





Article

Assessing the Viability of Integrating Evaporation and Solvent Extraction Systems for Lithium Recovery from Low-Grade Brines

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Abstract: In recent years, the demand for lithium, essential to the high-tech and battery sectors, has increased rapidly. The majority of lithium carbonate is now sourced from continental brines in Latin America, owing to the lower production costs and reduced environmental impact. In Europe, often overlooked but promising lithium resources could include highly mineralized underground waters. Therefore, this study investigates the enrichment of these low-grade solutions (<100 mg/L Li) through evaporation followed by solvent extraction (SX) processes under specific conditions. The effectiveness and the technical feasibility of lithium extraction were evaluated using binary synthetic, multicomponent semi-synthetic, and real brine samples. The popular tributyl phosphate/methyl isobutyl ketone (TBP/MIBK) system, supplemented with FeCl₃ and AlCl₃ as co-extractants, was employed as the organic phase. Evaporation resulted in significant lithium losses (up to 80%), reduced to ~10% by washing the crystallisate obtained during evaporation with ethanol. The results from SX tests revealed differences between the synthetic and real brines. While the synthetic brines exhibited satisfactory lithium extraction yields (91%), the real brines showed a significantly lower extraction efficiency (~32%), rendering the tested system ineffective. Solid phase precipitation during the SX trials was observed for both the synthetic and real brines, which were concentrated before the SX stage, highlighting the challenges in lithium-recovery processes. However, semi-synthetic brine trials yielded promising results, with a satisfactory extraction efficiency (76%), and the absence of physical problems (emulsion, long disengagement, etc.). This reveals the importance of the chemical composition of brines and emphasizes the need for varied procedural approaches in lithium-recovery processes.

Keywords: evaporation; solvent extraction; brine enrichment; lithium losses



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1. Introduction

The focus on green technologies in developed countries has led to a growing demand for sustainable energy solutions, highlighting the need to secure lithium supplies. Lithium plays a crucial role in the development of rechargeable lithium-ion batteries, essential for cleaner energy sources. Apart from its role in batteries, lithium is used in various industrial applications, such as the manufacturing of alloys, aircraft parts, ceramics, and glass, and the production of lubricants [1]. In 2020, it was recognized as a critical raw material due to its economic importance and the potential risk of supply shortages [2].

Lithium can be found in different natural sources such as hard rock pegmatite orebodies, sedimentary clay deposits, and saline subsurface waters (brines). Brines, especially in arid climates like the Lithium Triangle in South America, are particularly interesting due to their abundance. Industrial processing of brines for lithium recovery involves evaporative concentration followed by the precipitation of lithium carbonate [3]. While this approach

has the advantage of being relatively cost-effective and simple, it is time-consuming and depends on favorable weather conditions, unless alternative heat sources like geothermal energy are employed.

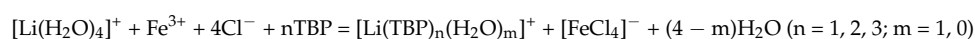
Simultaneously, there is the ongoing development of alternative methods known as Direct Lithium Extraction (DLE) processes, aiming to overcome the limitations of traditional approaches. These weather-independent methods use more advanced technologies, including adsorption on inorganic solvents, solvent extraction (SX), ion exchange (IX), and membrane-based processes, to concentrate lithium from a solution.

Among the various DLE methods, SX stands out as the most promising choice. This is mainly due to its versatility in effectively treating both concentrated and diluted solutions. Furthermore, SX shows potential in the efficient separation of lithium, enabling large-scale continuous operation, and requiring less time and energy [4].

However, the direct application of this method for treating low-concentration brines (<100 mg/L Li) would be impractical and uneconomical. Therefore, preconcentration of such solutions to a level that justifies the application of the SX method becomes necessary. Evaporation appears to be an appropriate way to achieve this, as it not only elevates lithium concentration but also aids in the partial removal of accompanying metal ions, such as Na⁺ and K⁺.

In recent decades, the most frequently studied organic extractants have included organophosphorus compounds, as well as, β-diketones, crown ethers, and ionic liquids [5–11]. Among them, the mixtures of tri-*n*-butyl phosphate (TBP) and FeCl₃ have gained popularity because of their relatively low cost, high lithium-recovery yields, and the high selectivity of this system when brines of high Mg/Li ratio are treated [12,13]. The mechanism of lithium extraction was explained broadly in several papers [14–18]. Generally, TBP can displace water molecules from the coordination sphere of the Li aqua complex to create a series of complex cations: [Li(TBP)]⁺, [Li(TBP)(H₂O)]⁺, [Li(TBP)₂]⁺, and [Li(TBP)₃]⁺. However, to balance the charge, a counter anion, such as [FeCl₄][−] is needed, because the transportation of Li⁺ into the organic phase through the coordination interaction between TBP and Li⁺ alone is not feasible.

