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Recovery of Lithium from Simulated Nanofiltration-Treated Seawater Desalination Brine Using Solvent Extraction and Selective Precipitation

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ABSTRACT

The world's seas and oceans contain vast amounts of lithium, but the low concentration hereof renders solvent extraction impractical for its recovery. By contrast, seawater desalination brine, after treatment by nanofiltration, contains a roughly ten-fold greater concentration of lithium than raw seawater. Hence, lithium can be effectively recovered from such streams using solvent extraction. Compared with other techniques to sequester lithium from dilute solutions, solvent extraction offers the advantages of simple operations, robust and well-established technology and high recovery yields. Thus, we propose a solvent-extraction based process to recover lithium from seawater desalination brine, treated by nanofiltration. The first step comprises the removal of magnesium and calcium using methyltrioctylammonium neodecanoate in *p*-cymene. This is followed by a lithium extraction step using the extractants Mextral 54–100 and Cyanex 923 in Shellsol D70 diluent. The lithium extract is then scrubbed with water and stripped with hydrochloric acid. Subsequently, residual alkaline earth metals are removed with sodium hydroxide in ethanol and finally lithium is precipitated using sodium carbonate. The solvent extraction, scrubbing and stripping steps were demonstrated on mini-pilot scale in continuous countercurrent mode (in mixer-settlers), while the precipitation steps were demonstrated in batch. The process was found to have an overall yield of 74%, affording a lithium carbonate product with a purity of 97 wt%.


KEYWORDS

Hydrometallurgy; solvent extraction; seawater desalination brine; lithium; mixer-settlers

Introduction

Although the concentration of lithium in seawater is low, the sheer volume of salt water present in the world's oceans implies that estimated oceanic reserves of lithium dwarf known continental reserves by a factor of 10^5 , as of 2022.^[1,2] Lithium concentrations vary around 0.1–0.2 ppm, depending on the source of

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the seawater.^[3] While concentrating seawater for the sake of extracting lithium or other minerals may not be economically viable, seawater desalination plants used for freshwater production offer a unique window of opportunity. The waste fraction produced by said plants comprises a concentrated brine, in which the lithium concentration is increased to about 0.3–0.5 ppm.^[4,5] The higher concentration of lithium in brines facilitates its extraction and expands the array of techniques that can be used for its recovery. As such, seawater desalination brine has become a widely considered resource for the recovery of not only lithium, but also sodium, magnesium and calcium salts, and trace minerals.^[5]

Membrane technologies currently constitute the most widely used methods to extract lithium from seawater-derived feeds.^[6,7] Nanofiltration (NF) and electrodialysis are the most common hereof, and allow for continuous operation with good selectivity. These two techniques are similar in the sense that ions are separated by differences in permeability of a membrane, but electrodialysis uses an electric field to drive ion mobility, as opposed to a pressure gradient as used in nanofiltration.^[7] The most performant membranes applied in these processes are cation exchangers, which attain an electrochemical and diffusive (Donnan) equilibrium state with a positive internal potential by exchanging ions with feed solution.^[7] However, other membranes are also effective at excluding larger, highly charged cations from diffusing across the membrane, as a result of surface polarization and steric effects.^[7–9] While nanofiltration is applied at an industrial scale, membrane fouling remains an issue for all membrane technologies, leading to selectivity and permeability loss over time.^[7] Moreover, operating costs are relatively high.^[10,11]

Ion exchange or adsorption is another well-studied techniques to sequester low concentrations of lithium from seawater desalination brines. It offers the promise of a simple, cost-effective solution to the lithium recovery problem. A variety of adsorbents have been studied, including both commercial organic resins and derivatives thereof, and inorganic organic ion exchangers such as manganese oxide, zirconium phosphate and alumina.^[6,12] Ideally, these materials should have both a high capacity and a high selectivity for lithium over other elements present in the brine matrix, and fully reversible desorption. While materials exist in which these conditions are met to a certain extent, the regeneration and long-term stability of adsorbents remains a challenge, especially in a desalination brine matrix.^[5,10]

A number of “battery-based” electrochemical systems have also been described to recover lithium from brine solutions. Their name stems from the fact that cells are used which are nearly identical to lithium-ion batteries, with the brine serving as the electrolyte. During capture, lithium ions move to a cathode made of a lithium-intercalating material. Lithium is stripped by switching the polarity of the electrodes, releasing lithium back into the electrolyte solution.^[10,11] These systems are promising due to their high

selectivity, lithium recovery and reversibility, but upscaling is nontrivial, processing rates are relatively slow and the low capacity of the electrode material implies high material costs.^[10,11]

Because of the vast complexity of the seawater matrix and the low ratio of lithium to other alkali and alkaline earth cations, many of the aforementioned processes only succeed in producing a lithium concentrate, and precipitation is still required to obtain a product of battery-grade purity.^[10,13] Treatment of desalination brine by a single stage of nanofiltration can increase the concentration of lithium in seawater desalination brine by a factor of about 3, yielding lithium concentrations of up to 1.5 ppm, while concurrently removing a significant fraction of the contaminating divalent cations, Ca^{2+} and Mg^{2+} .^[14,15] This brings the lithium concentration into a range in which solvent extraction becomes a practical option. This rapid and simple techniques is widely used in industry to separate metals in more concentrated feeds, affording high product yields at a low cost.^[10]

Many papers have reported on the selective extraction of lithium using systems based on FeCl_3 -loaded tributyl-*n*-phosphate (TBP).^[16–23] Extraction is driven by the complexation of Li^+ by TBP and coordination of chloride to FeCl_3 . Unfortunately, these systems suffer from competitive extraction of Na^+ and are prone to iron losses during stripping, requiring impractical phase ratios in order to minimize said losses.^[19,24] Alternatively, lithium can be extracted by a synergistic system of a β -diketone and a phosphoryl-containing synergist, wherein the β -diketone functions as cation exchanger and synergist serves to saturate the coordination sphere of the extracted Li^+ ions.^[25–30] Unlike the TBP/ FeCl_3 -based systems, the β -diketone/synergist systems are not selective for lithium over the alkaline earth metals, and thus require prior removal of divalent ions. This can be easily achieved using most cation exchangers, as cation exchangers usually extract ions in order of their charge density.^[31]

In this work, we present a flowsheet (Figure 1) for the recovery of lithium from simulated nanofiltration-treated seawater desalination brine, based on solvent extraction and carbonate precipitation. Mg^{2+} and Ca^{2+} are first removed using a basic extractant, methyltrioctylammonium neodecanoate ([A336][V10]), which extracts the alkaline earths as neutral ion pairs and does not require any pH control of the brine.^[32] Lithium is then extracted using Mextral 54–100, a β -diketone extractant, in synergism with Cyanex 923, a commercial mixture of phosphine oxides. After stripping of the organic phase with HCl, the stripping liquor is further purified by precipitation of the remaining alkaline earth ions using sodium hydroxide in ethanol, and lithium is finally selectively precipitated using sodium carbonate. The solvent extraction process was demonstrated on mini-pilot scale using a continuous multi-stage countercurrent mixer-settler setup. The precipitation steps were carried out in batch. The composition of the synthetic feed solution

