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Review

Selective Recovery Lithium from Mother Liquor via Solvent Extraction: A Review on Extractants, Mechanisms, and Efficiency

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Abstract

With the rapid expansion of the global lithium battery industry, the demand for lithium as a critical raw material continues to grow. Lithium precipitation mother liquor still contains considerable concentrations of lithium ions (Li^+), but they generally exhibit a high sodium-to-lithium ratio, which makes the separation of lithium from sodium particularly challenging. Solvent extraction is recognized as a viable approach for challenging Li^+/Na^+ separation due to its high selectivity, operational flexibility, and scalability. A comprehensive assessment and comparison of various extraction systems are therefore essential to facilitate the sustainable recovery of lithium from precipitation mother liquor. This review summarizes the commonly used extraction systems, including organophosphorus extractants, ketone-based extractants, macrocyclic compounds, ionic liquids, and deep eutectic solvents. A systematic analysis is provided regarding their extraction mechanisms, applicable conditions, and respective advantages and disadvantages. Finally, perspectives and suggestions are offered on future research directions and improvement strategies for different extraction systems, along with an outlook on the potential of combined enhancement technologies.

Keywords: mother liquor from lithium precipitation; sodium ion; lithium recovery; extraction method; extraction agent; separation

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1. Introduction

Energy transition represents an inevitable pathway for the economic development of all nations. Renewable sources such as wind, wave, and solar power have become major components of the energy mix. However, the transportation of these energy forms and the balancing of power grids still rely on energy storage systems. Among these, lithium-ion batteries have emerged as the preferred technology, driving continuous growth in their demand [1–4]. At present, more than 85% of China's lithium resources are found in salt lake brines, which are characterized by high magnesium-lithium ratios and complex compositional features, including varying lithium grades across different salt lakes. These factors increase the difficulty of extraction and hinder industrialization, resulting in a

heavy reliance on imports to meet domestic lithium demand [5,6]. Therefore, improving the comprehensive utilization efficiency of lithium resources and reducing the loss of recoverable lithium is essential to satisfy the industrial market's demand for lithium. This issue has become a key focus of current research [7–9].

The lithium precipitation mother liquor is a liquid by-product generated during the extraction and refining of lithium resources (Figure 1). Due to solubility constraints, this solution typically contains significant amounts of lithium, sodium, potassium, and other impurities. Its physicochemical properties vary considerably depending on the type of lithium ore and the refining process employed [10,11]. Previous studies have reported that the lithium concentration in the mother liquor generally ranges from 1.3 g/L to 2 g/L, while the sodium ion (Na^+) content often exceeds 50 g/L. Moreover, as pH adjustment is commonly involved in lithium extraction, the mother liquor is usually alkaline. Direct reuse of this solution would not only lower the raw material grade but also compromise the quality of the final product. Hence, developing a sustainable process for recovering lithium from the lithium precipitation mother liquor is of great importance [12–17].

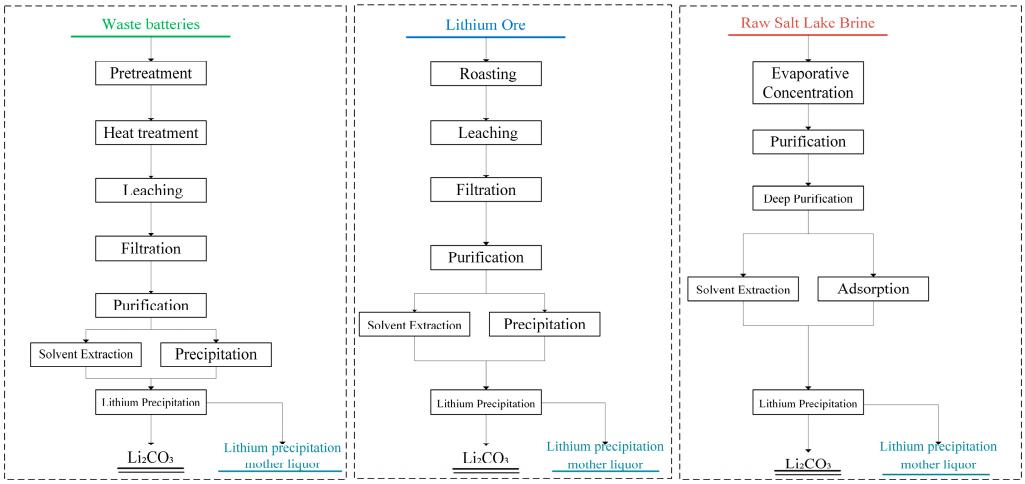

Figure 1. Generation of lithium precipitation mother liquor.

