Multi-pass Nanofiltration for Lithium Separation with High Selectivity and Recovery

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ABSTRACT

Nanofiltration (NF) is a promising and sustainable process to extract Li^+ from brine lakes with high Mg^{2+} to Li^+ mass ratios. However, a tradeoff between Li/Mg selectivity and Li recovery exists at the process-scale, and the Li/Mg selectivity of commercially and lab-made NF membranes in a single-pass NF process is insufficient to achieve the industrially required Li purity. To overcome this challenge, we propose a multi-pass NF process with brine recirculation to achieve high selectivity without sacrificing Li recovery. We experimentally demonstrate that Li/Mg selectivity of a three-pass NF process with a commercial NF membrane can exceed 1,000, despite the compromised Li recovery due to co-existing cations. Our theoretical analysis further predicts that a four-pass NF process with brine recirculation can simultaneously achieve an ultra-high Li/Mg selectivity of over 4,500 and a Li recovery of over 95%. This proposed process could potentially facilitate efficient NF-based solute-solute separations of all kinds and contribute to the development of novel membrane-based separation technologies.

KEYWORDS: nanofiltration, lithium extraction, selective separation, solute-solute separation

SYNOPSIS

Multi-pass nanofiltration with brine circulation using commercial membranes can achieve exceptional performance in lithium-magnesium separation with high selectivity and lithium recovery.

INTRODUCTION

Lithium (Li) has become one of the most valuable resources in the 21st century with a sharp increase in demand due to its applications in battery for electrifying transportation and sustainable energy-storage.[1,2] Li^+ is abundant in salt lake brine, though at a relatively low concentration compared to other co-existing cations, especially magnesium (Mg), which often exists at a concentration one to three orders of magnitude higher than Li.[3] In a typical treatment train for Li extraction (from brine), Li^+ is recovered at the final precipitation step in the form of hydroxide or carbonate compounds. Because $Mg(OH)_2$ or $MgCO_3$ also has low solubility and will thus co-precipitate (with LiOH or Li_2CO_3), separating Li^+ from Mg^{2+} in previous steps is critical to achieving a final product with high purity. Conventional solar evaporation/precipitation-based Li extraction process requires a large footprint and substantial use of chemicals and cannot effectively handle brines with high Mg^{2+} to Li^+ mass ratio (MLR).[2,4] Nanofiltration (NF), which can separate monovalent and divalent ions, has been explored for Li/Mg separation due to its separation effectiveness, modularity, and process sustainability.[5] As direct lithium extraction is challenging for NF due to the high ionic strength, complex feed composition and high scaling potential, NF is typically integrated with other pre- and post-treatment unit processes to assemble a complete treatment train. Sodium and potassium precipitation (e.g., KCl fertilizer production) and Li-selective adsorption are typical pre-treatment units preceding NF, during which Li is pre-enriched from the original brine lakes. Reverse osmosis can be applied as a post-treatment to concentrate the Li-enriched stream from NF permeate for the final precipitation step and recover the water for next-cycle dilution of brine before it enters the NF process.

NF membranes have sub-nanometer pores and charged functional groups that allow them to selectively exclude ions by steric, dielectric, Donnan exclusions, and dehydration mechanisms. The selectivity of monovalent and divalent ions stems from the difference in ion size, valence, and mobility. The Li/Mg selectivity of most commercial and lab-made NF membranes is typically lower than 30, with some exceptional membranes achieving 80~100.[6–12] Such a selectivity corresponds to a Li purity (i.e., mass ratio of Li over the sum of Li and Mg in the permeate) of 10%~90% when treating a typical brine with high MLR (e.g., 10~120) in a single pass of filtration, which fails to meet the industrial requirements of Li product purity (e.g., 98%~99.9%) without additional chemical purification.

While the membrane's intrinsic ability to separate Li^+ and Mg^{2+} may be substantially improved with a better design of membrane material and structure (e.g., incorporating coordination chemistry),[7,12–15] an operational tradeoff always exists at the process scale between the two success criteria for Li extraction in a single-pass NF process: Li/Mg selectivity and Li recovery.[16] Specifically, selectivity inevitably decreases as more Li^+ is recovered.[16] Therefore, innovation and optimization of the current NF-based Li/Mg separation process are necessary to improve both Li/Mg selectivity (i.e., product purity) and Li recovery simultaneously, regardless of the intrinsic membrane performance.

Multi-pass filtration is an effective strategy to improve water purity in water treatment processes.[17] Two-pass or even three-pass reverse osmosis has been adopted in seawater desalination and wastewater purification as the feed streams contain small and neutral compounds (e.g., boron and some micropollutants) that cannot be sufficiently rejected in a single pass.[18,19] Similarly, a multi-pass NF process, where the permeate in each pass is repressurized to feed into the next pass (Figure 1), is hypothesized to achieve higher Li/Mg selectivity by rejecting the less permeable ion, Mg^{2+}, for multiple times. Similar approach has been employed in selective electrodialysis for Li/Mg separation. A four-stage electrodialysis module was validated experimentally to enhance the Li/Mg selectivity by orders of magnitude.[20]

However, the overall Li recovery can be compromised in a multi-pass NF process if the brines are disposed directly after each filtration pass, as achieving 100% water recovery or Li recovery is unlikely in any single pass. To address this issue, the brine of each pass beyond the 1st pass may cycle back to the previous pass to be part of its feed solution (dash arrows in Figure 1). With recirculation, the multi-pass process has only one main brine stream from the 1st pass, and one main permeate stream (i.e., product stream) from the last pass, thereby mitigating the loss of Li^+ in the process.