Hence, the efficient transport of Li⁺ into the organic phase is achieved by forming ion pairs as shown below:



Accordingly, it is important to ensure an appropriate amount (>6 mol/L) of chlorides in the aqueous phase, needed for the formation of FeCl₄[−] species, facilitating the transport of lithium into the organic phase. An increasing HCl concentration can elevate the chloride content, as well as prevent the hydrolysis of ferric ions; however, the competition reaction of Li⁺ and H⁺ with TBP occurs, resulting in a low extraction of Li⁺. Additionally, TBP can degrade in the presence of strong acids [19]. Therefore, it is suggested to introduce salt, which would be the source of Cl[−] ions, and at the same time, would act as a salting-out agent. For this goal, a few salts were considered, and nevertheless, MgCl₂ and AlCl₃ were the most common [14,15,18,20]. The advantage of using MgCl₂ is that it is a natural component of brines, but AlCl₃ can provide a sufficient Cl[−] content at relatively low acidities and cause a stronger salting-out effect [4].

Surprisingly, scientific papers concerning the SX of lithium using the TBP/FeCl₃ system rarely describe its application to real brine solutions [21–23]. Typically, the qualitative composition reported for genuine lithium sources includes elements with the highest concentrations, such as Na, Mg, K, and Li. Occasionally, Ca and B, as well as certain anions, are taken into consideration. However, synthetic brines, either multi-component, i.e., Na, K, Mg, Li [13,24–28], or binary, i.e., Li, Mg [29–32], are more commonly studied. The latter, in particular, are chosen due to the challenges associated with the industrial processing of brines with a high Mg/Li ratio.

In the above-cited literature, the composition of brines varies greatly. The concentration of lithium is typically at a level of 0.35 g/L in both synthetic and real solutions, although in the latter case, some authors investigate brines concentrated up to 8 g/L. The sodium

content ranges from 1.7 to 140 g/L in model solutions, whereas in real brines, the range is much narrower (from 1.3 to 5.7 g/L). Similarly, the range of potassium concentrations is wide for synthetic brines (from 0.6 to 156 g/L) and relatively narrow for real solutions (from 0.62 to 5.1 g/L). Magnesium contents exhibit significant variability, ranging from 2.5 to 118 g/L in synthetic brine, while in real brines, concentrations of this element are high and within a narrow range, i.e., between 85.8 and 115 g/L. Calcium, on the other hand, is rarely taken into account in the composition of brines, and its concentration varies (<40 mg/L or 4–160 g/L).

Usually, research on Li solvent extraction focuses on fundamental aspects of the studied extraction system, such as the extraction mechanisms, or the assessment of extraction efficiency and process selectivity. Less frequently, published works investigate the application of the SX process as an intermediate step in brine processing, with the ultimate goal of Li_2CO_3 precipitation. In this case, it is crucial to achieve the target Li concentration of at least 6 g/L [33]. This value is justified by the solubility of lithium carbonate (12.9 g/L at 25 °C, [34]), equivalent to 2420 mg/L of Li in the saturated solution. While some studies have reported high lithium concentrations (20–40 g/L) in stripping liquors [17,21,35,36], it is essential to note that reaching this target typically requires a multi-stage process (5–13 stages), including extraction, washing, scrubbing, and stripping [17,26,37,38]. It should be emphasized that obtaining high Li content in final solutions was feasible due to initially high lithium concentrations (2–9 g/L), resulting in a relatively moderate lithium concentration ratio (~4–10 times).

Enriching lithium-rich solutions by solvent extraction appears to present less difficulty compared to poor (<100 mg/L) lithium solutions, where achieving the expected concentration and purification levels is considerably more demanding.

Therefore, the main objective of the present work was to enrich low-grade lithium brines to a level sufficient for the precipitation of lithium carbonate product. To achieve this, and to examine the effect of elemental matrix on lithium recovery, synthetic, semi-synthetic, and real brines were treated by evaporation followed by solvent extraction. A common tributyl phosphate/methyl isobutyl ketone (TBP/MIBK) system, supplemented with FeCl_3 and AlCl_3 as co-extractants, was used as the organic phase. For this purpose, synthetic, semi-synthetic, and real brines were treated by evaporation followed by solvent extraction. The effectiveness of the individual methods, as well as the practical aspects of combined operations for lithium recovery, was assessed. Not only the Li-extraction efficiency, but also the technical feasibility of both processes, was discussed in detail.

2. Materials and Methods

2.1. Characterization of Brines (Samples)

Three types of brine solutions were studied: (a) synthetic binary solutions (S1–S4), (b) real brines (GR, PR), and (c) semi-synthetic brine solution (PR-doped with lithium). The GR and PR samples were collected, respectively, from the gas-production well settled in Permian dolomites and sandstones, from the depth interval of 1482–1500 m, and from the geothermal well settled in Jurassic sandstone at depth intervals 1509.9–1563.9 m and 1623.9–1647.9 m. Both wells are within the territory of western Poland. The sampling sites were selected by the BrineRIS project geology team. The project aims to identify Li-enriched deep geothermal brines across six European countries, including Poland. Criteria for selection were the lithium content of the archival assays, the availability of deep boreholes, and the technical feasibility of sampling volumes greater than 100 L. Due to the limited volume of real brines, the tests were initially conducted on synthetic solutions to match the test procedures to the water type. The simplified composition of lithium source solutions is given in Table 1, while the full analysis for real brines (GR, PR) is attached in the Appendix A (Table A1).

Table 1. The simplified content of the main components of tested brines.