Currently, the primary methods for recovering lithium from the mother liquor include evaporation crystallization, precipitation, solvent extraction, adsorption, and oxidation-reduction [18–26]. Among these, the evaporation crystallization process typically requires multiple cycles of concentrating the mother liquor to facilitate re-precipitation. A key drawback of this method is the generation of secondary precipitation filtrate due to solubility limitations. Furthermore, to minimize lithium loss, additional alkaline solutions are often introduced, leading to resource wastage [27]. The oxidation-reduction method for treating lithium-containing mother liquor usually requires first oxidizing the target element to convert it into a metal precipitate for separation. However, this method often introduces new ions into the lithium-containing mother liquor, increasing the difficulty of subsequent processing and reducing product quality [27]. The adsorption method is very effective for the separation of lithium metal [28–30]. Titanium-based adsorbents have been proven to be applicable in the industrial production process of lithium extraction from salt lakes, but the cost of titanium-based adsorbents is too high, limiting their large-scale application [31,32].

Solvent extraction is a well-established technology recognized for its strong selectivity, low energy consumption, operational simplicity, high recovery rate, large processing capacity, and suitability for continuous production [27,33–40]. It has been widely applied in lithium recovery from salt lake brines and lithium-containing mother liquors [25,41]. For instance, Xinghua Lithium Salt (Qinghai, China) commissioned a 5000-ton lithium carbonate production line utilizing solvent extraction to recover lithium

from the Dachaidan Salt Lake [42]. The principle of solvent extraction relies on the similarity in solubility: by selecting an organic phase with high selectivity toward target ions, and mixing it with the aqueous feed solution, lithium ions can be transferred into the organic phase ($R–H + Li^+ \rightarrow R–Li + H^+$), while other impurities remain in the raffinate. The loaded organic phase is then subjected to washing, stripping ($R–Li + H^+ \rightarrow R–H + Li^+$) to produce a purified and concentrated lithium-rich solution. Furthermore, the organic extractant can be regenerated and reused, which significantly lowers the overall process costs (Figure 2). The key to an efficient extraction process lies in the selection of an extractant that satisfies one or more of the following criteria: (1) ability to form a tetrahedral coordination structure with Li^+; (2) presence of chelating functional groups that form strong chemical bonds with Li^+; (3) coordination atoms being hard bases such as oxygen or nitrogen; and (4) formation of a stable chelate ring, preferably a six-membered ring [42,43]. Common extractants used in industrial lithium recovery include phosphate esters, ketones, crown ethers, ionic liquids, and phenolic compounds [44–47].

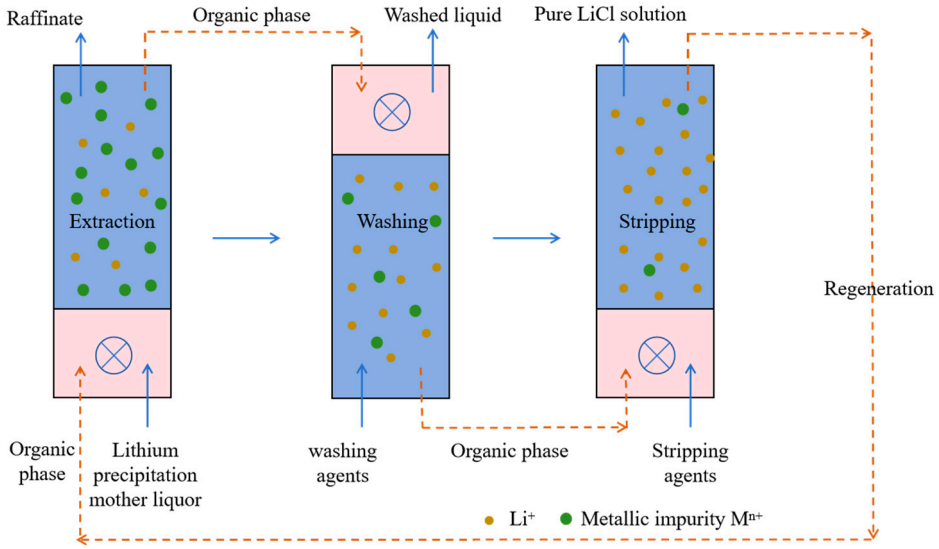

Figure 2. Process flow diagram of the solvent extraction process. Note: The blue arrow represents the aqueous phase, and the red arrow represents the organic phase. The pink area in the equipment represents the mixing chamber, and the blue area represents the clarification chamber.