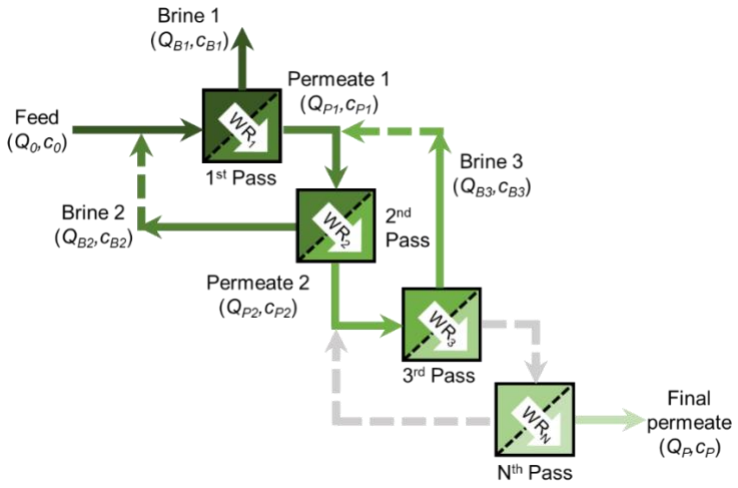

Fig. 1 Schematics of the multi-pass NF process for Li/Mg separation. The permeate of N^{th} pass is the feed of $(N+1)^{th}$ pass. The brine of N^{th} pass recirculates back to the feed of $(N-1)^{th}$ pass. Each pass can be operated at different pressures and water recovery. Passes between the 3rd and N^{th} pass, and pumps for pressurizing streams and recirculation are omitted for simplicity.

In this study, we first conduct experiments to evaluate the Li/Mg separation performance of a three-pass NF process without brine recirculation under varying operating pressures, using a simple Li/Mg mixture as the feed solution. We then investigate the impacts of co-existing cations and anions on Li/Mg selectivity and Li recovery of the multi-pass process. Finally, we extend the analysis to predicting the performance of multi-pass Li/Mg separation with brine recirculation by applying a module-scale NF model.

MATERIALS AND METHODS

Experiments of multi-pass NF without brine recirculation

Multi-pass Li/Mg NF separation experiments without brine recirculation were carried out using a commercial spiral-wound NF membrane module with polyamide membrane, NFX-1812 (Synder Filtration, USA, Table S1), in a crossflow filtration system. NFX membrane was selected in this study over other more commonly seen commercial NF membranes (e.g., NF270 and NF90 from Dupont) because NFX membrane is closer to the upper bound in the material tradeoff plot (Li/Mg permeability ratio vs Li/water permeability ratio),[16] which suggests NFX has potential to achieve moderate purity and Li recovery at the same time. The effective membrane area of the module is 0.37 m^2. Pure water permeability was first measured after pre-compaction of the membrane. Li/Mg separation was then conducted with synthetic brines at different pressures in a batch mode, i.e.,

circulating the brine stream back to the feed tank and collecting the permeate stream in a separate tank until the target water recovery was achieved. The target water recovery was set as 75% for the 1st pass (unless otherwise stated) to avoid a very low water flux at higher water recovery, as a low flux requires more membrane area in the real process to achieve the same target water recovery. The target water recovery was set as 85% for the 2nd and 3rd passes (unless otherwise stated), which was possible because the osmotic pressures for the 2nd and 3rd passes were much lower than that of the 1st pass. The determination of water recovery considers the solution dead volume in the membrane module and in the crossflow filtration loop. A balance was used to monitor the mass increase of permeate tank over time for water recovery estimation. In the batch mode where the water recovery of the small membrane coupon in each pass is negligible, the spatial variation of feed concentration in a real membrane module is mimicked by the temporal variation of feed concentration in the feed tank.

We focus the application scenario of NF on treating "old brines" (i.e., the brine after K and Na precipitation) or the elution solutions after a Li-selective adsorption pre-treatment step. Specifically, a simple mixture of 3.4 mM LiCl and 19.6 mM $MgCl_2$ was first used as the initial feed solution to evaluate multi-pass separation performance. The concentrations of Li^+ (23.8 mg L^{-1}) and Mg^{2+} (470.4 mg L^{-1}) represent a diluted brine with a MLR of 20. We note that the dilution of feed solution is typically necessary for two reasons: (1) to reduce the osmotic pressure so that a relatively low operating pressure can be used; and (2) to reduce the charge screening effect so that the Donnan effect can be leveraged for the selective separation of monovalent and divalent cations. We also note that the fresh water used for dilution can be recouped in the subsequent RO post-treatment for concentrating the NF permeate. The determination of the optimal dilution factor is beyond the scope of this study and requires more comprehensive analysis to account for separation performance, process cost, and the availability of fresh water to initiate the process.