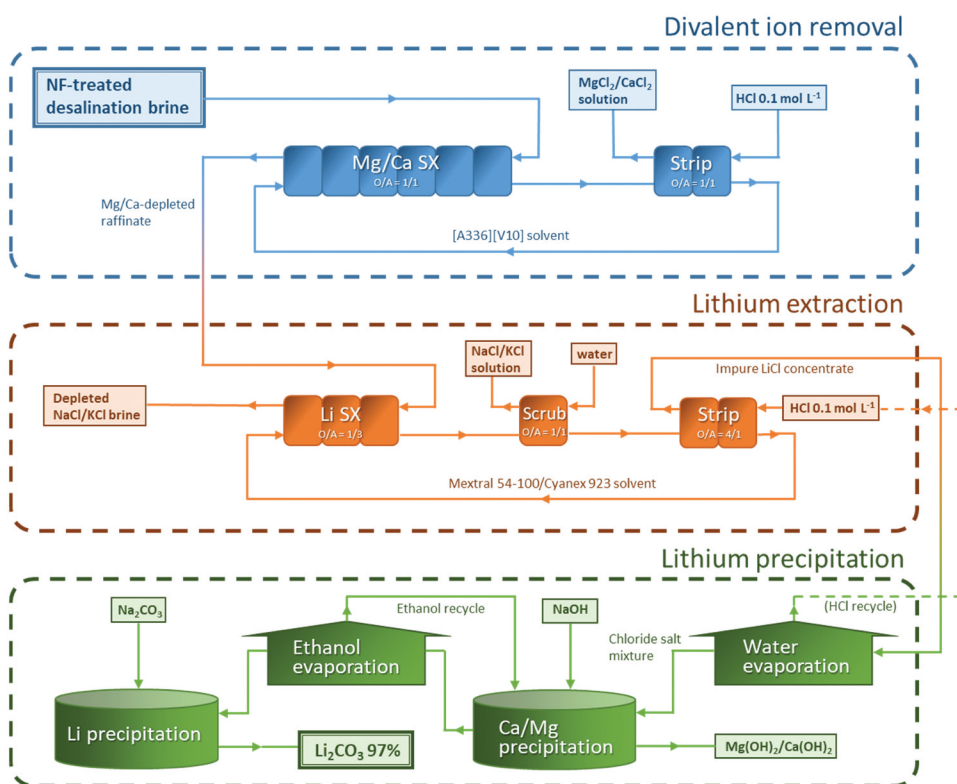


Figure 1. Flowsheet diagram for the proposed process to recover lithium carbonate from nanofiltration-treated seawater desalination brine.

used in this study was based on literature values for nanofiltration-treated seawater desalination brine.^[14,15]

We do not envision this process as a competing technology for state-of-the-art lithium extraction methods from salar brines and spodumene, as the very low concentration of lithium, even in concentrated seawater sources such as desalination brine, imply that the cost per ton of lithium will be significantly higher than for conventionally sourced lithium. However, if state-of-the-art methods can no longer satisfy the global demand for lithium, or if the international supply chain is disrupted due to geopolitical factors, rising lithium prices may render this process economically viable, allowing desalination brines to be used as an alternative source of lithium to meet market demands.

Experimental

Chemicals and reagents

Sodium hydroxide (pearl, analytical reagent grade), sodium chloride (analytical reagent grade), hydrochloric acid (37%, analytical reagent grade) and

absolute ethanol (99.8%, analytical reagent grade) were purchased from Thermo Fisher Scientific (Merelbeke, Belgium). Li, Na, K, Mg and Ca standard solutions for ICP-OES (1000 ppm Plasma HIQU) and for ion chromatography (1000 ppm Ion HIQU), potassium chloride (a.r.) and nitric acid (65%, a.r.) were obtained from Chem-Lab (Zedelgem, Belgium). Sodium carbonate (anhydrous) and calcium chloride dihydrate (AnalR Normapur) were acquired from VWR (Leuven, Belgium). *p*-Cymene (99+%) and Aliquat® 336 TG (~90%) were supplied by Acros Organics (Geel, Belgium). Magnesium chloride hexahydrate (for analysis) and 2,6-pyridinedicarboxylic acid (for ion chromatography) were purchased from Millipore Merck (Overijse, Belgium). Versatic® Acid 10 was provided by Hexion Research VAS B.V. (Louvain-La-Neuve, Belgium). Cyanex® 923 was supplied by Solvay (Brussels, Belgium). Shellsol® D70 was obtained from Shell Chemicals (Gent, Belgium). Mextral® 54–100, an optimized mixture of a β -diketone (as main ingredient), surfactant, modifier, and stabilizer, was purchased from Kopper Chemical Industry Co., Ltd. (Chongqing, China). Water used for dilutions was always of ultrapure quality (18.2 M Ω cm at 298.2 K). All chemicals were used as received, without any further purification.

Solvent extraction

All batch extraction experiments were carried out by contacting appropriate ratios of the aqueous phase with the organic phase in closed 4 mL vials. The vials were shaken at room temperature to equilibrate the phases. For the Mg²⁺/Ca²⁺ extraction experiments, this was carried out at 300 rpm for 30 min using a Kuhner ES-X laboratory shaker. For the Li extraction experiments, a Turbo Thermo TMS-200 was used for 5 min at 2000 rpm. After the extraction, separation of the phases was assisted by centrifugation for 3 min at 3000 rpm (Heraeus Labofuge 200). The aqueous phase was measured using inductively coupled plasma-optical emission spectrometry (ICP-OES) after the proper dilutions were made or ion chromatography (IC). The organic phase concentrations were calculated by means of the mass balance, according to Eq. (1):

$$[M]_{\text{org}} = \frac{V_{\text{aq}}([M]_0 - [M]_{\text{aq}})}{V_{\text{org}}} \quad (1)$$

Where $[M]_{\text{org}}$ represents the concentration of the metal in the organic phase, $[M]_0$ and $[M]_{\text{aq}}$ respectively denote the initial and final aqueous metal concentration, and V_{aq} and V_{org} are the aqueous and organic phase volumes, respectively.

The [A336][V10] extractant for magnesium and calcium removal was prepared according to a procedure reported by Li *et al.*^[32] Stoichiometric quantities of Aliquat® 336 and Versatic® Acid 10 were mixed, and this mixture

was then brought into contact with a freshly prepared 4 mol L⁻¹ NaOH solution in a 1:2 volume phase ratio. The amounts (in moles) added were estimated taking the purity of the commercial products into account. For Aliquat 336, the average molecular mass of 432 g mol⁻¹ and a purity of 97% were used. The following general reaction scheme is applicable for the synthesis:



with R' = CH₃, R = *n*-C₈H₁₇ or *n*-C₁₀H₂₁ and HA denotes Versatic Acid 10.

The mixture was agitated vigorously for 4 hours and subsequently allowed to separate. The organic layer was collected and washed three times with Milli-Q water to remove the remaining chloride ions. An acidified silver nitrate solution was used to test for remaining chloride anions in the washing water. The extractant was saturated with water and diluted to the desired concentration with *p*-cymene prior to use.

The organic phase for Li⁺ extraction was prepared by mixing the identical volumes of Mextral® 54–100 and Cyanex® 923 in ShellSol® D70. The vials were shaken at room temperature and 2000 rpm for 5 min using a laboratory shaker (Turbo Thermo TMS-200). The equilibrium pH (pH_{eq}) was adjusted using 10 mol L⁻¹ NaOH solution. After extraction, phase disengagement was accelerated by centrifuging at 3000 rpm for 2 minutes.

The *distribution ratio* *D* of a metal *M* is defined as:

$$D_M = \frac{[\text{M}]_{\text{org}}}{[\text{M}]_{\text{aq}}} \quad (3)$$

Since only the aqueous phase was analyzed after extraction, Eq. (3) can be rewritten by substituting Eq. (1) for [M]_{org}:

$$D_M = \frac{V_{\text{aq}} \left([\text{M}]_0 - [\text{M}]_{\text{aq}} \right)}{V_{\text{org}} [\text{M}]_{\text{aq}}} \quad (4)$$

The *percentage extraction* (%*E*) is defined as the amount of metal extracted to the organic phase over the initial amount of metal present in the aqueous phase:

$$\%E = \frac{V_{\text{org}} [\text{M}]_{\text{org}}}{V_{\text{aq}} [\text{M}]_0} \times 100 = \frac{[\text{M}]_0 - [\text{M}]_{\text{aq}}}{[\text{M}]_0} \times 100 \quad (5)$$

The separation efficiency between two metals is described by the *separation factor* *α*, which is defined as the ratio of the respective distribution ratios of two extractable solutes, measured under identical conditions:

$$\alpha_{M1,M2} = \frac{D_{M1}}{D_{M2}} \quad (6)$$

where D_{M1} and D_{M2} are the distribution ratios of metal M1 and M2, respectively. By definition, the value of the separation factor is always greater than unity ($D_{M1} > D_{M2}$).