Given the critical need for efficient and selective lithium recovery from such challenging matrices, this review aims to provide a systematic analysis of solvent extraction as a promising solution. The following sections will analyze specific extractants identified from 2000 to 2025 year representative lithium-sodium separation studies (sourced from Web of Science and CNKI), including organophosphorus compounds, β-diketones, ionic liquids, crown ethers, and others. For each category, the extraction mechanisms, operational efficiencies under various conditions, and their comparative advantages and limitations will be critically examined. Finally, based on the current state of research, perspectives on future development directions and potential enhancement strategies for the solvent extraction process will be offered (Figure 3).

The innovation of this work lies in being the first to systematically review and compare the performance and mechanisms of multiple classes of extractants in solvent extraction for the specific and challenging system of high Na/Li ratio alkaline lithium precipitation mother liquor. Beyond covering common systems, it particularly highlights the evaluation of their practical applicability, economic cost, and industrialization potential. By elucidating the relationship between extractant structure, performance, and application, this review fills the gap in the previous literature where systematic analysis of this specific system was

lacking, offering a clear technical roadmap and future research directions for achieving efficient and sustainable lithium recovery from this secondary resource.

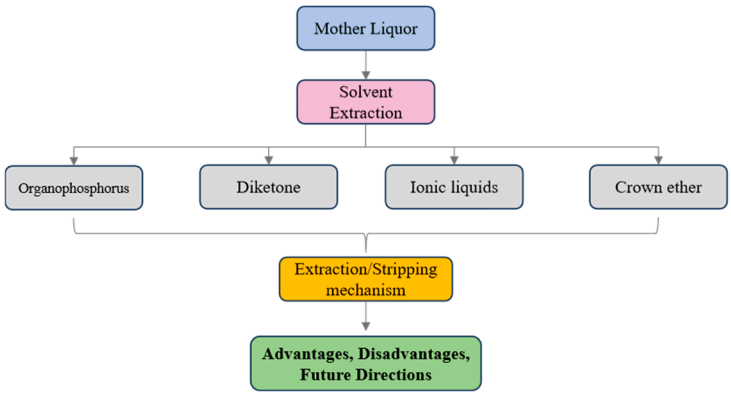

Figure 3. Roadmap of this review.

2. Organophosphorus Type Extractants Applied in the Extraction and Separation of Lithium from Mother Liquor

Organophosphorus extractants are a class of oil-soluble compounds that selectively separate metal ions through chelation or coordination reactions. These are mainly classified into acidic, neutral, and double-coordinated phosphorus compounds, with the latter exhibiting superior performance in strongly acidic media. Common neutral organophosphorus extractants include tributyl phosphate (TBP), trioctylphosphine oxide (TOPO), and trialkylphosphine oxide (TRPO/Cyanex 923), as illustrated in Figure 4 [43,48,49]. Among these, TBP is the most extensively studied neutral extractant in the phosphate ester system and has been widely applied in lithium recovery from salt lake brines and leaching solutions [43,48,49]. The extraction mechanism typically involves coordination between the metal ion and the phosphoryl oxygen atom, a process that occurs effectively in nitric or hydrochloric acid media but shows limited applicability in alkaline environments such as lithium-rich brine solutions. Li et al. [50] investigated the influence of coexisting ions (Mg^{2+}, K^+, Na^+, and B^{3+}) on the extraction efficiency of the TBP system. Their results indicated that increasing Na^+ concentration leads to competition with Li^+ for complex formation—e.g., forming species such as $[Na(TBP)_n][PF_6]^+$—which reduces lithium extraction efficiency while enhancing sodium co-extraction, thereby impairing Li/Na separation. Therefore, neutral extractants such as TBP, TOPO, and TRPO are usually not used as extractants to extract lithium from alkaline solutions such as lithium-rich brine solutions, but are used as co-extractants with ketone and phenolic extractants to form a co-extraction system for the separation of lithium and sodium in lithium-rich brine solutions [11,46,51–53]. Hano et al. [54] reported that when TBP was used as synergists in acidic organophosphorus systems (e.g., with D_2EPHA (di-2-ethylhexylphosphoric acid) or MEHPA (2-ethylhexyl-phosphonic acid 2-ethylhexyl ester), both lithium and sodium extraction increased, though TOPO alone showed no synergistic effect—a phenomenon attributed to interference from chloride and silicate ions. In contrast, Zhang [25] et al. observed a notable synergistic effect when TOPO and TBP were introduced into a ketone-based system employing benzoyltrifluoroacetone (HBTA). Further studies by Zhang et al. [43] suggested that the P=O group in TOPO, influenced by branched alkyl chains, possesses the strongest electron-donating ability, whereas in TBP, the P=O group is slightly less electron-donating due to alkoxy substituents. Nevertheless, both demonstrate stronger synergistic performance compared to C=O or N=O-based synergists.

