Lithium Recovery via Chemical Precipitation

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Lithium is a vital raw material used for a wide range of applications, such as the fabrication of glass, ceramics, pharmaceuticals, and batteries for electric cars. The accelerating electrification transition and the global commitment to decarbonization have caused an increasing demand for lithium. The current supply derived from brines and hard rock ores is not enough to meet the global demand unless alternate resources and efficient techniques to recover this valuable metal are implemented.

Keywords: lithium ; lithium recovery ; chemical precipitation

1. Introduction

Chemical precipitation is a method used in wastewater treatment to remove ionic components from aqueous wastes by adding counter-ions to reduce their solubility, thereby changing a dissolved material in water into solid particles. It is considered the most efficient technology for the removal of trace metals and rare earth elements from wastewater. The method is relatively simple and inexpensive to operate. The adjustment of pH is an essential step in the precipitation process. For instance, in some scenarios, basic conditions usually allow the dissolved metal to be converted into solid metal hydroxide, which is separated by sedimentation or filtration [1].

Lithium recovery via chemical precipitation has been the object of study in the past few decades. Different approaches have been developed, such as the carbonate precipitation method, phosphate precipitation method, and aluminate precipitation method.

2. Current Technology and Challenges

As previously mentioned, the traditional evaporation method requires large evaporation ponds, is time intensive, and is not suitable for all geographical locations, as it requires a dry climate and abundant sunlight. On the other hand, the efficiency of lithium recovery depends on the brine composition, as these aquifers contain high concentrations of other ions, and the co-precipitation of these impurities makes Li extraction more complicated. For example, lithium and magnesium are both alkali/alkaline earth metals and share similar ionic properties, as their ionic size is almost the same. Additionally, their radii are similar: 72 pm for Mg^{2+} and 76 pm for Li^{+}. Therefore, mining Li from brines with a high Mg/Li ratio has been a decades-long technical challenge. A high Mg/Li ratio requires large amounts of precipitant, which results in a huge amount of solid waste generation and high costs. Additionally, the method has a low recovery rate, as lithium is lost due to co-precipitation [2][3].

Carbonate precipitation is the current technology used for lithium extraction from brines at an industrial scale. However, this conventional process is ineffective for most new brine discoveries, with a low concentration of lithium. To obtain a significant level of lithium recovery, the initial Li concentration should be greater than 20 g/L [4]. In addition, the solubility of the precipitate Li_2CO_3 is still considerably high (Ksp = 8.15×10^{-4}); therefore, a large amount of Na_2CO_3 is used. In addition, a high temperature (~100 °C) is required to precipitate Li as Li_2CO_3, due to its lower solubility at higher temperatures. Such processes make the mining of Li from brines challenging when it is at a low concentration [5][6][7].

3. Current Advancements

In the past few decades, the chemical precipitation of lithium has been intensively studied from an economical and scientific perspective. Different materials have been used, such as carbonate, phosphate, and aluminate, in the precipitation method.

Several studies have been conducted using sodium phosphate salts, such as Di-sodium phosphate (Na_2HPO_4), tri-sodium phosphate (Na_3PO_4), sodium pyro-phosphate ($Na_4P_2O_7$), and sodium tri-polyphosphate ($Na_5P_3O_{10}$) [8][9][10][11].

The results obtained by Alsabbagh, Aljarrah [8] show that the four types of salts studied can be used as lithium-precipitating reagents, as the lithium recovery achieved was between 23% and 27%. However, the highest percentage of lithium recovery was achieved by using tri-sodium phosphate (TSP). The research obtained a 40% recovery rate using TSP in a Dead Sea evaporated end brine with an initial lithium concentration of 40 mg/L [8]. Alsabbagh, Aljarrah [8] studied the effects of operating conditions, and the results show that the amount of precipitating reagent had a significant effect on the percentage of Li extracted. In this phase, 1 to 10 g of TSP was used, and 7 g achieved the highest recovery. The stirring speed was adjusted from 150 to 1000 rpm and the ANOVA statistical analysis showed that the stirring speed had a substantial effect. The best percentage extracted was reached at 450 rpm. The time was studied from 30 to 180 min, and the results show that the Li extraction rate did not change significantly with time, and two hours is enough for the process. Finally, the study on the influence of the temperature showed that at 40 °C, the percentage of Li extracted was slightly better than that at other temperatures (25–70 °C). Accordingly, at optimum conditions, more than 40% of the lithium was extracted from Dead Sea evaporated end brine using TSP.