Stripping experiments were carried out in a manner identical to the extraction experiments. The *percentage stripping* (%S) in the stripping phase can be defined as:

$$\%S = \frac{V_{\text{aq}}[M]_{\text{aq}}}{V_{\text{org}}[M]_{\text{org},0}} \times 100 \quad (7)$$

Continuous experiments were performed in Rousselet PTFE lab-scale mixer – settler units of universal type (Model UX 1.1), having a mixer volume of 35 mL, a settler volume of 143 mL and a settler area of 49 cm². One baffle and two coalescence plates were placed in each settler. Peristaltic pumps of type Masterflex® L/S Variable-Speed Digital Drive with Remote I/O (Cole – Palmer) were used to pump the aqueous and organic phases via high density polyethylene plastic tubes. Rotors were operating at 1500 rpm. All operations were conducted in aqueous continuous mode. The mixing and settling chambers were first filled with appropriate quantities of the aqueous and organic phases to match the desired phase ratio. Subsequently, the pumps and stirrers were started. The flow rates were chosen to match the desired phase ratio. During the first 2 hours of operation, the height of the weirs was adjusted to set the phase ratio. The raffinate was periodically sampled from the aqueous outlet and quantitatively analyzed by ICP-OES to monitor the performance of the mixer-settlers.

Precipitation

A mixture of chloride salts was prepared to mimic the residue obtained after evaporation of the lithium stripping liquor, based on the analysis thereof. To this end, a 10 mL aliquot of the stripping solution (0.1 mol L⁻¹ HCl) was evaporated to dryness in a HDPE container by heating to 80°C under a jet of air, to remove all HCl. The residue was redissolved in 10 mL of ultrapure water, and analyzed using IC. Next, weighed quantities of each salt were ground together using a mortar and pestle, to obtain a mixture mimicking evaporated stripping liquor. The effective composition of the mixture was determined by ion chromatography of a solution thereof (996 mg in 100 mL, diluted 20-fold), as the hygroscopic starting materials may contain traces of water.

The precipitation of residual Mg²⁺ and Ca²⁺ was achieved by a following a method published by Avdibegović *et al.*^[33] Three 10 g aliquots of the salt mixture were placed in 50 mL PPE centrifuge tubes. To each sample, 102 mL

of a 845.2 mM NaOH solution in 95% ethanol was added. This corresponds to a 2% molar excess of NaOH with respect to Ca^{2+} and Mg^{2+} . The samples were shaken for 30 minutes at 300 rpm using an orbital shaker (Kuhner Shaker ES-X). Afterwards, the samples were centrifuged for 3 minutes at 5000 rpm in an Eppendorf 5804 centrifuge.

Samples were taken from the supernatant fluids obtained after $\text{Ca}^{2+}/\text{Mg}^{2+}$ precipitation. These were combined into a 500 mL HDPE bottle. The final mixture had a volume of 120 mL. The composition calculated as the weighted average of the constituent solutions. The HDPE bottle was suspended in a water bath set at 60°C. The bottle was placed in the flow of a jet of compressed air to aid in evaporation and prevent aerosols from contaminating the sample. The sample was evaporated to dryness, and the residue was redissolved in 5 mL of ultrapure water. To the resulting solution, 5 mL of a 1.35 mol L⁻¹ solution of Na_2CO_3 was added, which corresponds to a 10% molar excess of carbonate with respect to lithium. The resultant slurry was heated to 60°C in a water bath and filtered over a sintered glass filter (diameter 30 mm, vacuum 200 mbar). The precipitate was further washed with 2 mL of water (60°C).

Elemental analysis

After each extraction, metal concentrations in the aqueous phase were determined by either inductively coupled plasma-optical emission spectroscopy (ICP-OES) or ion chromatography (IC). ICP-OES was used to determine metals with highly disparate concentrations (e.g. 1 ppm Li in 80 000 ppm Na), due to the tolerance of this technique towards high salt concentrations. Ion chromatography was preferred for the analysis of samples in which the concentrations of the analytes were of similar magnitude, because of the absence of ionization effects in IC. In further discussions, ICP-OES is implied to be used unless explicitly stated otherwise. Error bars correspond either to the standard deviation of a triplicate measurement (batch experiments) or the standard deviation on the measured lines in axial and radial mode (continuous experiments).

ICP-OES analyses were carried out on a PerkinElmer Avio 500 spectrometer equipped with GemCone High Solids Nebulizer, baffled cyclonic spray chamber, 2.0 mm inner diameter alumina injector and PerkinElmer Hybrid XLT torch. Due to the low Li^+ and Rb^+ concentration in the aqueous phase (<2 mg L⁻¹) with respect to the matrix, the standard addition method was applied to their analysis. For each sample, 6 different solutions were prepared with a dilution factor of 10 in 2 vol% HNO_3 , five of which were respectively spiked with 0.1, 0.2, 0.3, 0.4 and 0.5 mg L⁻¹ of Li^+ or Rb^+ . The concentration is estimated as shown in Fig. S1 (Supplementary Material). A synthetic Li^+ solution was prepared mimicking the brine solution with concentration of 1.6 ppm and 4 replicates analyzed resulted in the following concentration

values 1.5, 1.7, 1.7 and 1.6 mg L⁻¹ with a standard deviation of 0.1 mg L⁻¹. For the determination of all other elements, an external calibration series was used. Samples from batch experiments were diluted appropriately in HNO₃-solution to obtain concentrations <40 ppm. For the analysis of the aqueous phase in continuous mixer settler tests, a 100-fold or 1000-fold dilution was made, depending on the concentrations of the analytes. The lines reported are 671 nm for Li, 559 nm for Na, 766 nm for K, 285 nm for Mg and 315 nm for Ca. All lines were recorded in axial viewing mode.

Ion chromatography was performed using a Shimadzu IC setup consisting of a CBM-40 system controller, DGU-403 degassing unit, LC-20Ai pump, SIL-20A autosampler, CTO-40C column oven and CDD-10A vp conductivity detector. A Metrohm Metrosep C4 column was used. The eluent consisted of 1.7 mmol L⁻¹ nitric acid and 0.7 mmol L⁻¹ pyridine-2,6-dicarboxylic acid in ultrapure water. The oven temperature was set at 25°C and the flow rate of the eluent was 0.9 mL min⁻¹. Samples were appropriately diluted in ultrapure water, such that the concentrations of the analytes were between 1 and 200 ppm. An external standard series was used for calibration.

Results and discussion

Magnesium/Calcium removal

The first step in the lithium isolation process is the removal of magnesium and calcium from the nanofiltration-treated seawater desalination brine by [A336][V10] diluted in *p*-cymene. This extractant consists of mixture of methyltrialkylammonium salts with neodecanoate counterions. The alkyl substituents on the cation have a length of eight to ten carbon atoms, while the neodecanoate anion may be any of a number of isomeric forms included in commercial Versatic Acid 10. These structures are shown in the Supplementary Material (Fig. S2). Li *et al.* investigated the selective extraction of Mg²⁺ over Li⁺ by this extractant and concluded that the extraction proceeds according to the following scheme, with overbars denoting species in the organic phase^[32]:



Prior to upscaling of this step, the extraction parameters were optimized. To this end, a number of smaller-scale, batch experiments were conducted, using a synthetic feed solution identical to that to be used in the continuous extraction trials. This solution contained 3.1 g L⁻¹ of Mg²⁺, 1.6 mg L⁻¹ of Li⁺, 76 g L⁻¹ of Na⁺, 3 g L⁻¹ of K⁺ and 0.3 g L⁻¹ of Ca²⁺, each added as its chloride salt. These concentrations are based on literature values for nanofiltration-treated seawater desalination brine.^[14] The first parameter to be optimized was the concentration of the extractant, [A336][V10]. The concentration was varied between 0.0 and 1.5 mol L⁻¹ at an organic-to-aqueous phase volume ratio (O/

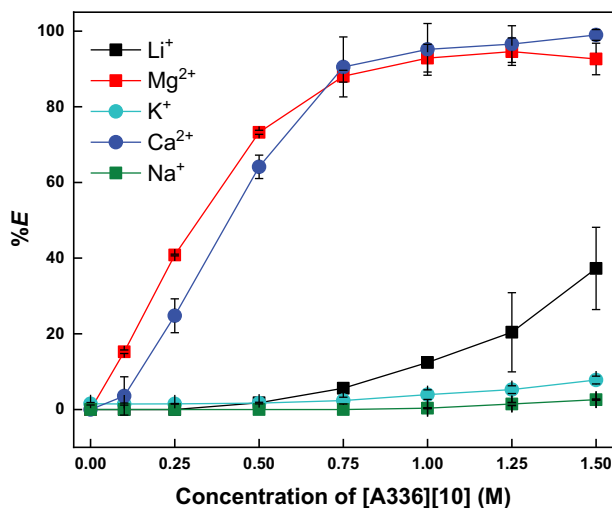


Figure 2. Effect of the [A336][V10] concentration on the extraction of Mg^{2+} , Ca^{2+} , Li^+ , Na^+ and K^+ from a chloride solution. Experimental conditions: [A336][V10] in p-cymene; O/A = 1/1; and equilibrium time 30 min.