Brine Source	Li	Na	Ca	Mg	K	Cl ⁻ (g/L)	pH
	mg/L						
S1–S4	35–50	70,000					8.7
PR	1.17	63,556	2451	913	266	64	8.7
GR	65	96,972	17,475	871	3176	140	5.5

2.2. Reagents and Solutions

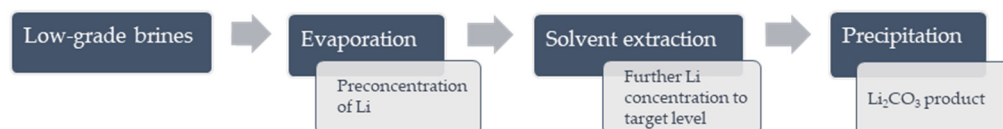
Model brine solutions were prepared by dissolving appropriate amounts of sodium chloride (NaCl, p.a., Eurochem BGD Sp. Z.o.o., Tarnów, Poland) and lithium chloride (LiCl, p.a., Sigma Aldrich, Saint Louis, MI, USA) in distilled water.

In solvent-extraction experiments, chloride salts of iron (FeCl₃·6H₂O, p.a., Chempur®, Piekary Śląskie, Poland) and aluminum (AlCl₃, p.a., Avantor Performance Materials Poland S.A., Gliwice, Poland) were added to the aqueous feed solutions as Li co-extractants. Additionally, HCl solution (35–38%, p.a., PPH STANLAB Sp. z o.o., Lublin, Poland) was added to correct the acidity of aqueous feed solutions.

The mixtures of 60% (v/v) tri-n-butyl phosphate (TBP, Sigma Aldrich, Saint Louis, MI, USA) in methyl isobutyl ketone (MIBK) (>99%, Merck, Darmstadt, Germany), kerosene (pure, Sigma Aldrich, Saint Louis, MI, USA), or 1,2-dichloroethane (1,2-DCE) (>99.5%, Avantor Performance Materials Poland S.A., Gliwice, Poland) served as organic phases.

2.3. The Concept of Work and Experimental Procedures

Considering the low concentrations of lithium observed in the tested brines, a two-stage concentration approach was implemented (Figure 1). Initially, the starting solution undergoes a preconcentration process through evaporation. Subsequently, lithium extraction is carried out from the partially concentrated brine. This sequential process aims to produce solutions with higher lithium content, suitable for the precipitation of lithium carbonate (Li₂CO₃) as the final product.

**Figure 1.** The general concept of low-grade brines treatment.

2.3.1. Evaporation

The synthetic solutions S1–S4 and real low-grade brine GR underwent evaporation according to the following procedure: a portion of the brine solution was placed into a beaker, mixed, and heated intensely on a hot plate for several hours. As the volume of the solution decreased, additional brine portions were incrementally added. Once a significant portion of the solution had evaporated, the content of the beaker was separated using a Büchner funnel under reduced pressure. The precipitate collected on the filter was dried, while the filtrate was reintroduced for further evaporation. This cycle was repeated until the desired volume was achieved. The concentrated brine solutions (CS_n) were then directed to solvent extraction testing.

In experiments where lithium losses were estimated, filter cake from evaporation was washed with ethanol according to the scheme presented in Figure 2.

Lithium distribution between liquid streams: concentrated brine and ethanol washings were calculated as D_{Li} (%) and lithium losses were assessed based on lithium contribution in the mentioned streams.

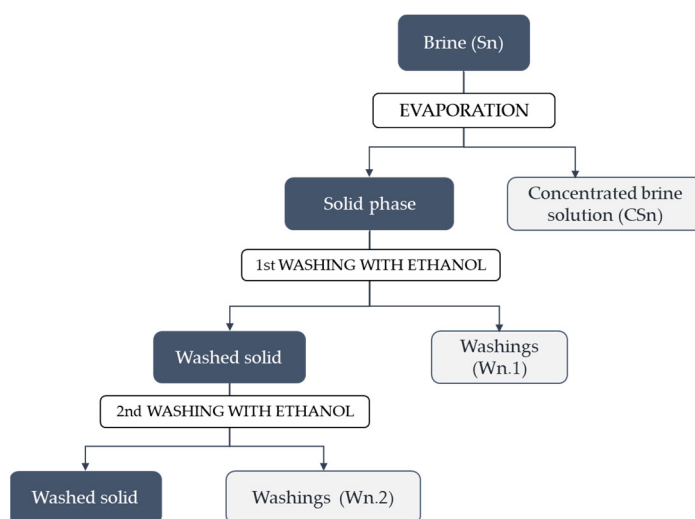


Figure 2. The overall concept of brines enrichment by evaporation, and recovery of lithium losses by washings with ethanol; n—number of treated S solution.