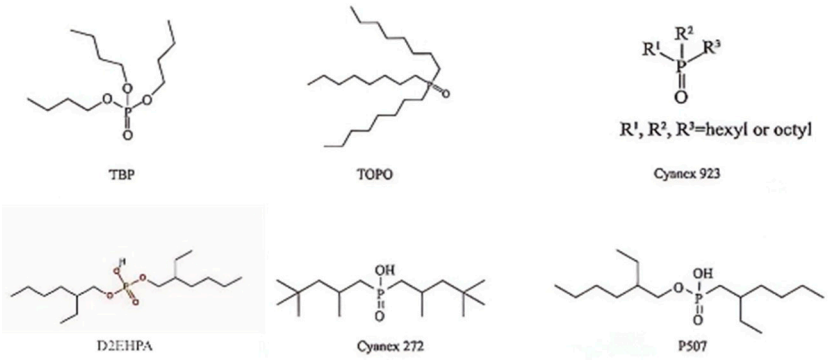

Figure 4. Common Organic Phosphorus-Based Extractants.

The extraction of lithium using acidic organophosphorus extractants typically proceeds via a cation exchange mechanism [53]. Commonly used extractants in this category include di(2-ethylhexyl) phosphoric acid (D2EHPA), bis(2,4,4-trimethylpentyl) phosphinic acid (Cyanex 272), and 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (P507), among others (Figure 3) [43,48,49]. Hano et al. [54] used D2EHPA or MEHPA to extract Li^+ from a mixture containing alkali and alkaline earth metals (Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+}). The results indicated that under neutral to weakly acidic conditions, both extractants achieved extraction efficiencies of approximately 70% for Li^+ and 50% for Na^+, demonstrating poor lithium-sodium separation selectivity. To enhance Li/Na separation, MEHPA was applied under acidic conditions; however, the lithium extraction efficiency dropped to around 40%, and the process required significant acid consumption to adjust the aqueous phase pH prior to extraction. In addition, when the medium contained divalent ions such as Mg^{2+} and Ca^{2+}, D2EHPA or MEHPA showed more advantageous effects, and the extraction rate of divalent metals such as Mg^{2+} and Ca^{2+} could reach over 90% [53]. Therefore, researchers usually use acidic extractants such as D2EHPA, P507, P204, P227, etc., to remove divalent impurity metals from the medium, rather than extracting monovalent metals [53,54].

3. Diketone Extractants Applied in the Extraction and Separation of Lithium from Mother Liquor

Both lithium and sodium are alkali metals. Their atoms readily lose the outermost s-electron to form monovalent cations. They have relatively strong metallic properties and significant variations in atomic size. Such differences in atomic size can also cause many differences in chemical behaviors, which limits the requirements for selecting extraction coordination groups for them. According to Pearson's hard-soft acid-base theory, alkali metal ions are all classified as hard acids, with hardness decreasing in the order: $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$. Consequently, these ions tend to form relatively stable complexes only with hard bases, such as extractants containing oxygen or nitrogen donor atoms [43].

While ketone-based extractants generally exhibit poor extraction efficiency for alkali metals such as lithium, β-diketones represent a notable exception. β-Diketone extractants contain two carbonyl groups and exist in a tautomeric equilibrium between the keto (I) and enol (II) forms. In the enol form, the active hydrogen is located on the hydroxyl group, whereas in the keto form, it resides on the methylene group between the carbonyls. The Li^+ ion can replace this active hydrogen and form a relatively stable chelate structure (III) with the β-diketone (Figure 5), thereby achieving the purpose of extracting lithium from ketone-based extraction agents [43,55,56]. However, since the dissociation of the active hydrogen requires alkaline conditions, this class of extractants is typically applied in alkaline aqueous systems or used in combination with alkaline saponification of the organic phase [53].