Two more complex and practical brine compositions (Table S2) were then tested to study the impacts of co-existing cations and anions on the multi-pass Li/Mg separation. Feed and permeate solutions were sampled at different water recovery values with a sampling volume of 1 mL per sample. The permeate flowing out of the spiral-wound module (before entering the permeate tank) and the permeate in the permeate tank (where permeate effluent mixes with existing solution in the tank) were sampled separately and were referred to as the 'local permeate' and

153 'cumulative permeate', respectively. Cation concentrations of collected samples were measured
154 by inductively coupled plasma optical emission spectroscopy. Anion concentrations were
155 measured by ion chromatography. For multi-pass filtration experiments without recirculation, each
156 pass was conducted sequentially with the permeate composition used as the feed composition for
157 the next pass.

158 The local permeate flux, J_{w}, at different water recovery was determined using the following
159 equation:

$$J_{\mathrm{w}} = \frac{\Delta m}{A \Delta t} \tag{1}$$

160 where Δm is the permeate tank mass change in a short time interval of Δt and A is the effective
161 filtration area of the membrane module. The observed local ion rejection at a certain water recovery
162 (WR), $R_i^{\mathrm{loc}}(WR)$, was calcualted as

$$R_i^{\mathrm{loc}}(WR) = 1 - \frac{c_{\mathrm{p},i}^{\mathrm{loc}}(WR)}{c_{\mathrm{b},i}(WR)} \tag{2}$$

163 where $c_{\mathrm{p},i}^{\mathrm{loc}}$ and $c_{\mathrm{b},i}$ are concentrations of the target ion in the local permeate (sampled at the outlet
164 of the permeate tube) and brine (a.k.a. retentate), respectively. While the cumulative ion rejection,
165 R_i^{cum}, was calcualted as

$$R_i^{\mathrm{cum}}(WR) = 1 - \frac{c_{\mathrm{p},i}^{\mathrm{cum}}(WR)}{c_{\mathrm{f},i}} \tag{3}$$

166 where $c_{\mathrm{p},i}^{\mathrm{cum}}$ is the concentration of the target ion in the cumulative permeate (sampled in the
167 permeate tank), and $c_{\mathrm{f},i}$ is the initial feed concentration of the current pass. The cumulative Li/Mg
168 selectivity or separation factor, $S_{\mathrm{Li/Mg}}$, is defined as[21]

$$S_{\mathrm{Li/Mg}} \equiv \frac{1 - R_{\mathrm{Li}}^{\mathrm{cum}}}{1 - R_{\mathrm{Mg}}^{\mathrm{cum}}} \tag{4}$$

169 Li purity (η_{Li}) is related to the MLR of the feed solution and the Li/Mg selectivity via the following
170 equation:

$$\eta_{\mathrm{Li}} = \frac{1}{1 + MLR/S_{\mathrm{Li/Mg}}} \quad (5)$$

Li recovery (LiR), defined as the mass fraction of Li^+ in the feed that is eventually recovered in the permeate, can be quantified by

$$LiR = WR(1 - R_{\mathrm{Li}}^{\mathrm{cum}}) \quad (6)$$

We note that $S_{\mathrm{Li/Mg}}$ (or η_{Li}) and LiR are both important performance metrics and a successful Li/Mg separation must achieve high $S_{\mathrm{Li/Mg}}$ and LiR simultaneously.[16]

Modeling multi-pass NF with brine recirculation

To validate multi-pass NF without brine recirculation, each filtration pass was conducted separately using a benchtop filtration system in the batch mode, as described in the previous section. However, for the validation of multi-pass NF with brine recirculation, a pilot-scale system is required, where a high value of water recovery can be achieved in a single pass, and the brine from each pass is recirculated to the feed of the previous pass to achieve steady-state operation. Therefore, in this study (without access to a pilot scale system), the performance of multi-pass NF with brine recirculation was simulated using a modeling approach.

A module-scale NF model for mixture solutions was applied to evaluate the Li/Mg separation performance of the multi-pass NF process, in which the local mass transport across the membrane was described by the solution diffusion electromigration model (SDEM) as described in the Supporting Information (Text S1).[22–24] For multi-pass filtration without brine recirculation, each pass can be solved sequentially with the permeate composition of one pass used as the feed to the next pass. For multi-pass filtration with brine recirculation, the feed of each pass between the 1st and the last pass (i.e., 2nd to (N-1)th pass) is a mixture of the permeate from the previous pass and the brine from the next pass (Figure 1). When steady state operation is achieved, the mass balance of water can be described as