Mulwanda, Senanayake [12] recovered lithium from an alkaline leach solution using phosphoric acid (H_3PO_4). With the purpose of increasing the efficiency of lithium extraction as Li_3PO_4, the study alternatively used H_3PO_4 instead of Na_3PO_4 to minimize the presence of sodium ions (Na^+) in the alkaline liquor. The Li-to-P molar ratio was varied from 3:1 to 3:2 to evaluate its effect on the lithium precipitation rate. The operating conditions were fixed to 90 °C, with a 2 h reaction time, initial pH of 12.5, and initial lithium concentration of 5.6 g/L. The highest precipitation efficiency (92%) was obtained at a Li:P ratio of 3:2; however, the XRD scan of the precipitate showed an additional phase in the solid, Li_2NaPO_4 (impurity). Therefore, the authors determined a molar ratio of Li:P = 3:1.6 as the most desirable, achieving around 83% recovery as Li_3PO_4.

As a new resource of lithium, Shin, Jeong [13] used the waste Li solution generated from the cathode manufacturing process. The recovery of Li as Li_3PO_4 was achieved by using phosphoric acid with the Li/PO_4 molar ratio of three. The effects of the initial Li concentration and the reaction time were studied in a synthetic solution at room temperature for three days. At various Li concentrations of 100, 250, 500, 1000, 2000, and 3000 mg/L, the results indicate that no precipitation was observed when the initial concentration was lower than 250 mg/L; once it was increased from 500 mg/L to 1000 and above, the precipitation reaction started increasing, reaching equilibrium within 12 h.

Shin, Jeong [13] concluded that the number of lithium and phosphorus ions in the solution can be a relevant factor to the precipitation rate of Li_3PO_4; therefore, at concentrations lower than 1000 mg/L, precipitation was not achieved due to a low number of Li-P nuclei. In contrast, at initial Li concentrations of 1000, 2000, and 3000 mg/L, the precipitation efficiencies achieved were 87%, 96%, and 97%, respectively, after three days of reaction. The study tested the phosphoric acid at the Li/PO_4 molar ratio of 3 in a real Li waste solution with a concentration of 2174 mg/L. The experiment was conducted at pH values of 7.0, 9.2, 11.0, and 12.4, and the precipitation efficiency achieved went from 0.2 to 81%, which indicated that the higher the pH, the higher the precipitation efficiency of Li_3PO_4. In the same study, tri-sodium phosphate was tested to evaluate the precipitation efficiency of each precipitating reagent. The experiment was conducted at a Li/PO_4 molar ratio of 3, initial Li concentration of 2000 mg/L, and initial pH of 12.9. After 24 h of reaction, the results revealed that H_3PO_4 had 92% precipitation efficiency, whereas the Na_3PO_4 recovered was 87%.

The precipitation of lithium with activated aluminum-based alloys was proposed by Li, Zhao [14]. Li was recovered as $LiCl{\cdot}Al(OH)_3{\cdot}xH_2O$. At first, Al−Ca alloy and Al−Fe alloy, each with 70% aluminum contents, were assessed to determine the lithium precipitation performance. The experiment was conducted with an initial Li concentration of 1 g/L, at 70 °C, 4:1 Al/Li ratio, and with a three-hour reaction time. The results obtained show that the precipitation rate of lithium with Al−Ca alloy was 93.6%, whereas the Al−Fe alloy achieved only 23.8%. In the subsequent experiments, the effects of the molar ratio of Al to Li, the Ca content of the Al−Ca alloy, the initial Li concentration, the reaction temperature, and the reaction time were evaluated to determine the optimum conditions.