A) of 1/1. As can be seen from the results shown in [Figure 2](#), extraction of Ca^{2+} and Mg^{2+} nears 100% at extractant concentrations above approx. 1 mol L^{-1} , but Li^+ losses are significant. In order to minimize losses of lithium while retaining adequate extraction of Mg^{2+} and Ca^{2+} , a concentration of 0.5 mol L^{-1} was selected for further studies. Subsequently, a variation of the phase ratio was conducted, using an extractant concentration of 0.5 mol L^{-1} . The O/A was varied from 11/1 to 1/11. The results of this study are shown in the Supplementary Material (Fig. S3). Based on similar considerations as above, an O/A of 1/1 was chosen for further studies.

With the optimal extractant concentration and O/A as input parameters, a distribution isotherm was determined for Mg^{2+} . In turn, this isotherm was used to estimate the required number of stages in a multistage countercurrent extraction process, using the McCabe-Thiele method. The distribution isotherm was constructed by varying O/A between 11/1 and 1/3. A feed solution with a higher magnesium concentration was used in this instance, containing 4 g/L of Mg^{2+} , 1.6 mg/L of Li^+ , 76 g/L of Na^+ , 3 g/L of K^+ and 0.3 g/L of Ca^{2+} . The higher aqueous magnesium concentration allowed higher loading of the organic phase to be achieved at lower phase ratios, reducing the error on the calculation of the organic magnesium concentration. Ion chromatography (IC) was used for the determination of the aqueous Mg^{2+} concentration and each sample was prepared and measured in triplicate. The distribution isotherm and derived McCabe-Thiele diagram are shown in [Figure 3](#). An estimated four stages would be needed to fully remove Mg^{2+} from the feed solution.

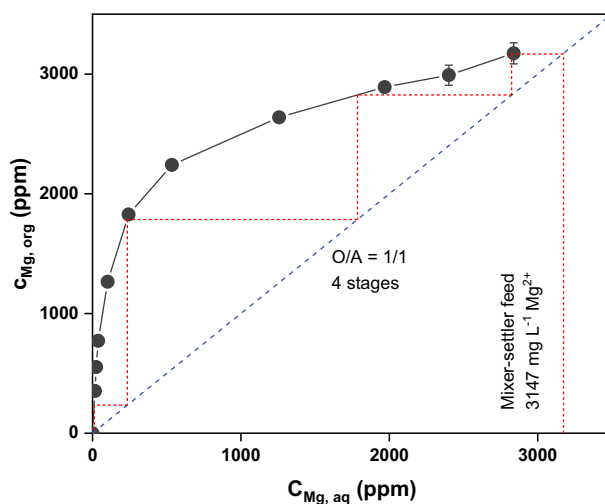


Figure 3. McCabe – Thiele diagram for Mg²⁺ extraction. The operating line is constructed for O/A = 1/1. Experimental condition: 0.5 mol L⁻¹ of [A336][V10] in p-cymene.

To ensure that the proposed process is suitable for upscaling in continuous countercurrent mode, the apparent kinetics and settling time of the system were studied, the mutual miscibility of the phases was determined and a five-stage countercurrent process was simulated in batch mode. The results hereof are discussed in the Supplementary Material (Fig. S4-S5). In summary, the extraction kinetics and settling times are sufficiently rapid that mixer-settler operations are feasible, and the batch countercurrent simulation demonstrated full removal of Ca²⁺ and Mg²⁺ after five stages (Fig. S6).

The extraction process was then scaled up in continuous countercurrent mode. The O/A was set to 1/1. The flow rate for both the aqueous and the organic phase was 12 mL min⁻¹. The residence time in each mixer was 1.45 min (calculated as the active mixer volume divided by the total flow rate). Based on the McCabe – Thiele diagram, four stages are theoretically required for quantitative extraction of Mg²⁺ at an O/A of 1/1 (Figure 4) According to the batch countercurrent experiments, five stages are needed in practice using a O/A of 1/1 (Fig. S6).

As shown in Figure 4, extraction efficiency of Mg²⁺ and Ca²⁺ increased over time for 5 hours and remained constant afterward. This means the steady state was reached after about 5 hours of operation. Both Mg²⁺ and Ca²⁺ were selectively extracted from the brine solution. The co-extraction of the impurities was only 0.39% Li⁺, 0.69% Na⁺, and 0.32% K⁺, respectively. Unfortunately, only 94% Mg²⁺ and 96% Ca²⁺ were extracted during the five-stage mixer-settler test. As a consequence, 199 mg/L Mg²⁺ and 12 mg/L Ca²⁺ remained in the raffinate. Reducing the flow rate of both the aqueous and organic phases to 6 mL min⁻¹ (increasing the residence time in each mixer to

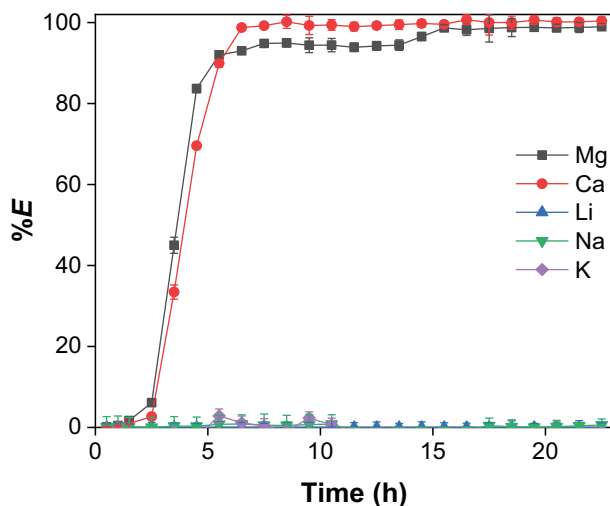


Figure 4. Percentage extraction of metals as a function of time in five/six-stage continuous countercurrent mixer-settler mode. Conditions: aqueous: synthetic brine solution (flow rate = 12 mL min⁻¹), 3174 mg L⁻¹ Mg²⁺, 325 mg L⁻¹ Ca²⁺, 1.628 mg L⁻¹ Li⁺, 75305 mg L⁻¹ Na⁺, 3048 mg L⁻¹ K⁺; organic: 0.5 mol L⁻¹ [A336][v10]/p-cymene (flow rate = 12 mL/min); O/A = 1/1; 298 K; 1500 rpm; residence time 1.45 min per mixer.