$$Q_n = \begin{cases} Q_0 + Q_2(1 - WR_2), & \text{for } n = 1 \\ Q_{n-1}WR_{n-1} + Q_{n+1}(1 - WR_{n+1}), & \text{for } n = 2 \sim N-1 \\ Q_{n-1}WR_{n-1}, & \text{for } n = N \end{cases} \quad (7)$$

where N is number of passes, Q_n and WR_n are the feed flow rate and water recovery of pass n, respectively, Q_0 is the initial feed flow rate. Q_n is a function of Q_0 and water recovery of each pass and can be solved analytically. The mass balance of ions can be described as

$$c_{\mathrm{f},n} = \begin{cases} Q_0 c_0 + Q_2(1 - WR_2)c_{\mathrm{b},2}, & \text{for } n = 1 \\ Q_{n-1} WR_{n-1} c_{\mathrm{p},n-1} + Q_{n+1}(1 - WR_{n+1})c_{\mathrm{b},n+1}, & \text{for } n = 2 \sim N-1 \\ c_{\mathrm{p},n-1}, & \text{for } n = N \end{cases} \quad (8)$$

where $c_{\mathrm{f},n}$, $c_{\mathrm{p},n}$, and $c_{\mathrm{b},n}$ are feed, permeate, and brine concentrations of pass n, respectively. $c_{\mathrm{f},n}$ depends on both $c_{\mathrm{p},n-1}$ and $c_{\mathrm{b},n+1}$, and is thus solved iteratively until the steady state is found. The module-scale NF model was first validated by comparing predictions to the experimental results of multi-pass NF without recirculation. The analysis was then extended to the multi-pass system with recirculation for different numbers of passes.

RESULTS AND DISCUSSION

Tradeoff between selectivity and recovery in multi-pass Li/Mg separation *without* brine recirculation

Li/Mg separation performance of a three-pass NF process without recirculation was first tested with the simple Li/Mg feed without other cation species. Both cumulative and local Li^+ rejections increase with number of passes, while Mg^{2+} rejections decrease (Figure 2A and 2B). Negative rejection of Li^+ is common in NF with mixed-salt feed solution as a result of maintaining Donnan equilibrium when the feed solution is abundant in the strongly rejected Mg^{2+} while Cl^- can easily permeate through the membrane.[24–26] The permeation of Cl^- promotes the transport of Li^+ to maintain charge neutrality in the permeate. The local Li^+ rejection in the 1st pass can be strongly negative when water recovery increases (Figure 2A), mainly due to both the increasing local MLR and decreasing local water flux (Figure S1) as the driving force diminishes with the increasing brine osmotic pressure. Li^+ rejection becomes positive in the 2nd pass and further increases in the 3rd pass as most Mg^{2+} is rejected in the 1st pass. The MLR of the feed solution (which is the permeate of the last pass, except for the 1st pass) drops by an order of magnitude after each pass (Figure S2).

NFX membrane has slightly negative charges near neutral pH (e.g., isoelectric point around pH 5). A recent study has shown that the adsorption of multivalent cations (e.g., Mg^{2+}) to

carboxylic functional groups may lead to charge reversal, i.e., the membrane may become positively charged,[27] which in turn benefits the rejection of Mg^{2+} and thus increases Li/Mg selectivity. With substantially reduced Mg^{2+} concentrations in feed solutions of the 2nd and 3rd passes (Figure S2), the charge reversal effect may be weakened and thus the membrane becomes less positively charged, which is a possible explanation of the reduced Mg^{2+} rejection in later passes. Another possibility is that the Mg^{2+} adsorption is not enough to cause charge reversal so that the membrane remains negatively charged in later passes. The enhanced Donnan effect due to the reduced feed ionic strength in later passes leads to the reduced Mg^{2+} rejection.