With an initial lithium concentration of 1 g/L, a 3 h reaction time, at 70 °C, and with a 30% Ca content in the Al−Ca alloy, the results show that the molar ratio of Al/Li had a significant effect on the lithium precipitation rate. At the Al-to-Li ratio of 2:1, the recovery achieved was only 72.1%. However, the precipitation rate was improved as the molar ratio was adjusted to higher values, and at an Al/Li of 3.5:1, the process achieved 93.8% recovery. However, as the molar ratio continued to increase, an insignificant improvement in the precipitation rate was obtained. The calcium content in the Al–Ca alloy also played an important part in the precipitation process. In this phase, the Ca content was varied from 10% to 40%, and the results showed a significant increase in the Li extraction rate, from 87.1% to 94.7%, as the Ca content was adjusted from 10% to 35%. This improvement was attributed to an Al−Ca alloy with a larger surface area as the Ca content was increased.

The initial lithium concentration did not show a major effect on the precipitation rate. The recovery achieved went from 71.3% to 95.3% when the lithium-ion concentration was adjusted from 0.4 to 0.8 g/L. Still, greater values did not exhibit better recovery rates. When the temperature was evaluated, it was found that at temperatures over 70 °C, the lithium precipitation rate significantly dropped, going from 93.6% to 66% once the temperature was raised from 70 to 90 °C.

This phenomenon was attributed to thermal motion at high temperatures, where part of the $LiCl{\cdot}Al(OH)_3{\cdot}xH_2O$ decomposes and LiCl dissolves. Finally, with the previous parameters evaluated, the effect of the reaction time was studied, from 0.5 to 3 h under the conditions of a 3.5:1 Al/Li molar ratio, 35% Ca content, 8 g/L initial Li concentration, and 70 °C. The precipitation reaction was very fast, and after 1 h, 94.6% of the lithium was extracted from brine using the Al−Ca alloy.

As mentioned in the previous section, the extraction of lithium in brines with high Mg/Li mass ratio is one of the main challenges of the precipitation process. The study conducted by Liu, Zhong [3] tested aluminum-based materials in a salt-lake brine, to evaluate the influence of the Mg/Li mass ratio, among other parameters, on the Li precipitation rate. The Al-based materials showed good results, as the extraction rate achieved was 64.8% of Li and only 0.8% of Mg, in a solution containing 1 mol/L LiCl and 1 mol/L $MgCl_2$.

The following experiments were conducted using a solution containing an initial Li concentration of 1 g/L and 20 g/L of Mg. The temperature is an important factor in the precipitation process, and in this case had a significant effect when it was increased from 20 to 90 °C. The Li precipitation rate reached 65.8% at 80 °C, whereas only 18.14% was acquired at 20 °C. Interestingly, the result shows that Mg is independent of the change in temperature, as its precipitation rates at various temperatures remained below 0.16%. The reaction time was evaluated, and the results show that from 60 to 180 min, the precipitation rate improved from 34.8% to 62.8%. However, when the reaction time was above 180 min, an insubstantial change was obtained. The concentration of Mg was fixed at 20 g/L to study the effect of lithium initial concentration on the extraction of Li. As the lithium concentration was adjusted from 0.2 to 1 g/L, an evident increase in the precipitation was observed, from 30% to 64.8%. However, it dropped to 52.3% when the Li concentration was 1.5 g/L. The authors determined that as a large number of precipitates are formed at a higher Li concentration, the surface of the Al-based materials gets coated, which decreases the reaction performance. The incrementation of the initial concentration of Mg^{2+} was studied to determine its effect on the Li precipitation rate. The results reveal that an excess of Mg^{2+} in the solution had detrimental effects on the precipitation of Li. The Li precipitation rate dropped from 78.3% to 49.4% when the Mg initial concentration was increased from 15 to 40 g/L.

The production of high-purity lithium carbonate with the current technology requires re-dissolution and re-precipitation of the already precipitated Li_2CO_3. This method consumes large amounts of freshwater and chemicals. Additionally, a high Li concentration is needed to obtain a high Li recovery rate. Zhao, Zhang [6] proposed a potential approach to recover lithium from a low-concentration Li solution and obtain industrial-grade Li_2CO_3 by a one-step precipitation method, with the use of ultrasound. Initially, a comparison of ultrasound and a stirring method at different initial lithium concentrations was conducted to assess the effects of both technologies on the Li recovery rate and purity grade of Li_2CO_3. The results show that at an initial Li concentration of 10 g/L, the Li recovery rate by the ultrasound method outstripped that of the traditional technology, as more than 80% of the Li was extracted. In addition, the Li_2CO_3 produced exceeded industrial-grade purity. On the other hand, the traditional stirring method recovered over 80% of Li only when the initial Li concentration was raised to 20 g/L. Moreover, this technology did not achieve the desirable purity for industrial-grade Li_2CO_3.