2.92 min), did not enhance the percentage extraction, implying that the issue was not related to kinetics. Therefore, one additional stage was added to the mixer-settler setup after 8 hours of operation. Near-quantitative extraction of 99.0% Mg²⁺ and 99.2% Ca²⁺ was achieved during the six-stage countercurrent mixer-settlers operation. Moreover, the co-extraction of impurities was limited to 0.09% Li⁺, 0.73% Na⁺, and 0.28% K⁺. Compared to the batch tests, the loss of Li⁺ is significantly diminished from 20% to 0.09% using mixer-settlers. Accordingly, the separation factor of $\alpha_{\text{Mg}^{2+}/\text{Li}^{+}}$ increased from 485 in batch test up to $1.13 \times 10^{[5]}$ in the six-stage mixer-settler operation. A minimal amount of 32 mg L⁻¹ Mg²⁺ and 1.8 mg L⁻¹ Ca²⁺ was detected in the raffinate. The evolution of the percentages extraction over time in the raffinate is shown in Figure 4. The concentration profile of Mg²⁺ and Ca²⁺ extracted across the mixer – settler battery are shown in the Supplementary Material (Fig. S7). The mixer-settler operation was halted after 22.5 hours of operation. No precipitate nor third phase formation was observed during the entirety of the operation. The concentrations of the feed, raffinate and loaded organic phases after 6 hours of operation are shown in Table 1.

The combined loaded organic phases from all previous extraction experiments, containing an average of 3057 mg L⁻¹ of Mg²⁺, 296 mg L⁻¹ of Ca²⁺, <0.002 mg L⁻¹ of Li⁺, 500 of mg L⁻¹ Na⁺ and 6.0 of mg L⁻¹ K⁺, was used for stripping studies. Stripping of the loaded organic phase was investigated using HCl solutions with variable concentrations (0–2 mol L⁻¹) in an O/A volume phase ratio of 1/1 (Figure 5). A stripping

Table 1. Concentration of each element in the feed, raffinate and loaded organic phase after 6 hours of magnesium and calcium removal in continuous counter-current mode. Values are given in mg L^{-1} .

	Mg^{2+}	Ca^{2+}	Li^+	Na^+	K^+
Feed	3147	325	1.6	$75.3 \cdot 10^3$	$3.0 \cdot 10^3$
Raffinate	32.4	1.7	1.6	$74.8 \cdot 10^3$	$3.0 \cdot 10^3$
Loaded organic	3141	323	0.0	550	8.5

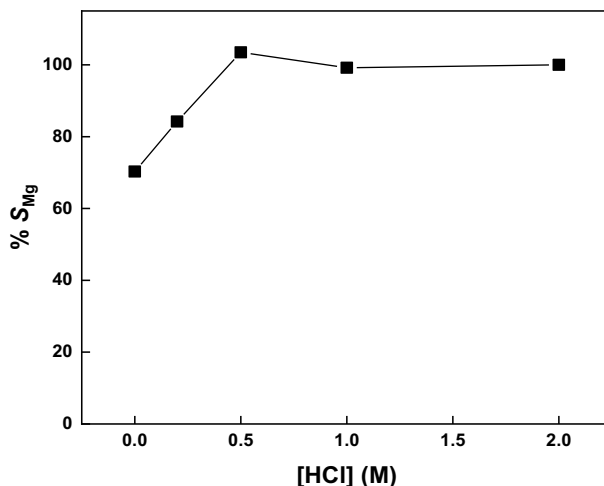


Figure 5. Effect of the HCl concentration on the stripping of the loaded organic phase. Experimental conditions for extraction: 0.5 mol L^{-1} of [A336][V10] in *p*-cymene; O/A = 1/1.

percentage of 100% is obtained at HCl concentrations of 0.5 mol L^{-1} or more. However, high HCl concentrations will reverse Eq. (2), leading to decomposition of the extractant. Stripping with water is therefore preferred.

The stripping process was then scaled up in a two-stage continuous countercurrent setup, with an O/A of 1/1 and a flow rate of 12 ml min^{-1} for each phase. First, water without HCl was used as stripping agent. The stripping behavior of the metals is presented in Figure 6. An upward trend of the percentage stripping was observed during the first 3 hours of operation. Afterward, the percentage stripping plateaued as it reached a steady state. Unfortunately, only 83% Mg^{2+} and 88% Ca^{2+} could be stripped with water. The percentage stripping of Mg^{2+} and Ca^{2+} did not improve upon decreasing the flow rate to 6 mL min^{-1} and using a slightly acidic solution of 0.01 mol L^{-1} HCl. After 9 hours of operation, the acidity of stripping liquor was increased to 0.1 mol L^{-1} HCl. As a result, the recovery of Mg^{2+} and Ca^{2+} was quantitative ($\%S_{\text{Mg}} = \%S_{\text{Ca}} = 100\%$) after 12 hours of operation. A final stripping solution was produced containing 3053 mg L^{-1} of Mg^{2+} , 296 mg L^{-1} of Ca^{2+} , 488 mg L^{-1} of Na and 6 mg L^{-1} of K^+ . No Li^+ was detected in the stripping solution.

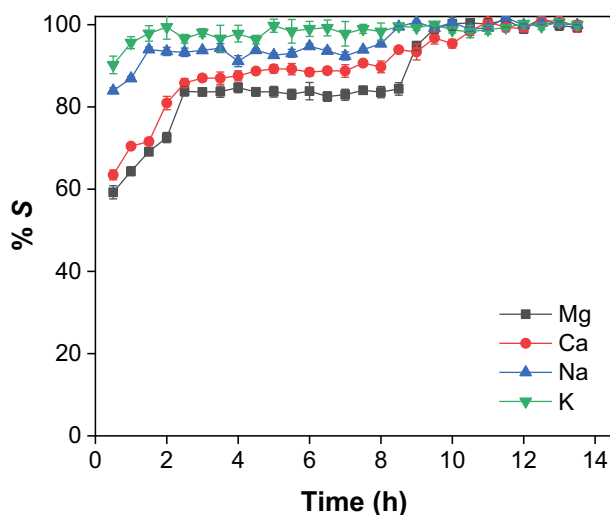
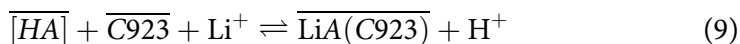


Figure 6. Percentage stripping of metals from loaded organic [A336][V10] as a function of time in two-stage continuous countercurrent mode. Conditions: aqueous: water and 0.1 mol L^{-1} HCl (flow rate = 12 mL min^{-1}); Loaded organic: 0.5 M [A336][v10]/p-cymene (flow rate = 12 mL min^{-1}), $3057 \text{ mg L}^{-1} \text{ Mg}^{2+}$, $296 \text{ mg L}^{-1} \text{ Ca}^{2+}$, $<0.002 \text{ mg L}^{-1} \text{ Li}^{+}$, $500 \text{ mg L}^{-1} \text{ Na}^{+}$, $6.0 \text{ mg L}^{-1} \text{ K}^{+}$; O/A = 1/1; 298 K; 1500 rpm; residence time 1.45 min.

Lithium extraction

The second step in the lithium isolation process is the selective extraction of lithium from the Mg^{2+} -depleted brine by the synergistic combination of the extractants Mextral 54–100 and Cyanex 923, diluted in ShellSol D70. Mextral 54–100 has a structure identical to that of LIX 54–100, consisting of a mixture of 6 isomeric 1-phenyldecane-1,3-diones.^[34] Cyanex 923 consists of trialkyl phosphine oxides, with a chain length of six to eight carbon atoms. The structures of these extractants are shown in the Supplementary Material (Fig. S8). Pranolo *et.al.* determined the mechanism of extraction by this synergistic extractant combination to be that represented by Eq. (9), with HA denoting acidic Mextral 54–100 and overbars denoting species in the organic phase.^[35] Mextral 54 acts as a bidetate acidic extractant, while Cyanex 923 partially saturates the coordination sphere of Li^{+} . Steric constraints appear to prevent the formation of a four-coordinate Li species:



Again, the extraction parameters were optimized prior to upscaling, using a synthetic feed solution with a composition similar to the raffinate after the removal of divalent ions (1.55 mg L^{-1} of Li^{+} , 76 g L^{-1} of Na^{+} and 3 g L^{-1} of K^{+}), beginning with the equilibrium aqueous pH. The effect of the pH was investigated using 0.5 vol% Mextral 54–100 and 0.5 vol% Cyanex 923 in ShellSol D70 at an O/A volume phase ratio of 1/1. As shown in Figure 7, the extraction