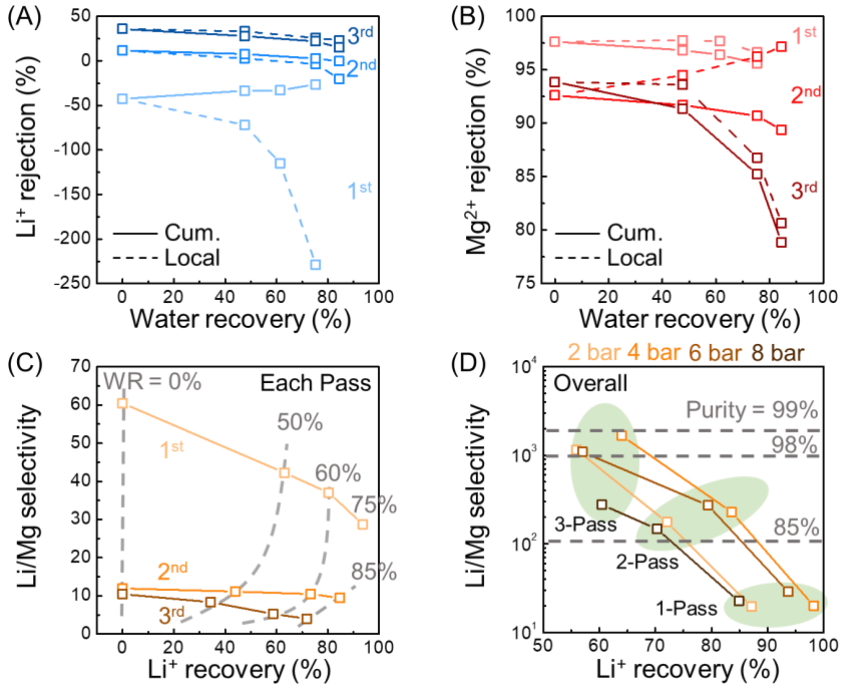

Fig. 2 Performance of a three-pass Li/Mg separation process without brine recirculation. (A-B) Local and cumulative Li^+ rejection (A) and Mg^{2+} rejection (B) as a function of water recovery in each pass. (C) Li/Mg selectivity versus Li recovery in each pass. Pressure in panels (A-C) was 6 bar. (D) Overall Li/Mg selectivity and Li recovery variation with number of passes using different pressures. Feed solution was the simple $LiCl/MgCl_2$ mixture. Water recovery was 75% for the 1st pass and 85% for the rest.

Li/Mg selectivity is sensitive to Mg^{2+} rejection due to how selectivity is defined based on Eq. 4, especially when Mg^{2+} is well rejected (e.g., $R_{Mg} > 95\%$). Thus, the tradeoff between Li/Mg selectivity and Li recovery is most obvious in the 1st pass where the selectivity drops from 60 to less than 30 as Li recovery increases from 0 to over 90% (Figure 2C). The tradeoff still exists in the 2nd and 3rd passes, although Li/Mg selectivity becomes less sensitive to Li recovery (Figure 2C). The selectivity for the 2nd and 3rd passes (<15) is much lower than that of the 1st pass due to

the reduced Mg^{2+} rejection and increased Li^{+} rejection caused by roughly an order of magnitude reduction in MLR following each pass. In other words, we can achieve high Li recovery in 2nd and 3rd pass without sacrificing too much selectivity in the same pass, even though the selectivity is relatively low compared to that of the 1st pass.

The tradeoff between selectivity and recovery is affected by applied pressure or permeate flux (Figure S3). Although a higher pressure allows to achieve a higher water recovery, especially in the 1st pass where the osmotic pressure increases rapidly at high water recovery, the higher water flux resulting from a higher operating pressure can be detrimental to Li recovery: if water permeation is much faster than Li^{+} permeation, only a small fraction of Li^{+} in the feed solution can be recovered in the permeate.[16]

According to our recent work, the operating pressure also has a non-monotonic impact on the Li/Mg selectivity.[16] The lower selectivity in the low-pressure range is due to the weakened "dilution effect": the low water flux reduces the Mg^{2+} rejection to which the Li/Mg selectivity is very sensitive. The lower selectivity in the high-pressure range is a result of enhanced concentration polarization (CP) which increases the MLR at the membrane interface. The optimal pressure or water flux for optimal Li/Mg selectivity depends on both the membrane properties and feed solution composition (and was 4 bar in our case based on the results shown in Figure 2D). Overall, the Li/Mg selectivity exceeds 100 with the two passes for all tested pressure and can even exceed 1,000~2,000 (equivalent to a purity of 98%~99%) with three passes except when 8 bar was applied (Figure 2D). However, the cumulative loss of Li recovery (~40%) is also substantially higher than the single-pass process, which may be mitigated by recovering more water in each pass and by introducing the brine recirculation strategy.

Impacts of co-existing cations and anions on multi-pass Li/Mg separation

Real salt-lake brines are complex multicomponent solutions with high salinities, containing a variety of cations (e.g., Li^{+}, Mg^{2+}, Ca^{2+}, K^{+} and Na^{+}, etc.), in contrast to the simple dual cation feed solution with only LiCl and $MgCl_2$ as used in most prior studies. The presence of Ca^{2+} in the permeate of NF process would directly deteriorate the product purity as $CaCO_3$ is insoluble. While the presence of K^{+} and Na^{+} is less harmful to the Li purity, it can still compromise Li recovery due

to competitive transport in the NF process. Furthermore, the existence of other cations also changes the rejections of Li^+ and Mg^{2+} as compared to that in a simple Li/Mg feed, ultimately impacting the Li/Mg selectivity and Li recovery. A mixture of LiCl, $MgCl_2$, $CaCl_2$, KCl, and NaCl (complex 1 in Table S2) was tested as the feed to validate the effectiveness of multi-pass NF for enhancing Li/Mg selectivity in a more practical scenario. Mg^{2+} shows the highest rejections (85%~95%), while Ca^{2+} rejection is lower but still over 80%. Na^+ and K^+ have similar rejections as Li^+ (Table S3). Both Mg/Li and Ca/Li mass ratio drops by an order of magnitude after each pass, while Na/Li and K/Li mass ratio maintains almost unchanged over the three passes (Figure 3A). Therefore, the NFX membrane is effective to separate monovalent ions from divalent ions, but it shows no selectivity to monovalent cation pairs.