2.3.2. Solvent Extraction

In all solvent-extraction experiments, aqueous and organic phases were contacted for 10 min in a separatory funnel at an A/O (aqueous/organic) ratio of 1 at ambient temperature. After phase separation (30 min), a sample of the raffinate was collected for analysis. The lithium content in the organic phase ($m_{Li,org}$) was determined through mass balance, representing the difference between the initial lithium mass in the aqueous feed solution ($m_{Li,aq}^{in}$) and the remaining lithium mass in the raffinate solution ($m_{Li,aq}^{out}$). Lithium-extraction yields (E_{Li}) and partition coefficients (P_{Li}) were calculated according to the following equations:

$$E_{Li}(\%) = \frac{m_{Li,org}}{m_{Li,aq}^{in}} \cdot 100\% = \frac{m_{Li,aq}^{in} - m_{Li,aq}^{out}}{m_{Li,aq}^{in}} \cdot 100\% \quad (1)$$

$$P_{Li} = \frac{[Li]_{org}}{[Li]_{aq}^{out}} \quad (2)$$

where $[Li]_{aq}^{out}$ and $[Li]_{org}$ denote lithium concentrations (mg/L) in raffinate and loaded organic phases, respectively.

2.4. Measurements of Li Concentrations

The concentration of lithium (c_{Li}) was determined in all aqueous solutions using atomic absorption spectrometry with the Varian SpectraAA 20Plus instrument (Varian Australia Pty. Ltd., Melbourne, VIC, Australia). Measurements were performed in absorption mode at a wavelength of 670.8 nm using an external 5-point standard curve. Both standard and sample solutions were prepared by appropriate dilutions by weight to avoid differences in their densities. The experimentally determined values for the limit of detection (LOD) and limit of quantification (LOQ) of lithium (in mg/L) are 0.00634 and 0.0190, respectively.

3. Results and Discussion

The analysis of brine composition (Appendix A, Table A1) indicates that the available natural sources have low lithium concentrations and contain significant amounts of sodium and calcium. Both the PR and GR brines have rich elemental matrices, which may pose a substantial challenge in the context of lithium recovery.

3.1. Evaporation Trials

The evaporation method uses the high solubility of lithium chloride in water (845 g LiCl/L H₂O at 20 °C), thanks to which, part of the remaining components—mainly, alkali metal chlorides of lower solubility (360 g/L NaCl [39] and 355 g/L KCl [40])—precipitate from the solution. As a consequence, a solution with a higher Li content is obtained. However, it is necessary to consider the losses of lithium in the precipitate. Thus, evaporation experiments were conducted in an attempt to estimate lithium losses. For the first trial, the synthetic lithium solution (S1) was used, with a Li concentration of 50 mg/L. The dependence of the lithium concentration and its losses during evaporation on the volume of brine are presented in Figure 3.

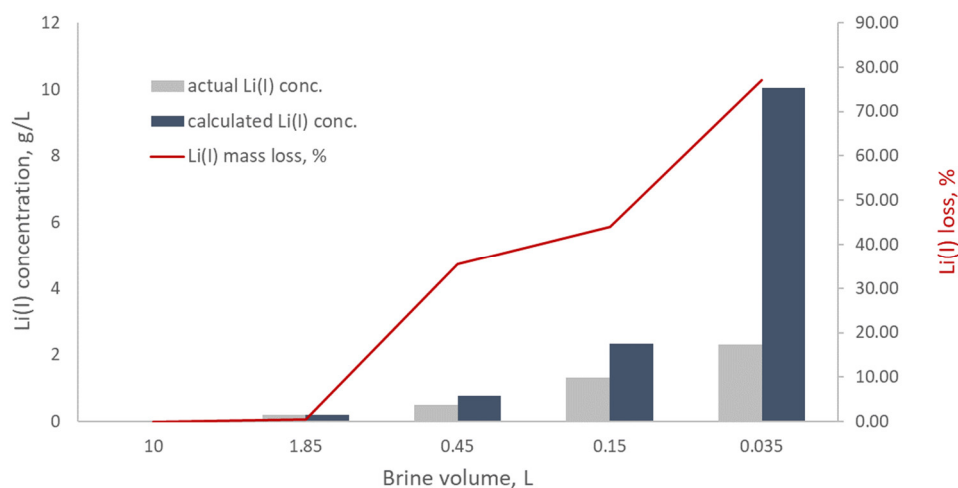


Figure 3. The dependence of lithium(I) concentration and its losses during evaporation on the volume of brine.

It was observed that during the reduction of the solution volume, the concentration of lithium increases. However, in the first stage of evaporation (volume reduction from 10 to 1.85 L), there are no lithium losses. Further volume reduction results in significant lithium losses, causing a substantial decrease (close to 80%) in the mass of lithium in the solution. This weight loss may be attributed to incomplete phase separation, resulting in the retention of a portion of the solution within the solid phase.

This conclusion corresponds well with the observations of other authors, who have demonstrated that lithium losses increase with the degree of brine concentration during progressive evaporation. In the study [41], the degree of concentration during brine boiling was examined by measuring the height of evaporated water. It was found that lithium losses can reach up to 80%, which is related to brine retention in the crystallized phase. Similar observations were noted in [42], where it was shown that at concentration ratios up to 20, lithium losses are negligible, but above this value, they can reach up to 60%, depending on the final lithium concentration in the brine. Other authors [43], investigating the evaporation of real brines under natural sunlight, demonstrated minimal lithium losses (<0.004%), although the concentration ratio was rather low, i.e., around 5.

It is important to note that the losses are affected not only by the degree of brine concentration but also by the initial lithium concentration in the brine undergoing evaporation. With similar concentration ratios, greater losses can be expected for brines with higher initial lithium concentrations.