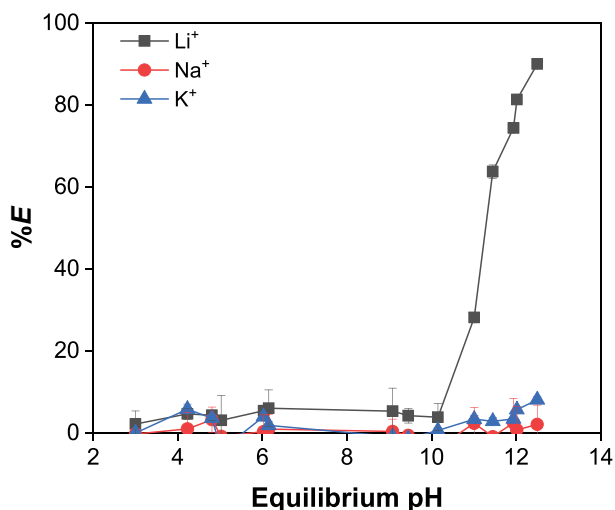


Figure 7. Effect of the equilibrium pH on the percentage extraction of Li^+ . Aqueous: 1.55 mg L^{-1} Li^+ , 76 g L^{-1} Na^+ and 3 g L^{-1} K^+ ($\text{pH}_{\text{ini}} = 2.94$; equilibrium pH adjusted by adding 10 mol L^{-1} NaOH); Organic phase: 0.5 vol% Mextral 54–100 and 0.5 vol% Cyanex 923 in ShellSol D70; O/A = 1/1; 298 K; equilibrium time 5 min.

of lithium is very low ($\%E < 5\%$) at equilibrium pH (pH_{eq}) values below 10. At higher equilibrium pH values, Li^+ extraction increases sharply. In further batch studies, the equilibrium pH was adjusted to this value by the addition of 10 mol L^{-1} NaOH. Next, the effect of the extractant concentration was investigated in the range of 0.5 vol% to 2.0 vol% Mextral 54–100 and Cyanex 923. The results hereof are shown in Figure 8. Increasing the concentration of extractant from 0.5 vol% to 1.5 vol% Mextral 54–100 and Cyanex 923 resulted in a limited increase in the percentage extraction of Li^+ , while the co-extraction of Na^+ and K^+ remained very low. There was no added value in a further increase of the extractant concentration to 2 vol%, and hence the a concentration of 1.5 vol% was chosen for further study. A lower extractant concentration has the added advantage of minimizing extractant losses to the raffinate. We declined to use a higher extractant concentration at an even lower O/A, as it is difficult to maintain the proper phase ratio and phase continuity during mixer-settler operation with an O/A beyond 1/3 or 3/1.

A distribution isotherm was constructed using the previously determined optimum equilibrium pH and extractant concentration, by varying the O/A from 5/1 to 1/5. The aqueous feed solution used here was identical to that used for optimization studies. Subsequently, the McCabe-Thiele method was applied to obtain an estimate of the number of stages required for full extraction of Li^+ (Figure 9). It was estimated that three countercurrent stages are required to achieve quantitative extraction of Li^+ at an O/A of 1/3. A low O/A was chosen in order to concentrate the lithium solution during the extraction process. Three-stage countercurrent

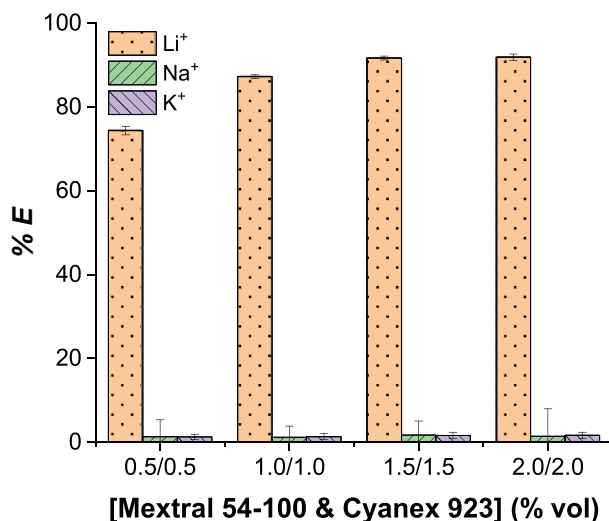


Figure 8. Effect of the extractant concentration on the percentage extraction of Li^+ . Aqueous: $1.553 \text{ mg L}^{-1} \text{ Li}^+$, $76 \text{ g L}^{-1} \text{ Na}^+$ and $3 \text{ g L}^{-1} \text{ K}^+$ ($\text{pH}_{\text{ini}} = 2.94$); $\text{pH}_{\text{eq}} = 12$ (adjusted by adding $10 \text{ mol L}^{-1} \text{ NaOH}$); Organic phase: 0.5–2.0 vol% Mextral 54–100 and 0.5–2.0 vol% Cyanex 923 in ShellSol D70; O/A = 1/1; 298 K; equilibrium time 5 min.

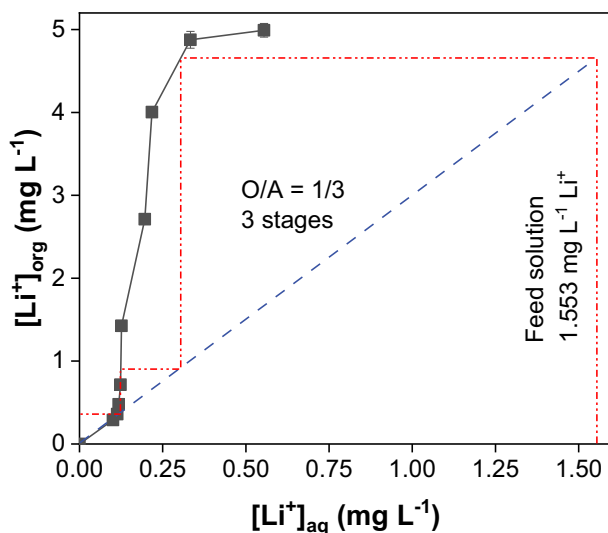


Figure 9. McCabe – Thiele diagram for Li^+ extraction. The operating line is constructed for O/A = 1/3. Experimental condition, aqueous: $1.553 \text{ mg L}^{-1} \text{ Li}^+$, $76 \text{ g L}^{-1} \text{ Na}^+$ and $3 \text{ g L}^{-1} \text{ K}^+$ ($\text{pH}_{\text{ini}} = 2.94$); $\text{pH}_{\text{eq}} = 12$ (adjusted by adding $10 \text{ mol L}^{-1} \text{ NaOH}$); Organic phase: 1.5 vol% Mextral 54–100 and 1.5 vol% Cyanex 923 in ShellSol D70; O/A = 1/5 to 5/1; 298 K; equilibrium time 5 min.

extraction was simulated in batch mode, demonstrating experimentally that three countercurrent stages are sufficient for near-quantitative extraction of lithium ($\%E = 98\%$). This is discussed in the Supplementary Material (Fig. S9–S10).

Stripping of Li^+ from the loaded organic phase was investigated using aqueous HCl solutions of various concentrations (Figure 10). The loaded organic phase collected after batch countercurrent extraction simulations were used as feed for these tests. HCl was chosen as stripping agent, as stripping with HCl produces LiCl , a common intermediate for the production of LiOH and Li_2CO_3 . Pure water is incapable of stripping Li^+ , but the percentage stripping rises sharply with increasing HCl concentrations. Full stripping of Li^+ ($\%S > 99.5\%$) is achieved using HCl concentrations $> 0.04 \text{ mol L}^{-1}$. On the other hand, Na^+ was quantitatively stripped with either water or diluted HCl solutions. It means that the co-extracted impurity, Na^+ , can be efficiently scrubbed from the loaded organic phase with water and selectively removed from Li^+ .

A distribution isotherm under stripping conditions (*i.e.* 0.1 mol L^{-1} HCl) was constructed by variation of the phase ratio. The McCabe-Thiele method was applied to obtain an estimate of the number of stages required for full stripping of Li^+ using the McCabe-Thiele method (Figure 11). It was found that three countercurrent stages are required to achieve quantitative extraction of Li^+ at an O/A of 4/1. A high O/A was chosen in order to concentrate the lithium solution during the stripping process. Two-stage countercurrent stripping of Li^+ was simulated in batch mode, demonstrating that quantitative stripping of Li^+ can be achieved in two countercurrent stages. This is discussed in the Supplementary Material (Fig. S11–S12).

