for Li production (Liu et al., 2014).

According to Garrett (2004), the basic process for recovering Li from brines are as follows: 1) solar evaporation, in which a large portion of the other salts (e.g. KCl, NaCl) are removed; 2) precipitation of impurities (B, sulfate, and Mg); and 3) precipitation of Li with soda ash. The drawbacks of the described method are that the recovery of Li is only 50% and that especially Mg makes the process unfavorable (Intaranont et al., 2014). An et al. (2012) have suggested an alternative process for brines having high Mg concentrations and some sulfate. Most of the Mg and Ca are precipitated with lime, B is adsorbed, and residual Ca and Mg are precipitated as oxalates. After these steps, evaporation and polishing purification (not described more closely) are still needed before Li_2CO_3 precipitation. Two patents by Boryta et al. (2002, 2010)

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suggest the use of conventional cation exchangers to purify the brine solutions after the Ca and Mg precipitation steps. Bukowsky et al. (1991) used chelating resins to remove Ca and Mg from the brine, and Nishihama et al. (2011) purified the brine of divalent metals with a strong cation exchanger. For the B removal step, solvent extraction with some alcohol is suggested (Brown and Boryta, 1993). However, in these conventional processes, the removal efficiency, especially that for Mg, in the final purification is not very high, and the Li losses are typically ten percent or higher.

The conventional precipitation purification containing processes are only able to produce Li_2CO_3 of 99.0–99.5% purity (An et al., 2012; Moreno, 2013), which is suitable for ceramic applications, but, for example, in production of the Li-ion batteries, over 99.9% pure Li_2CO_3 is needed. Solvent extraction is known to produce high purity raffinates in many cases but purification of Li-rich brine with solvent extraction has received surprisingly little attention. The only research article is by Bukowsky et al. (1992). In that paper, D2EHPA was successfully used for the task, and the discussion was mainly regarding the equilibrium data for Ca.

In this work the above described known challenges (Li purity and losses) in the Li brine concentrate purification are studied by solvent extraction. In addition to Ca removal presented in the paper by Bukowsky et al. (1992), emphasis is also in the typical challenge of Mg removal. The performance of the suggested purification process step is also studied in bench-scale continuous counter-current experiments in mixer-settlers to demonstrate the applicability of the suggested flowsheet in industrial type equipment. The goal was to reduce the Ca and Mg concentrations from ca. 1.3 g/L and 50 mg/L, respectively, to under 20 mg/L or desirably to the ppm level if possible while having significantly lower Li losses than in conventional precipitation purification. First, a comparison of three types of commercial cation exchangers based on laboratory-scale experiments is presented. Based on these fundamental data, continuous experiments were designed and run to study process dynamics and performance.

2. Experimental

2.1. Materials and reagents

LIX-984 (1:1 mixture of 5-dodecylsalicylaldoxime and 2-hydroxy-5-nonylacetophenone oxime), D2EHPA (di-(2-ethylhexyl)phosphoric acid), and Versatic 10 (neodecanoic acid) were used as solvent extraction reagents, and prior to the experiments, they were analyzed via titrations, and their concentrations in all experiments were 0.50, 0.52, and 0.53 mol/L, respectively. Exxsol D80 (Exxon Mobil) and Shellsol D70 (Shell Chemicals) were used as diluents. Both of these are similar hydrocarbon fluids with very low aromatics content, and they are thus expected to have the same performance in the systems studied. Other chemicals used in the experimental work were: LiCl (supplier VWR International, purity 98%), CaCl_2 (VWR International, 98%), NaCl (VWR International, 98%), $\text{MgCl}_2 \cdot 4.5\text{H}_2\text{O}$ (VWR International, 97%), 37% HCl (Merck KGaA, pro analysi), 65% HNO_3 (Merck KGaA, pro analysi), 25% NH_3 (Merck KGaA, pro analysi), NaOH (VWR International, 98%), and ethanol (Merck KGaA, 99%).

In all the experiments in this work, similar synthetic Li-rich brine solutions prepared with purified water were used as the feed aqueous phase. According to the analyses, their compositions were as follows: Li 26.0–34.0 g/L, Ca 1.17–1.55 g/L, Mg 0.022–0.075 g/L. The total chloride concentration was topped up to 200 g/L with NaCl, and the pH was 7.5. All metal analyses, both from the batch experiments and pilot runs, were carried out from 14% HNO_3 -media using inductively coupled plasma atomic emission spectroscopy (ICP-AES, device: IRIS Intrepid Duo, Thermo Electron Corporation). The organic phase metal concentrations were analyzed after stripping them with 14% HNO_3 (A/O = 10:1).