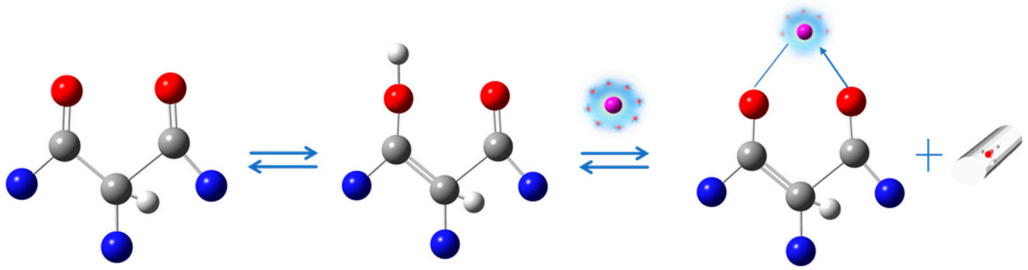

Figure 5. There exists an interconversion equilibrium between the keto form (I) and the enol form (II) of β-butanediol, as well as a chelating structure with Li^+ (Adapted from [43]). Note: Blue represents hydrogen atoms, grey represents carbon atoms, and red represents oxygen atoms.

Numerous studies have indicated that the use of beta-diketone extractants alone for lithium extraction is prone to interfacial precipitation and emulsification, thereby reducing extraction efficiency. In contrast, organophosphorus extractants, despite their stronger polarity, are prone to dissolution in the aqueous phase, resulting in the loss of the organic phase [55,56]. To address these limitations, recent research has focused on combining β-diketone extractants with organophosphorus synergists (e.g., TOPO) to form cooperative extraction systems for the selective separation of lithium from high Na/Li ratio media. Zhang et al. [55] investigated the effect of varying molar ratios of HTTA (β-diketone) to TOPO (organophosphine synergist) on lithium extraction. The results demonstrated that at an HTTA:TOPO ratio of 9:1, the system was prone to emulsification, with a lithium extraction rate below 10% and a separation coefficient (Li/Na) not exceeding 15.7. In contrast, at a balanced ratio of 5:5, emulsification was suppressed, and the lithium extraction efficiency exceeded 90%, with a separation coefficient as high as 768.1, indicating significantly enhanced performance. Duan [48] employed benzoylpropanoone (a diketone free of N, P, S, and F atoms) as the extractant, triisobutyl phosphate (TIBP) as the synergist, and 2-octanol as the diluent. After saponification with 80% NaOH, lithium was extracted from a mother liquor containing 1.51 g/L Li^+, achieving an extraction rate of 89.79% following stripping. Healy et al. [57] proposed that in such synergistic systems, each metal ion complexes with one molecule of β-diketone and two molecules of the synergist, forming a complex of the form M·TTA·2S (where M = Li, Na, K, Cs), which exhibits greater stability than complexes formed with the β-diketone alone. Common β-diketone extractants include benzoyltrifluoroacetone (HBTA), 2-thenoyltrifluoroacetone (HTTA), 1-heptyl-3-phenyl-1,3-propanedione (LIX54), and 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone (PMBP) (Figure 6). These compounds are typically characterized by the presence of benzene and/or fluorine substituents. The electron-withdrawing capacity of substituents R_1 and R_2 adjacent to the carbonyl groups significantly influences extraction performance; stronger electron-withdrawing groups generally enhance extraction efficiency [43]. Seeley [58] studied alkali metal extraction in β-diketone systems and found that fluorine-substituted extractants (e.g., HTTA) exhibited superior lithium extraction capability compared to non-fluorinated analogs like HDBM and HDPM, with efficiency increasing with the number of fluorine atoms. Zhang et al. [43] studied the extraction effect of lithium using tri-octylphosphine oxide (TOPO) as a co-extractant and benzoyl trifluoropropionone (HBTA) in alkaline salt solutions. The separation factor of lithium and sodium reached >2100, and the lithium extraction rate was greater than 95%. Ishimori et al. [59] reported that in different diluents, using HTTA (nonyl trifluoropropionone) and PHEN (1,10-phenanthroline) as a co-extraction system, using toluene, benzene, chlorobenzene or ortho-chlorobenzene as solvents, lithium was well separated from sodium solutions in sodium chloride and potassium solutions. However, ketone extractants with three-fluorine substituents such as HBTA usually have a higher price, which also limits its industrial prospects.

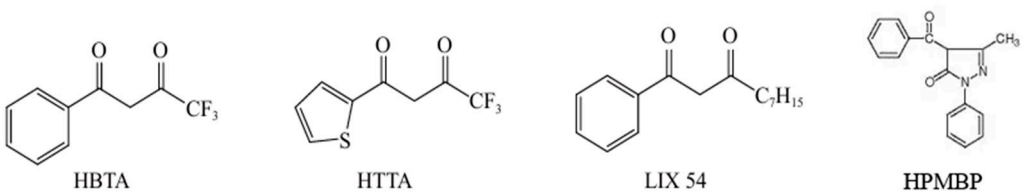

Figure 6. Structures of Common Diketone Extractants.