The full extraction-scrubbing-stripping process was then simultaneously scaled up in continuous countercurrent mode. The raffinate obtained after removal of divalent ions was used as the feed in this experiment. The O/A was

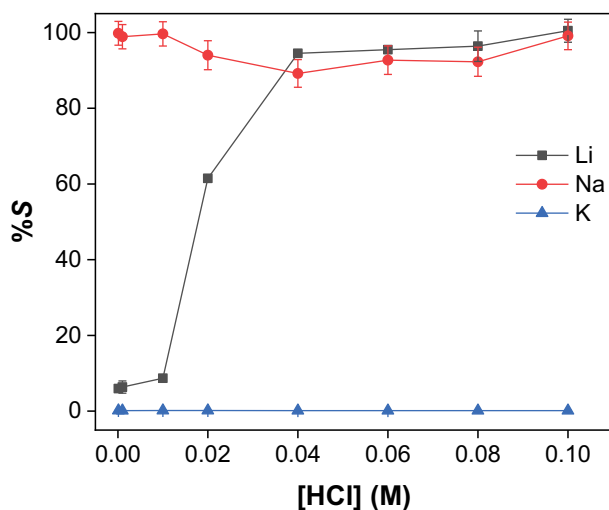


Figure 10. Effect of the HCl concentration on the percentage stripping of Li^+ , Na^+ and K^+ . Extraction: aqueous: $1.55 \text{ mg L}^{-1} \text{ Li}^+$, $76 \text{ g L}^{-1} \text{ Na}^+$ and $3 \text{ g L}^{-1} \text{ K}^+$ ($\text{pH}_{\text{ini}} = 2.94$); $\text{pH}_{\text{ini}} = 12.08$ (adjusted by adding $10 \text{ mol L}^{-1} \text{ NaOH}$); $\text{pH}_{\text{eq}} 1^{\text{st}}/2^{\text{nd}}/3^{\text{rd}} = 11.98/11.92/11.64$; Organic phase: 1.5 vol% Mextral 54–100 and 1.5 vol% Cyanex 923 in ShellSol D70; volume phase ratio O/A = 1/3; 298 K; equilibrium time 5 min. Stripping: aqueous: 10^{-4} – $10^{[1]}$ mol L^{-1} HCl; Loaded organic phase: $4.56 \text{ mg L}^{-1} \text{ Li}^+$, $1.3 \text{ g L}^{-1} \text{ Na}^+$, $0.45 \text{ g L}^{-1} \text{ K}^+$; volume phase ratio O/A = 1/1; 298 K; equilibrium time 5 min.

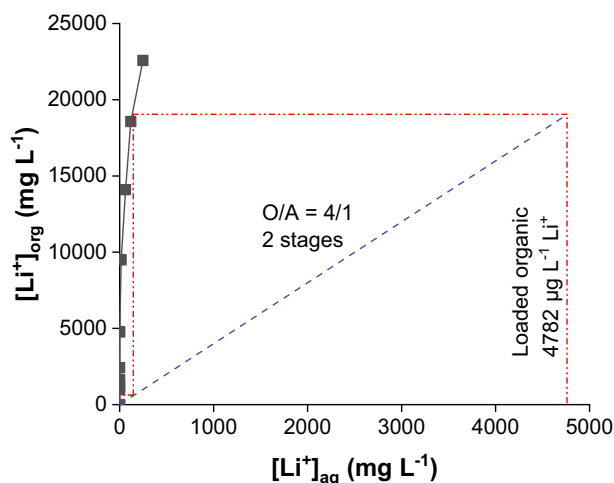


Figure 11. McCabe – Thiele diagram for Li^+ stripping. The operating line is constructed for $O/A = 4/1$. Experimental condition: aqueous: $0.1 \text{ mol L}^{-1} \text{ HCl}$; Scrubbed organic phase: $4.78 \text{ mg L}^{-1} \text{ Li}^+$, $9.2 \text{ mg L}^{-1} \text{ Na}^+$ and $0.24 \text{ mg L}^{-1} \text{ K}^+$; $O/A = 5/1$ to $1/5$; 298 K ; equilibrium time 5 min .

set to $1/3$, with a flow rate of 18 mL min^{-1} for the aqueous phase and 6 mL min^{-1} for the organic. The residence time in each mixer chamber was 1.45 min . As shown in Figure 12, more than 90% of Li^+ was extracted after 1 h. The quantitative extraction of Li^+ ($\%E = 99.9\%$) was achieved within 2 h. Thus, three stages suffice for full extraction of Li^+ as predicted by the distribution isotherm using the McCabe-Thiele method.

Concurrently, co-extracted Na^+ and K^+ were scrubbed and Li^+ was stripped from the organic phase. One cross-current scrubbing stage was employed for the removal of Na^+ and K^+ , using water as scrubbing agent. The O/A in this stage was $1/1$ and the flow rate of both phases was 6 mL min^{-1} , with a residence time of 2.92 min in the mixing chamber. The steady state for scrubbing was reached within 2.5 hours. As shown in Figure 13, both Na^+ and K^+ were efficiently removed ($\%Sc > 91\%$) from the loaded organic phase in a single contact. The mass loss of Li^+ was negligible, less than 0.89% . During scrubbing, the phase disengagement was good, without third phase or crud formation. The scrubbing stage was followed by two countercurrent stripping stages with $0.1 \text{ mol L}^{-1} \text{ HCl}$ as stripping agent. The O/A in these stages was $4/1$, with an aqueous flow rate of 1.5 mL min^{-1} and an organic flow rate of 6 mL min^{-1} , at a residence time of 4.67 min per mixer chamber. As shown in Figure 14, the stripping efficiency of Li^+ and other impurities (*i.e.* Mg^{2+} , Ca^{2+} , and Na^+) increased substantially in the first four hours of operation. At the steady state, most of the metals were quantitatively recovered.

The mixer-settler test was stopped after 12 hours of operation. No precipitation nor third-phase formation was observed during the entirety of the operation. The concentrations of each metal at the steady state in each stream are shown in Table 2. Taking into account the phase ratios of the extraction

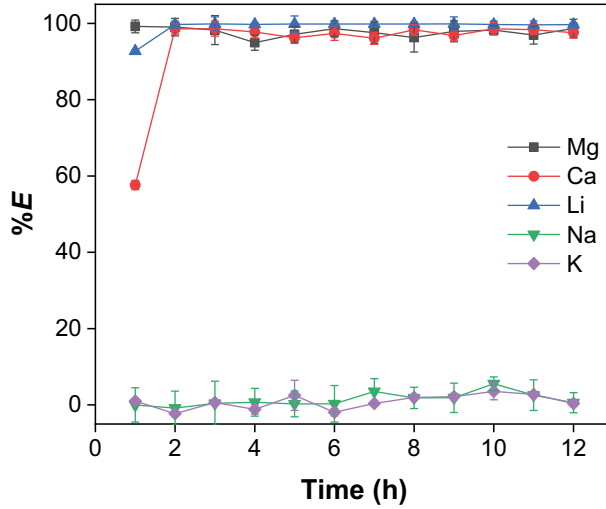


Figure 12. Percentage extraction of metals as a function of time in three-stage continuous countercurrent mode. Aqueous: brine solution after Mg/Ca removal (flow rate = 18 mL min^{-1}); organic: 1.5 vol% Mextral 54–100 and 1.5 vol% Cyanex 923 in Shellsol D70 (flow rate = 6 mL min^{-1}); O/A = 1/3; 298 K; 1500 rpm; $\text{pH}_{\text{eq}} = 11.8$; residence time 1.45 min per each mixer.