Ultrasonic radiation was used to increase the efficiency of the precipitation reaction. The reason involves the formation of cavitation bubbles that provide hot spots with very high temperature and pressure gradients, and these spots can enhance mixing and particle collisions and facilitate the chemical reaction. As part of the study of the ultrasound technology, the power was varied from 90 to 300 W, at 20 KHz, to improve the recovery rate of Li. The results show an increase of more than 10% when the power was incremented from 0 until 150 W. However, at values above 150 W, minor changes were obtained.

The influences of the amount of precipitant reagent (Na_2CO_3) on the lithium precipitation rate and the purity of Li_2CO_3 were evaluated. The dosage was changed from 1 to 1.4 Na/Li (molar ratio). In this phase, the Li recovery rate increased, but the purity of Li_2CO_3 declined. The authors deduced that the increase in carbonate ions in the solution will accelerate the chemical reaction and improve the extraction of lithium. However, the presence of more ions could increase the probability of being trapped in the Li_2CO_3 complex, which increases impurities in the final product and reduces its purity. It is important to highlight that the study investigated the difference between dosing solid Na_2CO_3 versus a highly concentrated Na_2CO_3 solution in the Li recovery. The solid precipitant achieved a higher lithium recovery rate than the saturated solution. Therefore, the solid Na_2CO_3 was used throughout the whole study.

The effect of the reaction temperature was evaluated, and the results showed that the increase in the temperature accelerated the rate of the chemical reaction. When it was raised from 25 to 80 °C, the Li recovery went from 64 to 82%. Moreover, the reaction reached equilibrium in only 5 min at high temperatures. The purity of the Li_2CO_3 also improved from 96% to 99%. Such an increase was attributed to the high temperature, as Na_2CO_3 remained in solution without affecting the precipitate composition, whereas at low temperatures, the Na_2CO_3 dissolved gradually, and some of the undissolved particles were wrapped in the Li_2CO_3 precipitate.

At optimum conditions of 10 g/L of Li, solid Na_2CO_3, ultrasonic power of 150 W, and 35 min reaction time at 80 °C, the lithium recovery rate reached 82.62%, and the Li_2CO_3 was 99.01% pure. The recovery of residual lithium (2 g/L) in the filtrate was consequently extracted by the Na_3PO_4 precipitation method. Therefore, the overall recovery rate reached by the researchers was 97.4%.

3.1. Materials Used in the Recovery Process

In the past few decades, the chemical precipitation of lithium from aqueous sources has been intensively studied, and different materials and methods have been proposed—in particular, carbonate precipitation, phosphate precipitation and aluminate precipitation.

3.2. Operating Conditions and Performance

The lithium recovery rate and the operation conditions can differ considerably among precipitant materials. Additionally, the nature of the Li-bearing solution appears to be a determining factor that influences the operating conditions, as the selection of the optimum parameters for the chemical precipitation will benefit the extraction of Li rather than other ions.

Influence of pH on Lithium Precipitation

pH is a key parameter in the chemical precipitation process, and finding its optimum value is crucial to efficiently extract lithium. Li, Li [9] examined the influence of pH on the lithium precipitation rate by the phosphate precipitation method. The authors concluded that the Li extraction rate increases as the pH value reaches the basic range. When the reaction pH is above 8, the lithium extraction rate stabilizes, at nearly 80%. In acidic conditions, soluble Li compounds are formed, as the many H^+ molecules in the solution react with PO_4^{3-} to produce HPO_4^- and $H_2PO_4^-$; subsequently, Li^+ reacts with HPO_4^- and H_2PO_4 to produce Li_2HPO_4 and LiH_2PO_4, which are highly soluble in water and therefore affect the precipitation of lithium.