Entrapped lithium can potentially be recovered by washing the solid with specific solvents that exhibit differing solubilities for LiCl and NaCl. An example of such a solvent is ethanol, with a solubility of lithium chloride of 243 g/L [34] and sodium chloride of 0.65 g/L [44].

To verify this concept, two attempts were made, according to the scheme presented in Figure 2. In both trials (S2, S3), 1 L of a model brine was evaporated, reducing the volume

to 140 mL and 93 mL, respectively, resulting in two concentrated brine solutions: CS2 and CS3. The precipitated sodium chloride phase was separated from the solution and washed twice with a portion of ethanol (>99.5%, Merck). The results of the chemical analysis of the obtained solutions are presented in Tables 2 and 3.

Table 2. The balance of lithium content in the evaporation and ethanol washing trials for S2 brine.

Solution	Volume (mL)	c_{Li} (mg/L)	m_{Li} (mg)	D_{Li} (%)
S2	1000	50.0	50.0	100
CS2	140	201.5	28.2	56
Washings W2.1	147	98.4	14.5	29
Washings W2.2	73	20.9	1.53	3.0

Table 3. The balance of lithium content in the evaporation and ethanol washing trials for S3 brine.

Solution	Volume (mL)	c_{Li} (mg/L)	m_{Li} (mg)	D_{Li} (%)
S3	1000	50.0	50.0	100
CS3	93.0	248.5	23.1	46.2
Washings W3.1	153	133.3	20.4	40.8
Washings W3.2	82.0	32.6	2.7	5.4

As shown in Table 2, the initial volume of the S2 brine underwent a 7-fold reduction, resulting in the lithium concentration in the final solution (CS2) slightly exceeding 200 mg/L. Unfortunately, this was significantly below the expected value equal to 350 mg/L. This discrepancy was attributed to a considerable loss of solution within the separated wet sodium-chloride sludge, leading to a notable depletion of lithium, estimated at around 44%. The double washing of the precipitate with ethanol facilitated the recovery of lithium to a level of 32%.

In the second trial (Table 3), the model brine S3 was concentrated to a volume of 93 mL (CS3). The precipitated sodium chloride was washed, as in the previous experiment. The higher degree of brine enrichment resulted in an elevated lithium concentration (up to 248 mg/L). However, this also led to a higher loss of lithium in the wet chloride precipitate (up to 53.6%). The lithium mass balances presented in Tables 2 and 3 suggest that ethanol washing of the evaporative solid by-product can lessen lithium losses to 10–12% of their original levels. This can be achieved by blending both liquid streams and, subsequently, separating this mixture through alcohol distillation. Consequently, the ethanol could be recycled and reused.

Based on the above results, two subsequent attempts were made to concentrate the real GR brine. In both trials, 1 L of the raw brine, containing ca. 65 mg/L of lithium and the original elemental matrix (as shown in Table A1, Appendix A), was used. In this case, the distribution ratio of lithium (D_{Li}) between two liquid streams (concentrated brine/washings) was estimated. The obtained results are presented in Table 4.

Table 4. The evaporation parameters for real GR brine treatment.

Solution	Volume Reduction Ratio	c_{Li} (mg/L)	D_{Li} (%)
CGR1	7	376.7	80/20
CGR2	14	478.0	56/44

Similarly to synthetic brines, the evaporation treatment of natural brine solutions leads to lithium losses in the solid phase. As shown in Table 4, the greater the reduction in brine volume, the higher the lithium concentration in the final solution and the higher losses of lithium in the precipitate. Thus, in optimizing the processes involving evaporation, the consideration of metal losses for mass balance is crucial.

3.2. Solvent Extraction Experiments

3.2.1. Lithium Extraction from Synthetic Solution

In our studies, we aimed to assess the efficiency of lithium(I) extraction using different organic solutions: Org 1: TBP + MIBK, Org 2: TBP + kerosene, and Org 3: TBP + dichloroethane. In each organic phase, the concentration of TBP was maintained at 60% (*v/v*), as the most optimal for Li extraction [36,45,46]. Low-grade lithium(I) brine (S4), containing substantial amounts of Na, was concentrated by evaporation and used as the aqueous feed phase (CS4) for the SX tests. The initial experiments were conducted on two-component solutions (Li, Na), with no additives.

In the subsequent experiments, AlCl₃ and FeCl₃ were added to the aqueous feed to assess their effect on Li extraction performance. Various research studies have indicated that the Fe/Li mole ratio required for satisfactory extraction ranges from 1 to 3 [14,17,24,26]. Previous investigations have identified 2 mol/L (M) AlCl₃ as an optimal concentration [18]. Thus, in our studies, the concentration of AlCl₃ was held constant at 2 M, while the Fe/Li ratio varied from 1 to 3. The acidity of the aqueous feed phase was regulated by the addition of an HCl solution to achieve a pH level of 0.5. The results obtained for the synthetic (CS4) brine are summarized in Table 5 and Figure 4.

Table 5. Lithium-extraction efficiencies with TBP systems for synthetic brine after evaporation (CS4).