The impact of each co-existing cation (e.g., Ca^{2+}, K^+ and Na^+) on the Li/Mg selectivity has been investigated individually in the literature usually at the coupon-scale (i.e., zero water recovery),[28] but rarely tested in a mixture and with a high value of water recovery. The existence of Ca^{2+} is reported to increase Li/Mg selectivity,[28] as Ca^{2+} usually has a similar rejection as Mg^{2+} which increases the divalent/monovalent cation ratio and thus forces Li^+ rejection to be more negative to balance the transport of Cl^-. Meanwhile, the existence of other monovalent cations, Na^+ or K^+, is reported to decrease Li/Mg selectivity,[28] because both Na^+ and K^+ have a smaller hydrated radius than Li^+ and thus are preferably transferred across the membrane with less hindrance in both interfacial partition and intra-pore transport. When Ca^{2+}, K^+ and Na^+ co-exist in the feed mixture as chloride salts, their opposite individual impacts on Li/Mg selectivity offset each other to some extent, and thus the observed overall Li/Mg selectivity after each pass is similar to, or even higher than, that measured with the simple Li/Mg feed (Figure 3B). The overall Li/Mg selectivity with complex feed 1 approaches 2000 (equivalent to 99% purity) after the 3rd pass. However, Li recovery is further reduced when Ca^{2+}, K^+ and Na^+ co-exist, mainly due to the preferable transport of K^+ and Na^+ over Li^+. When SO_4^{2-} and Cl^- co-exist as anions (complex feed 2 in Table S2), rejections of cations (especially monovalent cations) increased due to the reduced total anion flux as SO_4^{2-} has lower permeance compared to Cl^-. As a result, both Li/Mg selectivity and Li recovery in the three-pass NF process were compromised as compared to the case where SO_4^{2-} was in absence (Figure 3B), consistent with a recent study showing that Li/Mg selectivity in coupon-scale experiments would be overestimated in the absence of SO_4^{2-}.[29] The Li-specific energy consumption (SEC_{Li}) of the three-pass NF process without brine recirculation is estimated

for the simple feed (0.23 kWh mol^{-1}), complex feed 1 (0.30 kWh mol^{-1}), and complex feed 2 (0.42 kWh mol^{-1}), which increases as less Li was recovered (Table S4).

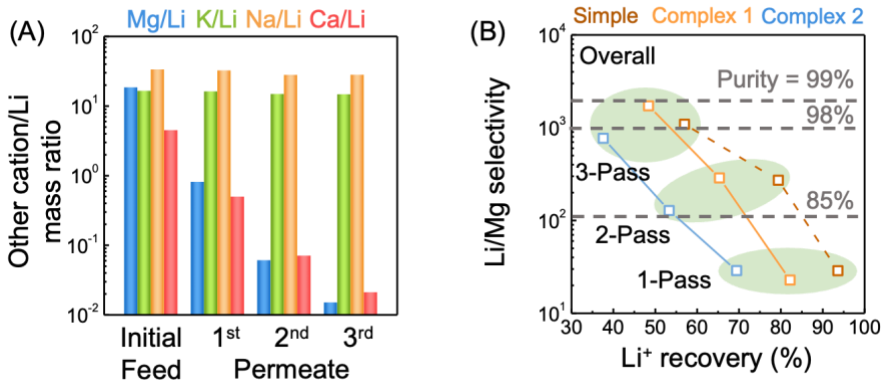

Fig. 3 Impacts of co-existing cations and anions on the performance of a three-pass Li/Mg separation process. (A) Mass ratio of co-existing cations to Li^+ in the feed and the permeate of each pass. Results of complex feed 1 (chloride as the only anion) were presented. (B) Overall Li/Mg selectivity and Li recovery variation with number of passes for simple and complex feed solutions. Complex 1 is sulfate-free and complex 2 contains sulfate. Water recovery was 75% for the 1st pass and 85% for the rest. Pressure was 6 bar.

High selectivity and recovery achieved simultaneously *with* brine recirculation

The Li/Mg separation performance of a four-pass NF process with brine recirculation was analyzed via module-scale modeling. The experimental validation of multi-pass NF with brine recirculation requires a pilot-scale system where a high value of water recovery can be achieved in a single pass and was thus not performed in this study due to the lack of access to pilot-test infrastructure. The local ion transport across the membrane in the module-scale NF model is characterized by ion permeabilities in the SDEM model. Ion permeability depends on both membrane properties and solution composition. Experimental results of the three-pass filtration without recirculation were used to fit Li^+ and Mg^{2+} ion permeabilities under different pressures and water recovery values. Mg^{2+} permeability increases by over an order of magnitude over the three passes, corresponding to the rejection reduction from 95% to 80% in Figure 2B, while Li^+ permeability variation is less substantial (Table S5). An empirical correlation (Eq. S4 and Table S6) successfully captures the dependence of ion permeability variation on Li^+ and Mg^{2+} concentrations in the brine stream after accounting for concentration polarization (Figure 4A). The module-scale NF model was then validated by predicting similar Li/Mg selectivity and Li recovery in a three-pass process without

brine recirculation for which we have collected experimental results (Figure 4B, in which the experimental curve is one of the curves reported in Figure 2D).