In addition to fluorine substituents, β-diketone extractants bearing phenyl substituents also demonstrate remarkable lithium extraction performance. Wang et al. [16] developed a synergistic solvent extraction system consisting of 1-phenyl-3-heptyl-1,3-propanedione (PHPD) and trialkylphosphine oxide (Cyanex923) for recovering lithium from lithium precipitation mother liquor. The system achieved a single-stage extraction efficiency of 97.83% and a Li/Na separation factor of 475.06. Pranolo et al. [46] investigated the separation of lithium from sodium in brine using α-acetyl-di-tert-dodecylacetophenone (Lix54) as the extractant. Their study revealed a strong synergistic effect when Lix54 was combined with Cyanex923. Under equilibrium pH 11 conditions, a single-stage lithium extraction efficiency of 97% was attained, along with a Li/Na separation factor of 1560. Zhao et al. [60] employed an optimized system comprising dibenzoylmethane (DBM) and tributyl phosphate (TBP). Under the conditions of 0.4 mol/L DBM, 1.2 mol/L TBP, and an O/A ratio of 1:1, the single-stage lithium extraction rate reached 99.96%, with an exceptionally high separation factor exceeding 160,000, indicating outstanding lithium-sodium separation performance.

4. Ionic Liquids Extractant Applied in the Extraction and Separation of Lithium from Mother Liquor

Wilkes et al. first synthesized stable ionic liquids in air and water, providing possible conditions for the industrial application of ionic liquids [61,62]. Unlike traditional solvents, ionic liquids consist of organic cations and organic/inorganic anions. The commonly used cations mainly include quaternary ammonium salts, imidazoles, phosphonium salts, and pyridines. Owing to the significant size disparity between the cations and anions, ionic liquids exhibit low melting points, with most remaining in the liquid state at room temperature [63,64]. Wang et al. [65] synthesized functional ionic liquids using trialkyl methylammonium as the cation and diketone acid as the anion. Compared with the traditional HTTA extractant, the ionic liquid [A336][TTA] demonstrated higher extraction efficiency, with an applicable pH range extending from 1.26 to 10.17. After a three-stage extraction process, the Li^+ recovery rate reached 97.16%. The alkyl substituents on the anion of the ionic liquid may exert steric hindrance effects on the extraction of Li^+ or Na^+. Due to the reduced steric hindrance associated with anions bearing shorter alkyl chains, the corresponding ionic liquids exhibit higher extraction efficiency (Figure 7). Shi et al. [66,67] synthesized phosphate-based functional ionic liquids using phosphate groups as anions and ammonium chloride as cations, and the phosphonium salt type ionic liquid [P4444][BTMPP] based on Cyanex 272. Under identical aqueous phase pH conditions, these ionic liquids demonstrated significantly higher lithium extraction efficiency compared to Cyanex 272. This enhancement may be attributed to the synergistic extraction effect exerted by $[P4444]^+$ on the complex formed during the coordination between $[BTMPP]^-$ and Li^+. Although ionic liquids have stable properties and low volatility, due to their production cost being much higher than other available extractants, they have not been widely used in the industrial production of lithium extraction.

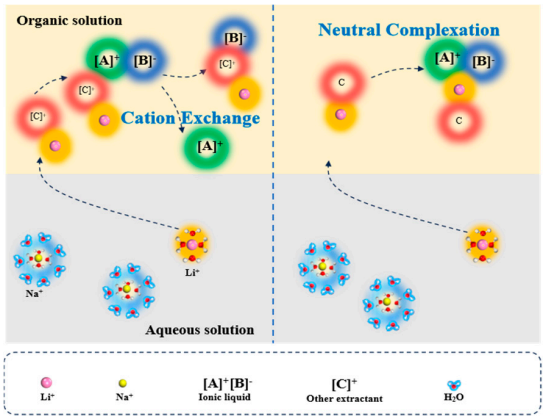

Figure 7. Mechanism of lithium-sodium separation by ionic liquid [A336][TTA] (Adapted from [65]).