CS4 Composition	SX Conditions		E_{Li} (%)	P_{Li}
	Organic Phase	Aqueous Phase		
Li: 917 mg/L Na: saturated		CS4 & no additives	-	-
	Org 1: 60% TBP + MIBK	CS4 + FeCl ₃ (Fe/Li = 1) + 2 M AlCl ₃	59.0	1.197
		CS4 + FeCl ₃ (Fe/Li = 2) + 2 M AlCl ₃	73.0	2.437
		CS4 + FeCl ₃ (Fe/Li = 3) + 2 M AlCl ₃	91.2	10.395
		CS4 + FeCl ₃ (Fe/Li = 3)	49.7	0.986
	Org 2: 60% TBP + kerosene	CS4 + FeCl ₃ (Fe/Li = 3) + 2 M AlCl ₃	84.3	5.927
	Org 3: 60% TBP + 1,2-DCE	CS4 + FeCl ₃ (Fe/Li = 3) + 2 M AlCl ₃	87.4	7.168

These results demonstrate that the SX experiment conducted with no additions of co-extractants yielded no Li extraction. However, the successive addition of Fe and Al chlorides lead to an increase in lithium(I)-extraction efficiency and a partition coefficient of up to 90% and 10.395, respectively. In the case where only FeCl₃ was added, a considerable decrease in efficiency, of ~40%, was observed. It is worth noting that the requirement for a sufficient chloride ions concentration was met, as the saturated NaCl solution yields at least 10 M of Cl⁻ ions. This primarily ensures the formation of [FeCl₄]⁻ in the aqueous phase, which complexes with TBP in the organic phase, thus preventing the back-transport of iron ions from the organic to the aqueous phase [4]. However, the contribution of AlCl₃ to the overall extraction process turned out to be significant, indicating its important role as a salting-out agent. The above findings agree with those of Cui et al. [18], who noted that the presence of FeCl₃ and AlCl₃ has a synergistic effect on lithium extraction. In general, the addition of salts can be beneficial for the extraction of metal ions, and this phenomenon correlates with the position of anions and cations in Hofmeister sequences. For anions, they can be arranged as: OH⁻ ≈ SO₄²⁻ ≈ CO₃²⁻ > ClO₃⁻ ≈ BrO₃⁻ ≈ Cl⁻ ≈ OAc⁻ ≈ IO₃⁻ > Br⁻ ≈ I⁻ > NO₃⁻. Similarly, for cations, the order is as follows: N(CH₃)₄⁺ > (CH₃)₂NH₂⁺ > NH₄⁺ > K⁺ > Na⁺ > Cs⁺ > Li⁺ > Mg²⁺ > Ca²⁺ > Ba²⁺. Anions positioned toward the left side of the sequence generally tend to reduce the solubility of nonpolar molecules in water. This trend applies also to cations, although their effects tend to be more diverse and dependent on the nature of the solute [47–49].

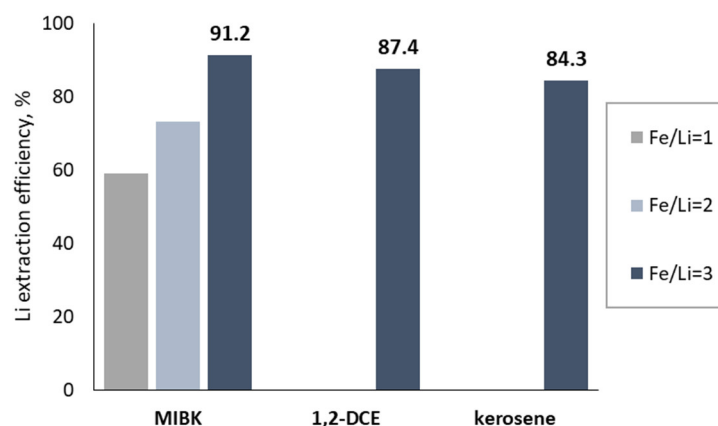


Figure 4. The effect of Fe/Li ratio and the type of diluent on Li(I) extraction from synthetic brine after evaporation (CS4).

The observed synergistic effect does not solely originate from the constituents of the aqueous phase but can also be partially attributed to solvent–diluent interactions. MIBK has been identified as the co-extracting agent, primarily due to the presence of the $-C=O$ functional group [36]. It has been noted that the functional group of TBP ($-P=O$) was stronger than that of MIBK [19,36]. To verify this observation, MIBK was replaced by kerosene and 1,2-dichloroethane, while the parameters of the aqueous phase remained constant. The obtained results (Table 5 and Figure 4) confirm these observations. The change of the diluent leads to a slightly lower efficiency of the extraction process—87.4 and 84.3, respectively, for dichloroethane and kerosene. It can be inferred from the above study that altering the diluent in the organic phase (containing 60% (*v/v*) TBP) is less crucial for achieving successful Li extraction.

The key aspect of any SX process is its physical behavior, such as susceptibility to the formation of third phase/crud, or progressive deterioration in phase separation. In our experiments, during the preparation of the aqueous feeds, a white solid was observed and subsequently filtered out before extraction. XRF analysis (Appendix A, Table A2) of the collected precipitate indicated that it was mainly the mixture of Na, Al, Mg, and Ca chlorides—likely a result of exceeding their solubility limit during the introduction of chloride ions into the saturated brine solution. The appearance of the precipitate was also noted during the disengagement of aqueous and organic phases. The precipitation of the solid phase complicates the liquid–liquid extraction process, as it requires an additional operation for its separation. However, it is worth noting that no third phase was observed.