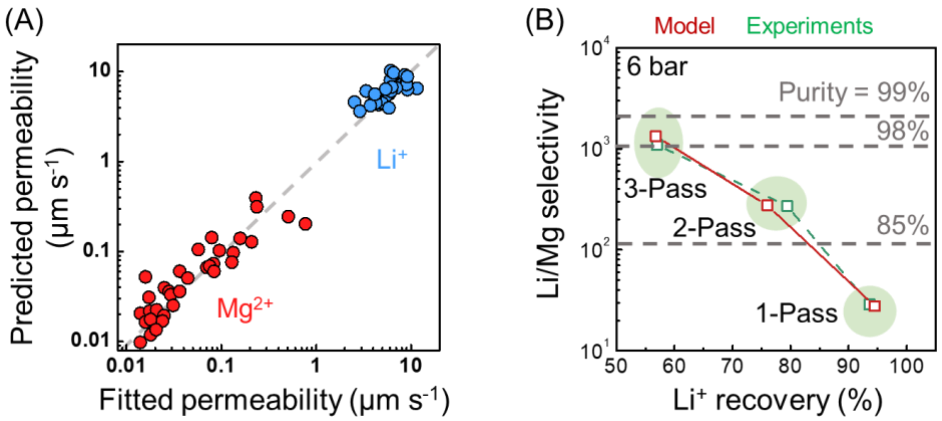

Fig. 4 Modeling module-scale performance of Li/Mg separation by NF. (A) Correlation of predicted and fitted ion permeabilities. Fitted ion permeabilities are from three-pass filtration experiments without recirculation. (B) Validation of the module-scale model by comparing performance predictions of the three-pass filtration process to experimental results. Model used same conditions as the experiments. Feed composition was 3.4 mM LiCl and 19.6 mM $MgCl_2$, water recovery was 75% for 1st pass and 85% for 2nd and 3rd passes, and pressure was 6 bar.

With a validated model that can reasonably predict module-scale performance, the effect of brine recirculation was analyzed. The overall water recovery can maintain at near 80% over four passes when brine is recirculated, while less than 60% of feed water can be recovered without recirculation, which causes substantial Li loss (Figure 5A). With brine recirculation, Li^+ concentrations in the permeate of each pass are higher than those without recirculation (Figure 5B), while Mg^{2+} concentrations in the permeates remain similar (Figure 5C). Our simulation predicts that the Li/Mg selectivity can exceed 4,000 (equivalent to 99.5% purity) with a four-pass filtration without brine recirculation, but at the cost of substantial Li loss of around 15~20% in each pass of the 2nd to 4th passes (dash line in Figure 5D). A high Li/Mg selectivity (4,889) and high Li recovery (96.6%) can be achieved simultaneously with four passes and brine recirculation (solid line in Figure 5D). Thus, the tradeoff between selectivity and recovery can be overcome with brine recirculation. As long as we can achieve high Li recovery in the 1st pass (where brine is not recirculated), the configuration of multi-pass with recirculation can achieve extremely high Li/Mg selectivity while maintaining a high Li recovery. Additionally, the high Li recovery achieved by brine recirculation also results in the reduction of energy consumption from 0.30 kWh mol^{-1} to 0.18 kWh mol^{-1} in the four-pass NF process (Table S4), though having recirculation adds process

complexity and capital cost. A comprehensive techno-economic analysis is necessary to fairly compare the potential economic benefit of the multi-pass NF process with other different Li/Mg separation technologies after accounting for pre- and post-treatment unit processes in complete Li extraction treatment trains, which is beyond the scope of the current study.