High concentrations of other ions have a significant effect on the pH adjustment. To effectively precipitate Li and avoid the co-precipitation of impurities, the adjustment of pH is an essential step in the Li extraction. The recovery of Li from leach liquors could be quite challenging, as these solutions contain various dissolved species. Xiao and Zeng [7] recovered lithium from a Li-containing leach solution using Na_3PO_4. During the step of pH adjustment, the researchers noticed a substantial reduction in the concentration of ferric ions (Fe^{3+}) instead of lithium, when the pH was varied from 0 to 5.5. The rationale behind the change involves the formation of $FePO_4$, as phosphate preferentially precipitates ferric ions rather than Li ions at pH values from 0 to 5.5.

Shin, Jeong [13] recovered lithium from a lithium waste solution using phosphoric acid. The effect of the pH on the Li precipitation rate was evaluated using pH levels of 7.0, 9.2, and 12.4. The results show a significant improvement in the lithium precipitation rate as the pH became more basic. The precipitation efficiency went from 0.2 to 81% as the pH of the solution increased from 6.4 to 12.4.

Increasing the pH might not be a critical step when using aluminum-based materials. Liu, Zhong's [3] study is a case in point. They achieved a 78.3% lithium recovery rate by adding aluminum-based materials, and the pH value (5.5) of the brine remained unchanged throughout the precipitation process. The authors highlighted that a change in pH in the brine could lead to negative effects within the salt-lake ecosystem.

Influence of Temperature on Lithium Precipitation

According to the collision theory of reactivity, chemical reactions occur when reactant particles "effectively collide". Moreover, an effective molecular collision requires a minimum amount of kinetic energy in the molecule. A high temperature increases the average kinetic energy of the reactant molecules and causes molecules to move faster, increasing the rate of intermolecular collisions. These collisions promote more molecules to interact in the reaction and increase the reaction rate. Thus, in theory, the precipitation rate of lithium should increase with the increase in the temperature.

For example, Shin, Joo [10] used Na_3PO_4 to study the effect of the temperature on the Li precipitation rate, at 30, 60, and 90 °C. The results showed that at 90 °C, the precipitation rate obtained was over 90% in only 5 min of reaction time, regardless of the initial Li concentration (1.7, 4.0 and, 7 g/L). At 30 °C, the lithium extracted was only 70% over the same period of time, and high recovery was only achieved at the highest Li concentration.

The maximum precipitation rate of Li, Li [9] was reached at 70 °C, using Na_3PO_4 as the precipitant, in a Li solution containing 262.43 mg/L of lithium. When the temperature was increased from 50 to 70 °C, the extraction increased from about 77% to 86.57%. The authors observed that the higher the temperature, the better the Na_3PO_4 precipitation of lithium. However, once the temperature was raised from 70 to 90 °C, the extraction rate plateaued.

Li, Zhao [14] extracted lithium as $LiCl{\cdot}Al(OH)_3{\cdot}xH_2O$ from a salt-lake brine using aluminum-based alloys. The increase in the temperature (50 to 90 °C) did not have a positive effect on the lithium recovery rate. First, there was no significant difference in the Li extraction efficiency when the temperature was raised from 50 to 70 °C. As the temperature was increased from 70 to 90 °C, a significant decline in the Li precipitation rate was observed, dropping from 93.6 to 66%. The authors stated that at more than 70 °C, $LiCl{\cdot}Al(OH)_3{\cdot}xH_2O$ disintegrates and LiCl dissolves in water, decreasing the extraction rate of Li.

About 90% of Li was extracted from Dead Sea brine as lithium aluminate, using aluminum chloride ($AlCl_3{\cdot}6H_2O$). The highest yields were achieved at room temperature, and as the temperature was increased, the lithium recovery declined [15][16]. Theoretically, a high temperature increases the rate of a reaction; however, temperature does not exhibit the same behavior in all precipitation methods. High lithium recovery can be achieved at room temperature and prolonged reaction times when the initial Li concentration is high.

The solubility product of the precipitate plays an important part in the selection of the reaction temperature. For example, the solubility product of Li_2CO_3 is relatively high, 8.15×10^{-4} (pKsp = 2.2), in comparison with Li_3PO_4, 2.37×10^{-11} (pKsp = 10.63) [9]. Therefore, the carbonate precipitation method is usually conducted in the range of 80 to 100 °C, as the solubility of Li_2CO_3 decreases as the temperature rises [17][18].