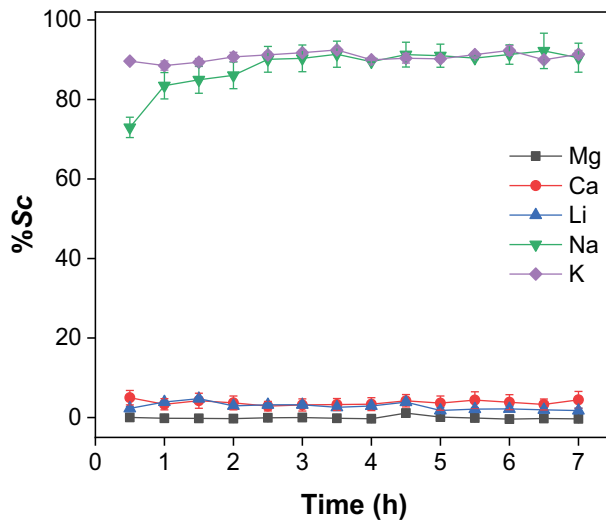


Figure 13. Percentage scrubbing of metals as a function of time in one-stage continuous countercurrent mode. Aqueous: water (flow rate = 6 mL min^{-1}); loaded organic: 1.5 vol% Mextral 54–100 and 1.5 vol% Cyanex 923 in Shellsol D70 (flow rate = 6 mL min^{-1}); O/A = 1/1; 298 K; 1500 rpm; residence time 2.92 min per each mixer.

process (O/A = 1/3 during extraction and 4/1 during stripping), no significant losses of lithium are incurred during the process, and the extraction and stripping steps can be considered to have a quantitative yield. Losses to the scrubbing liquor amount to less than 1%.

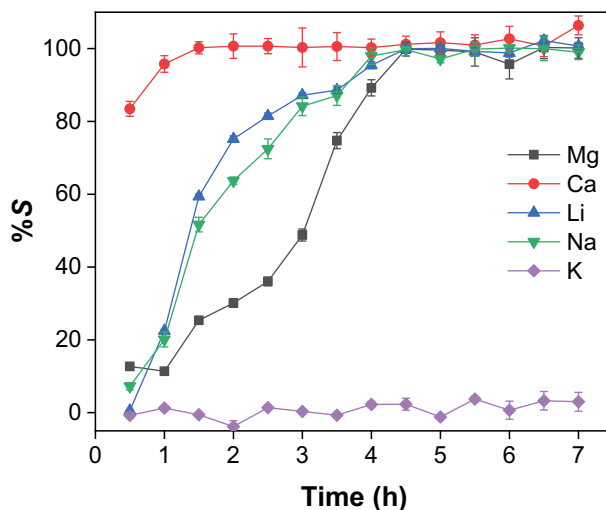


Figure 14. Percentage stripping of metals as a function of time during two-stage continuous countercurrent mode. Aqueous: 0.1 mol L^{-1} HCl (flow rate = 1.5 mL min^{-1}); scrubbed organic: 1.5 vol% Mextral 54–100 and 1.5 vol% Cyanex 923 in Shellsol D70 (flow rate = 6 mL min^{-1}); O/A = 4/1; 298 K; 1500 rpm; residence time 4.67 min per each mixer.

Table 2. Concentration of each element in the feed, raffinate, loaded organic phase, scrubbing liquor and stripping liquor after 6 hours of magnesium and calcium removal in continuous countercurrent mode. Values are given in mg L^{-1} .

	Mg^{2+}	Ca^{2+}	Li^+	Na^+	K^+
Feed	32.4	1.8	1.6	$74.8 \cdot 10^3$	$3.0 \cdot 10^3$
Raffinate	<0.01	0.1	<0.01	$77.2 \cdot 10^3$	$3.0 \cdot 10^3$
Loaded organic	30.7	8.2	4.9	435	20.9
Scrubbing liquor	<0.01	<0.01	0.04	414	17.0
Stripping liquor	121	31.7	19.1	37.5	0.2

Selective precipitation of lithium carbonate

The stripping liquor still contains appreciable amounts of monovalent and divalent impurities. The divalent impurities were separated from the monovalent ions by precipitation using ethanolic sodium hydroxide. Subsequently, lithium was isolated by precipitation as lithium carbonate. Ethanolic NaOH was used as $\text{Ca}(\text{OH})_2$ is far less soluble in ethanol than in water, wherein a large excess of NaOH would be needed to fully remove Ca^{2+} as its hydroxide.^[33] This comes with the disadvantage of having to invest energy in the removal of water from the feed solution in order to change solvents. Likewise, ethanol must be distilled off after precipitation of the alkaline earth elements in order to switch back to an aqueous solution.

A mixture of chloride salts was prepared to mimic the residue obtained after evaporation of the lithium stripping solution, based on IC analysis thereof. Evaporation of the stripping liquor is necessary as the quantitative precipitation of Ca^{2+} by sodium hydroxide is only possible in organic media, necessitating

Table 3. Composition of the supernatant fluid and percentage recovery of each element.

	Li ⁺	Na ⁺	Ca ²⁺	Mg ²⁺
Concentration (ppm)	1.37·10 ³	3.36·10 ³	0.0	0.0
% dissolved	96.0	80.3	0.0	0.0
Wt% in precipitate ^a	0.49	8.42	29.4	61.6

^aMetal basis.

a change of solvent. Three 10 g aliquots of the mixture were each shaken in 102 mL of ethanolic sodium hydroxide (845.2 mM, 95 vol% ethanol), corresponding to a 2% molar excess with respect to Ca²⁺ and Mg²⁺. Analysis of the supernatant fluid after shaking and centrifuging shows that while nearly all LiCl was recovered (96.0%), the solution was devoid of divalent metals. This implies that the precipitation of magnesium and calcium hydroxides was highly efficient in ethanol with only a minor excess of sodium hydroxide being required. The composition of the supernatant fluid and the precipitate, and the percentage recovery of each element are given in Table 3. The composition of the residue was determined using the mass balance.

The organic solvent is subsequently removed from the purified lithium chloride by evaporation, followed by dissolution of the lithium chloride in water to a concentration of approx. 2 g L⁻¹ (5 mL). An equal volume of sodium carbonate solution was then added (1.35 mol L⁻¹), corresponding to a 10% molar excess. The solution was heated to 60°C to further reduce the solubility of lithium carbonate, filtered and finally washed with water (2 mL) at 60°C. Based on the concentration in the filtrate, it was determined that 79.8% of lithium was precipitated as the carbonate. By washing, a 3.2% loss was incurred, resulting in a final precipitation yield of 76.6%. The purity of the final product (expressed as the weight percent Li₂CO₃) was 97.2%. Preliminary tests showed a similar residual lithium concentration when the filtration was conducted at room temperature. Hence, heating to 60°C prior to filtration is not warranted. Most likely, a higher final purity can be obtained by further washing of the precipitate, but this is only feasible on a larger scale due to the non-negligible solubility of the lithium carbonate precipitate.

Conclusion

A process to isolate lithium from simulated nanofiltration-treated seawater desalination brine was proposed. The process consists of a magnesium and calcium removal step using methyltrioctylammonium neodecanoate in *p*-cymene, a lithium extraction step using Mextral 54 and Cyanex 923 in Shellsol D70, scrubbing of the lithium extract with water, stripping of lithium with hydrochloric acid, removal of residual alkaline earth metals with sodium hydroxide in ethanol and precipitation of lithium using sodium carbonate. The solvent extraction, scrubbing and stripping steps were demonstrated on mini-pilot scale in

continuous countercurrent mode, while the precipitation steps were demonstrated in batch. Negligible quantities of lithium were lost during the magnesium and calcium removal step. Extraction and stripping of lithium were essentially quantitative, with losses to the scrubbing liquor amounting to less than 1%. A 4.0% loss of lithium was incurred during the removal of residual magnesium and calcium, and the yield of lithium carbonate precipitation was 76.6%. The total lithium carbonate yield of the process was thus 74%, at a purity of 97 wt%. Future work should focus on further upscaling of the process to pilot scale, and using this data to evaluate which market preconditions must be met in order to render this process economically viable. Longer-term studies with various desalination brine sources would allow the evaluation of solvent losses and poisoning.

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Disclosure statement

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