3.2.2. Lithium Extraction from Semi-Synthetic and Concentrated Real Brine

Based on the described experiments, the optimal conditions were selected. They include an organic mixture of 60% (*v/v*) TBP in MIBK, and an aqueous phase containing $FeCl_3$ at a molar ratio of $Fe/Li = 3$, along with 2M $AlCl_3$. However, it is important to note that the feed for extraction consisted of only two-component solutions. Therefore, it was decided to confirm the effectiveness of the chosen system for solutions of a richer composition (containing a mineral matrix)—similar to natural brines. Consequently, the optimal conditions were further verified on semi-synthetic and evaporated real brine (CGR2, Table 4) solutions. It should be noted that a semi-synthetic solution was prepared by blending real PR brine (composition given in Tables 1 and A1) with a synthetic LiCl solution, resulting in a multi-element solution with final lithium(I) concentration of around 350 mg/L. In this way, the composition of the aqueous phase was modified to reflect that of natural brines rich in lithium. The other solution (CGR2) was prepared by the evaporation of real GR brine (composition in Tables 1 and A1), following the procedure outlined in Section 2.3.1. As before, the appropriate amounts of $FeCl_3 \cdot 6H_2O$ and $AlCl_3$ were added to both solutions, along with an HCl solution for pH regulation, maintaining the extraction

parameters from the previous experiments. Additionally, for the natural brine, experiments with no additions, as well as successive additions of chloride salts were run. The obtained results for the processing of both semi-synthetic (PR-doped) and CGR2 brine are presented in Table 6.

Table 6. Lithium-extraction efficiency from semi-synthetic (PR-doped) and concentrated (CG2) brines with TBP-MIBK system.

Aq Phase Composition	c_{Li} (mg/L)	SX Conditions	E_{Li} (%)	P_{Li}
PR-doped	350	Org 1 Aq + FeCl ₃ (Fe/Li = 3) + 2 M AlCl ₃	76.1	3.179
		Org 1 Aq: no additives	1.0	0.010
CGR2	478	Org 1 Aq + FeCl ₃ (Fe/Li = 3)	13.1	0.151
		Org 1 Aq + FeCl ₃ (Fe/Li = 3) + 2 M AlCl ₃	32.2	0.388

As can be seen, the Li-extraction efficiency for semi-synthetic brine (PR-doped) was estimated at 76% after a one-stage SX process. It is worth noting that unlike in the extraction of lithium from evaporated synthetic solution (CS4), no physical issues were observed in this case. Thus, the treatment of high-grade brines containing full elemental matrix through SX with TBP–MIBK systems seems promising.

On the contrary, processing real brines concentrated through evaporation presents challenges. Similarly to preliminary studies on Li SX from CS4 solution, the introduction of chloride salts has been found beneficial in terms of extraction efficiency (increasing it from 1 to 32.2%). However, the partition coefficients in the real brine SX tests exhibited significantly lower values compared to those calculated for the binary solutions, contributing to the observed weaker extraction efficiency. Comparing the SX results for the brines concentrated by evaporation, namely, the semi-synthetic binary brine (PR-doped), and the real brine CGR2, a significant drop in the extraction efficiency, from 76.1 to 32.2%, is evident.

Additionally, as for the synthetic concentrated brine (CS4), the appearance of a solid precipitate was observed.

It should be noted that evaporation results in increased concentrations of brine constituents, thus leading to an increase in ionic strength values. By considering only the concentrations of main ions, we can simply calculate these values based on the classic equation ($I = 0.5 \cdot \sum(c_i \cdot z_i^2)$, where c_i is the molar concentration of ion i and z_i is the charge of that ion). The lowest ionic strength and the lowest initial Li content were observed in the PR brine doped with lithium (~15 M), while the concentrated GR brine had the highest value of ionic strength (~35 M). The model CS4 solution had the highest lithium concentration, and a composition limited to Na⁺, Fe³⁺, Al³⁺, and Cl[−] ions, but also a high ionic strength (~27 M) after the evaporation. These differences in ionic strength values result from the presence of metal cations (Me: K, Ca, and Mg) in real brines, which are absent in synthetic brines.

In published works on Li SX, the influence of ionic strength on SX performance is often omitted. Usually, discussions regarding ionic strength focus on evaporation and the proper calculations of salt solubilities in multicomponent solutions [50–53]. Studies on ionic strengths suggest that ion interactions in concentrated brines (of high I values) should be considered based on the analysis of specific ion effects [47,54,55].

In light of this, to explain the observed decrease in Li extraction yields, the composition of the semi-synthetic and real concentrated brines, in terms of Me/Li ratios, were compared (Table 7).

Table 7. The Me/Li concentration ratios in semi-synthetic (PR-doped) and real concentrated (CGR) brines.