5. Crown Ether Extractant Applied in the Extraction and Separation of Lithium from Mother Liquor

Crown ether extractants are a series of large-ring organic compounds containing multiple ether groups. Since Pedersen's successful synthesis in 1967 of a series of crown ethers capable of forming stable complexes with alkali metals while being readily soluble in organic solvents, these compounds have been gradually applied in lithium isotope separation [68,69]. Studies have shown [70–74] that the electronegative oxygen atoms in the crown ether ring can form stable complexes with metal ions through electrostatic interactions. When the radius of the metal ion is approximately 0.9 times the cavity radius of the crown ether, the resulting complexes exhibit maximum stability and optimal extraction efficiency. Under alkaline conditions, crown ethers containing protonatable functional groups on their side chains can provide enhanced affinity for Li^+, which enables them to form more stable complexes with Li^+ compared to neutral crown ethers. Wilcox et al. [75] investigated two chromogenic monoaza-crown ethers (13-crown-4 and 14-crown-4) and demonstrated their high selectivity for Li^+ in sodium-containing solutions. Torrejos et al. [76] synthesized a series of dihydroxy crown ethers via intermolecular cyclization of diepoxides and dihydroxybenzenes and applied them for lithium separation. The results revealed that these crown ethers exhibit high selectivity for lithium due to their ideal cavity size matching with Li^+ (Figure 8), with the lithium-sodium separation coefficient reaching up to 2514.

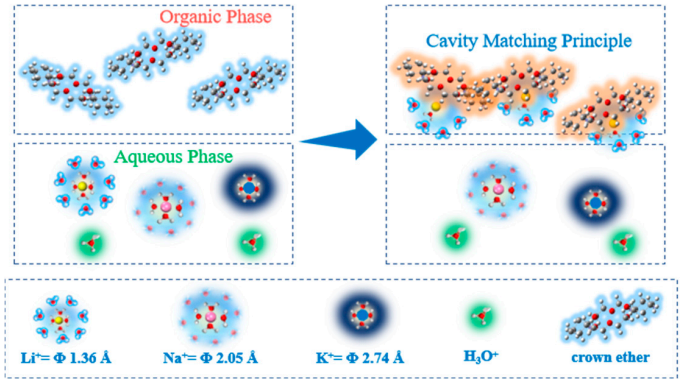

Figure 8. Mechanism of lithium-sodium separation using crown ether extractants (dihydroxy crown ether) (Adapted from [76]).

6. Other Extractant Applied in the Extraction and Separation of Lithium from Mother Liquor

Phenolic compounds refer to compounds formed by substituting hydrogen atoms on the aromatic ring of aromatic hydrocarbons with hydroxyl groups. Based on the number of

hydroxyl groups in the molecule, they could be classified into monophenols, diphenols, and polyphenols (those containing three or more phenolic hydroxyl groups) [77–79]. The hydroxyl groups of phenols are directly connected to the sp2-hybridized carbon atoms of the benzene ring, which is similar to the enol groups in aliphatic compounds. Zhao et al. [52] compared several common phenolic reagents such as tert-butyl catechol (TBHQ), 2,6-di-tert-butylphenol (2,6-DTBP), 2,4-di-tert-butylphenol (2,4-DTBP), nonylphenol (HA), and dodecylphenol (DP). The results showed that TBHQ theoretically exhibits the highest extraction efficiency for Li^+, but due to its two hydroxyl groups, its water solubility was high, leading to a significant dissolution loss in water. Nonylphenol itself exhibits no extraction capability for Li^+. However, after saponification to form sodium nonylphenolate, its HOMO-LUMO energy gap decreases and the electrostatic potential distribution becomes more asymmetric. This results in a stronger affinity of the nonylphenolate oxyanion for Li^+ compared to Na^+ (Figure 9). Through a 12-stage counter-current extraction process, the lithium extraction rate could reach 99%, with a maximum lithium-sodium separation coefficient ($\beta Li^+/Na^+$) as high as 114,799.73.

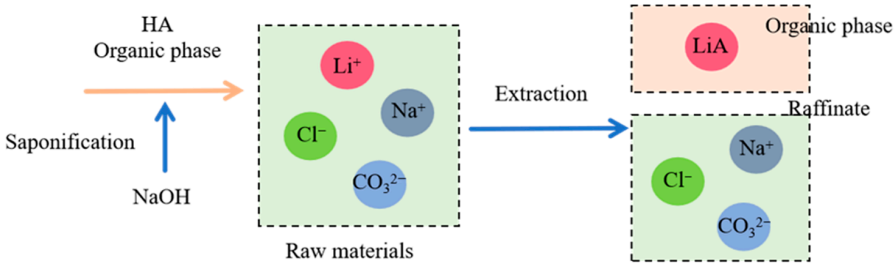

Figure 9. The mechanism of extraction and separation of lithium and sodium using phenolic extractants (nonylphenol) (Adapted from [54]).