Influence of Reaction Time on Lithium Precipitation

The reaction time may perhaps be linked to the initial Li concentration of the solution and the reaction temperature: high Li concentrations and high temperatures shorten the time required to achieve efficient lithium extraction. Shin, Joo [10] studied the precipitation efficiency of lithium over time at different temperatures and initial lithium concentrations. In only five minutes, more than 90% of the lithium was extracted at 90 °C, despite the initial Li concentration. At 30 °C, only 70% was extracted in the first five minutes; however, the precipitation efficiency of lithium increased gradually, given more time, and at higher Li concentrations. The authors indicated that to obtain the critical size in the crystallization of Li into Li_3PO_4, a longer period of time is needed. Therefore, the extraction rate of lithium as Li_3PO_4 is slow at low temperatures, and the higher the temperature, the faster the rate.

Xiao and Zeng [7] used Na_3PO_4 to extract lithium from a synthetic LiCl solution; the precipitation of Li reached 96.5% after 5 h of reaction time at 25 °C. Shin, Jeong [13] used phosphoric acid to recover Li from a LiOH solution. The experiment achieved around 92% precipitation efficiency after 24 h of reaction time at room temperature, with an initial Li concentration of 2000 mg/L. Evidently, a low reaction temperature requires a longer period of time to extract lithium as Li_3PO_4, and a high lithium concentration is key to obtaining a significant extraction rate.

4. Challenges and Outlook

Although much progress has been made in lithium recovery via chemical precipitation, there are still some challenges to overcome. Many studies have been conducted to separate lithium from magnesium in salt-lake brines; however, a high Mg/Li ratio requires large amounts of precipitant, which results in huge amount of solid waste generation and high costs [2]. The study of the aluminate precipitation method showed high lithium recovery. However, increasing the magnesium concentration to a Mg/Li mass ratio of 20:1 was detrimental to the precipitation process, and the lithium precipitation efficiency decreased [19]. To improve the precipitation separation of lithium from magnesium, the effects of various parameters on the precipitation process must be entirely and systematically studied.

The efficiency of lithium recovery depends on the Li-bearing composition. High concentrations of dissolved ions result in the co-precipitation of these impurities, making the Li extraction process more complicated. To efficiently harvest lithium from waste solutions, the characteristics of impurity removal and the interactions between the present ions must be

understood. Once the removal of impurities is achieved, Li can be recovered in a one-step precipitation process with a high recovery rate and high purity of the final Li product [20].

The phosphate precipitation method has shown promising results in recovering lithium from aqueous sources. However, the direct recovery of lithium from solutions with low concentrations of lithium faces serious challenges, such as low induction period and low efficiency. Additionally, the formation of a Li_3PO_4 precipitate requires large supersaturation and a high nucleation energy barrier [21]. To achieve a high recovery rate, the reaction temperature should be raised to 70 °C or higher, and the initial lithium concentration should be higher than 2 g/L [10][21][22]. Thus, a high recovery rate is still conditional on a high initial lithium concentration.

Even though the proposed chemical precipitation technologies are technically feasible, the majority of the reported materials are still at the bench scale. To prove the concept and evaluate the feasibility of the proposed methods, pilot-scale tests would be an important step.

Lanthanum compounds have received lots of attention in various applications because of their flexibility and multifunctionality. There is indeed significant evidence of La^{3+} ions being extensively used to remove toxic pollutants from wastewater [23][24][25]. Lanthanum reagents have shown several advantages over traditional precipitation methods, such as high performance with and without pH adjustment. Although it is called a rare earth element (RE), La is relatively abundant, which means it offers a potentially cost-effective option. RE technology for wastewater treatment does not have negative effects on the ecosystem. Moreover, the La precipitation method has favorable characteristics for closed-loop technology, as it can form insoluble complexes with carbonate (CO_3^{2-}), hydroxide (OH^-), and fluoride (F^-) [26], favoring its recovery for reuse. In summary, the RE technology exhibits promising features for precipitating Li from wastewater with closed-loop technology, which aligns with the circular economy principles.

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