Metal Ion	<i>Me/Li</i>	
	PR-Doped	CGR2
Ca	7.0	365
K	0.8	66
Mg	2.6	18
Na	181.6	296

Based on the results, the concentration ratios of the main metal cations to lithium (*Me/Li*) differ significantly, except for Na/Li. It can be assumed that the contribution of Na in the examined brines (PR-doped and CGR2) is comparable. Attention should be focused on the content of Ca, K, and Mg in both solutions. It appears that the reduced Li extraction yield can be attributed to the higher content of the accompanying ions, particularly calcium, which is present in much higher concentrations in the CGR2 than in the PR-doped brine. This observation agrees well with the position of calcium in the Hofmeister series. As mentioned earlier (Section 3.2.1), the position of ions in the series indicates their tendency toward salting-out (left-sided) or salting-in effects (right-sided). Considering the composition of the examined brine solutions, chloride ions are the main constituents playing the role of salting-out agents. Increased Cl^- concentration (due to additions of FeCl_3 and AlCl_3) has been shown to enhance Li SX efficiency. However, the decrease in efficiency for real concentrated brine (CGR), containing sufficient levels of chlorides, can be explained by the compensating salting-in effect of cations (Ca, K, and Mg), which were absent in the synthetic solution (CS4), or present at lower levels in the real doped PR brine.

4. Conclusions

The research aimed to show the potential advantages of integrating evaporation and solvent extraction techniques for the recovery of lithium from low-quality brines. Both the efficacy of individual methods and their practical feasibility were assessed. It was observed that evaporation resulted in significant lithium losses (up to 80%, depending on the concentration ratio) due to the solution retention within chloride crystallisate. This led to lower lithium concentration in solutions intended for further enrichment via solvent extraction. However, the loss could be minimized by washing the precipitate with ethanol and recycling it after distillation. The evaporated solutions are saturated in NaCl and contain elevated levels of other analytes present in the original solutions. The solvent extraction trials with the TBP–MIBK/ FeCl_3 extraction system yielded results consistent with the literature values for two-component synthetic brines. The beneficial effect of co-extractants, namely, iron and aluminum chlorides, on lithium extraction efficiency was confirmed. However, their introduction was noted to cause the formation of solid precipitates during the extraction stage, likely due to exceeding the saturation level of the aqueous phase.

In the case of real evaporated brines, the outcomes of the SX tests varied significantly, rendering the tested system ineffective. Only the results for the semi-synthetic brine with elevated lithium concentration and containing the original elemental matrix showed to be promising, both in terms of satisfactory extraction efficiency after a one-stage SX process (76%) and the absence of physical issues encountered during the processing of real brine.

In summary, the processing of low-grade lithium brines through the presented approach of combining evaporation and solvent extraction poses challenges for complex solutions with a rich elemental matrix. The complexity of lithium brines suggests a low potential for scaling up, particularly concerning the practical goal of achieving the target Li concentration necessary for the precipitation of the carbonate product. Further studies involving a broader variety of brine solutions with different elemental matrices are necessary

to enhance the understanding of lithium recovery from diverse sources. Additionally, an important direction for future research is addressing the problem of solid phase formation during SX experiments.

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Appendix A

Table A1. The physicochemical parameters and composition of GR and PR brines.

Indicator	Unit	Brine	
		GR	PR
pH-value (20.3 °C)		5.5	6.7
Total hardness, calc. as mg CaCO ₃ /L	mg/L	59,600	>500
Temperature	°C	20.3	21.8
Total alkalinity	mmol/L	0.93	2.9
Solid residue	mg/L	379,000	>250,000
Residue on ignition (600 °C)	mg/L	328,160	115,370
Redox potential	mV	82	98
Dissolved solids	mg/L	293,058	>250,000
Conductivity (20 °C)	µS/cm	210,000	132,000
TOC	mg/L	8.24	<1
TIC	mg/L	6.45	16.1
Oxygen (electrom.)	mg/L	3.9	9.8
Chloride (Cl)	mg/L	140,000	64,000
Fluoride (F)	mg/L	<5.00	<5.00
Sulfate (SO ₄)	mg/L	308	1200
Nitrate (NO ₃)	mg/L	<25.0	<10
Nitrite (NO ₂)	mg/L	<20.0	<5
Phosphate (PO ₄)	mg/L	<5.00	<10
Bromide (Br)	mg/L	989	>20
Hydrogen carbonate (HCO ₃)	mg/L	55.8	175
Carbonate (CO ₃)	mg/L	56.9	172
Sulfide (S), easily released	mg/L	<0.0400	<0.04
Hydrogen sulphide (H ₂ S) calc.	mg/L	<0.041	<0.028
Ammonium (NH ₄)	mg/L	130	24.9
Borate (calc. as BO ₃)	mg/L	132.783	53.93
Calcium (Ca)	mg/L	17,475	2451
Potassium (K)	mg/L	3176	266
Lithium (Li)	mg/L	65	1.17
Magnesium (Mg)	mg/L	871	913
Sodium (Na)	mg/L	96,972	63,556
Strontium (Sr)	mg/L	730.8	0.142
Boron (B)	mg/L	24.4	9.91
Manganese (Mn)	mg/L	13.2	1.85
Zinc (Zn)	mg/L	12.806	<0.05
Iron (Fe)	mg/L	106	0.366

Table A2. Main element composition of precipitate from SX test.

Element	m/m%
Cl	81.76
Na	11.76
Al	3.12
Ca	1.12
Mg	0.37
K	0.16

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