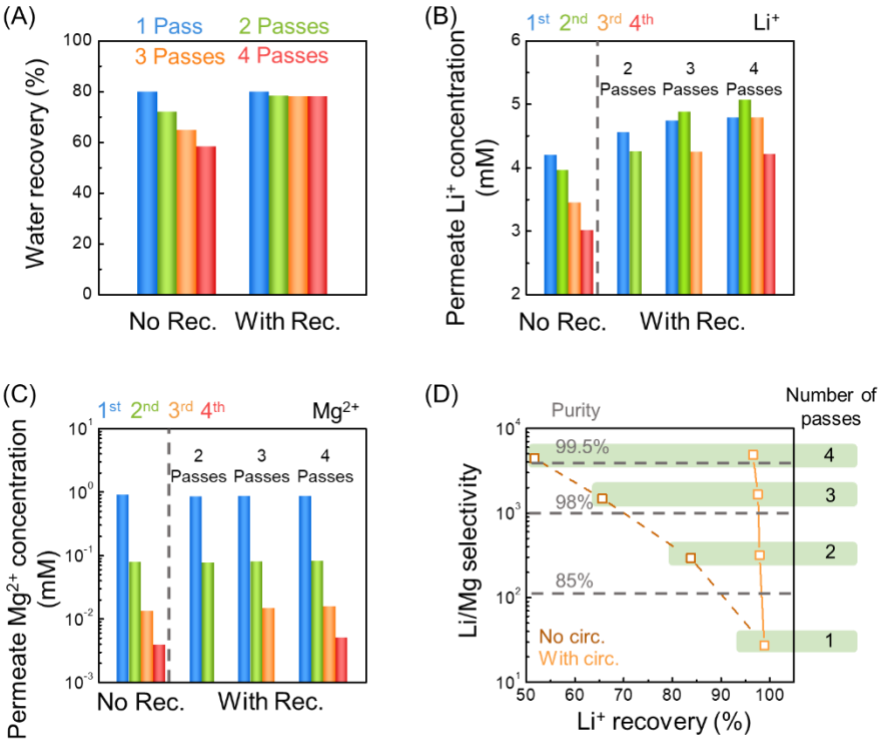

Fig. 5 Lithium recovery of multi-pass Li/Mg separation process enhanced by brine recirculation. (A) Water recovery with and without brine recirculation as a function of number of passes. (B) Li^+ and (C) Mg^{2+} concentration in the permeate of each pass in the multi-pass NF process with and without brine recirculation. (D) Overall Li/Mg selectivity and Li recovery with and without recirculation as a function of number of passes. Feed solution was the simple $LiCl/MgCl_2$ mixture. Pressure was 6 bar. Water recovery was set as 80% for the 1st pass and 90% for the rest. Mass transfer coefficient of 100 L m^{-2} h^{-1} was used to account for concentration polarization. The labels "No Rec." and "With Rec." in the x-axis stand for "without brine recirculation" and "with brine recirculation", respectively.

IMPLICATIONS

NF is a promising unit process in the treatment train for extracting Li^+ from brine lakes with high mass ratios of Mg^{2+} to Li^+. However, the Li/Mg selectivity of currently available NF membranes is not high enough to satisfy the industrial product purity requirements in a single-pass filtration. Advances in membrane material research may improve the situation but unlikely achieve satisfactory separation in a single pass. The multi-pass NF process with brine recirculation

proposed in this study can achieve ultra-high selectivity without sacrificing Li recovery. The performance may be further enhanced by optimizing the operating pressure and water recovery in each pass, and by applying novel NF membranes with better performance than the tested commercial NF membrane. We note that the feed solution used in this study is relatively dilute (corresponding to a large dilution factor), which shows benefits in separation performance, though from a practical point of view, will require a larger membrane area and a substantial amount of fresh water to initiate the process. Thus, performance of the multi-pass NF with more concentrated feed solutions needs further investigation to evaluate the proper dilution factor considering the potential tradeoff between separation performance and cost. Lastly, although the context of this study is on Li/Mg separation, the technical approach of multi-pass NF with recirculation is expected to be also effective for other types of solute-solute separations in resource extraction and recovery.

ASSOCIATED CONTENT

The Supporting Information is available free of charge at: XXX

Module-scale NF model for Li/Mg separation (Text S1); Properties of the commercial NF membrane used in this study(Table S1); Composition of the synthetic brines to study impacts of co-existing cations and anions (Table S2); Rejections of cations in the three-pass Li/Mg separation process (Table S3); Energy consumption of the multi-pass NF process for Li/Mg separation (Table S4); Fitted ion permeability at different concentrations and pressures (Table S5); Linear correlation coefficients for ion permeability (Table S6); Permeate flux at different water recovery under different operating pressures in the 1st pass (Figure S1); Ion mass concentration and MLR in the initial feed, and permeates of each pass (Figure S2); Li/Mg selectivity and Li recovery at different water recovery under different pressures (Figure S3).

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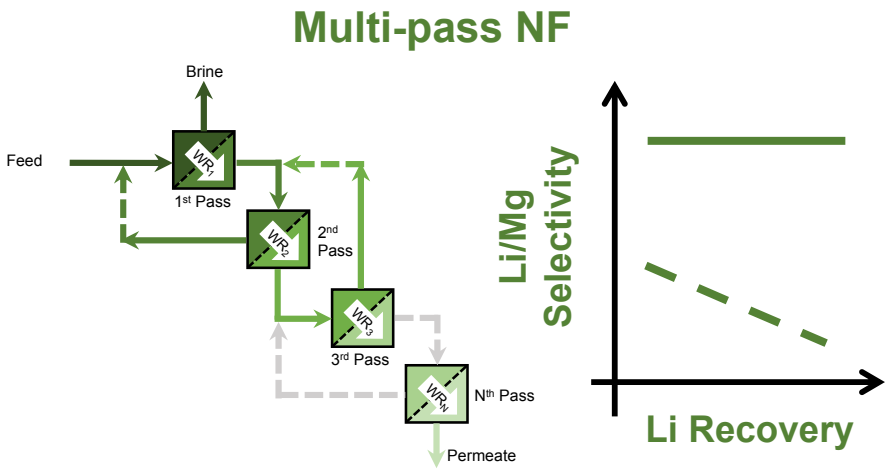
488 TOC Art



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