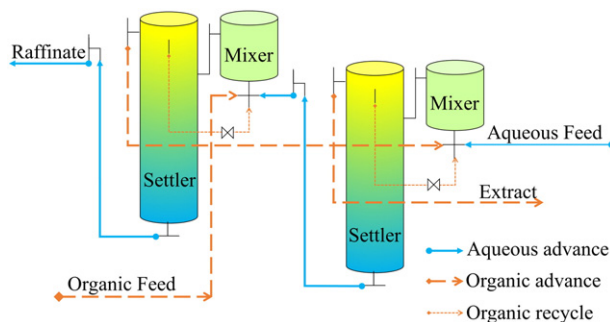


Fig. 1. Continuous counter-current solvent extraction mixer-settler setup for studying the purification of Li-rich brine.

2.2. Equilibrium and kinetic experiments

The effect of pH on the extent of Ca, Mg, and Li extraction from the brines with D2EHPA, Versatic 10, and LIX-984 was studied in a jacketed 1000 mL glass reactor at 23 and 35 °C. The pH of the aqueous phase was

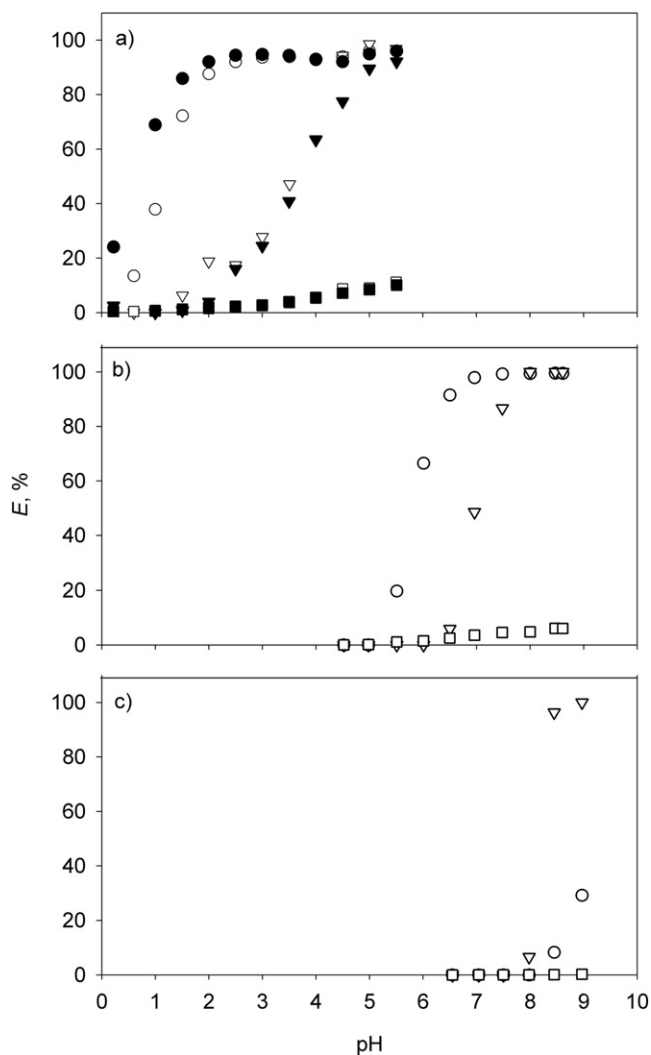


Fig. 2. The dependence of the metal extraction on pH with certain commercial solvent extraction reagents in the purification of Li-rich brine. The initial concentrations of the metals were Li 26.0 g/L, Ca 1.30 g/L, and Mg 0.022 g/L, and reagent concentrations were 0.52, 0.53, and 0.50 mol/L for D2EHPA, Versatic 10 and LIX-984, respectively. a): D2EHPA, b) Versatic 10, and c) LIX-984. Circles Ca, triangles Mg, and squares Li. Open symbols 35 °C, and closed symbols 23 °C.

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