Amide compounds have the property that the lone pair electrons on the N atom in the molecule undergo P-π conjugation with the carbonyl group, resulting in an increase in the electron cloud density on the oxygen of the carbonyl group, making them prone to combine with hydrogen ions or metal ions. Shi Dong [80] et al. combined the amide extractant N523 with TBP and sulfonated kerosene to form an extraction system for separating lithium, magnesium, sodium, and potassium ions from brine. It showed that three-stage countercurrent extraction could achieve an extraction rate of 99.53% for Li^+, while the extraction rates for magnesium, sodium, and potassium were only 0.17%, 1.78%, and 2.30%, respectively. This effectively separated metal Li from other impurity metals.

Deep Eutectic Solvents (DESs) are a new type of ionic liquid. It is formed though the hydrogen bonds between substances, creating a new substance characterized by a freezing point significantly lower than the melting points of its individual pure components [81]. Hanada et al. [82] used two different conventional extractants (HTTA and TOPO) to mix in an ultrasonic environment to form a liquid DES that can effectively produce a synergistic effect. The viscosity of this DES is lower than that of traditional hydrophobic ionic liquids, which showed a good extraction effect on lithium in brines containing lithium, sodium, and potassium.

The above extraction systems can achieve the extraction and separation of Li^+ to a certain extent (Tables 1 and 2), but compared with organic phosphine and diketone extractants, their production costs are generally higher than those of β-diketone and organophosphorus extractants, which limits their large-scale application in industrial settings [83–86]. Notably, across various extractant categories—including diketones, organophosphorus compounds, phenolic compounds, and ionic liquids—deionized water is widely adopted in the washing stage, and hydrochloric acid remains the most frequently used reagent in the stripping

stage. In the future, reducing the synthesis costs of extractants such as crown ethers, ionic liquids, and phenolic compounds will help promote the development of lithium extraction and separation from lithium precipitation mother liquor and enhance the industrial competitiveness of this technology.

Table 1. Common extraction systems are used for extracting and separating lithium and sodium metals.

Extractant	System	Lithium Concentration in Mother Liquor (g/L)	Sodium Concentration in Mother Liquor (g/L)	Feed pH	O/A	Lithium Extraction Percentage	Na	K	Ref.
Organophosphorus type extractants	ES-TRPO	1.856	60.60	13.5	1	99.5% (Three-stage)	1.2%	/	[51]
	TBP-HDES	1.52	56.82	-	1	76.80% (Single-Stage)	3.15 g/L	15.4	[11]
Diketone extractants	Lix54-Cyanex	1	23	11.2	1	97.3%	2.6%	1563	[46]
	Lix54-Cyanex	1	80	11.2	1	96.3%	2.5%	1123	[46]
	PMBP-TIBP	1.51	47.30	/	1	94.29%	/	988.55	[48]
	BA-TIBP	1.51	47.30	/	1	89.79%	/	/	[48]
	PHPD-Cyanex923	1.39	68.97	13.06	1	>97%	About 10%	475.06	[16]
	HBTA-TOPO	1.423	52.25	10.5	1	≥99.9% (Five-stage)	0.14 g/L	>25,000	[43]
	DEM-TBP	2.097	76.99	9.56	1	99.96%	<10%	>160,000	[60]
Amide-based extractants	N523-TBP	2.07	0.71	1–2	2	99.53% (Three-stage)	0.013 g/L		[80]
Ionic Liquids	[A336][TTA]-TRPO	1.41	63.23	13.11	1	97.16%	8%	/	[65]
	[OHEMIM][NTf2]	1.412	63.23	10.68	2	93.86%	15.81%	38.36	[87]
Phenolic extractants	HA	1.791	111.244	10.23	3	71.52% (Single-Stage)	−5.91%	−44.99	[52]

Table 2. Summary and Industrial Viability Evaluation of Lithium Extractants.

Extractant Category	Extraction Mechanism	Advantages	Disadvantages	Industrial Maturity Assessment
Organophosphorus	Neutral coordination/Cation Exchange	Low cost, extensive industrial experience.	Prone to degradation and emulsification under acidic conditions, corrosive to equipment; poor Li^+/Na^+ selectivity.	High (Traditional), but facing obsolescence for lithium recovery from precipitation mother liquor; mostly used as synergists.
Diketones	Cation Exchange	Exceptionally high Li^+/Na^+ selectivity	High cost; prone to emulsification; strongly dependent on high pH conditions; solvent loss issues.	Medium-High (Industrialization in Progress), currently the research and application hotspot for lithium recovery from mother liquor; relies on synergistic systems with organophosphorus esters to overcome drawbacks.
Ionic Liquids	Neutral coordination/Cation Exchange	Low volatility, high thermal stability; wide applicable pH range.	Extremely high synthesis cost; high viscosity.	Low (Transition from Lab to Pilot), high cost is the core barrier to industrialization; currently mainly used in high-value-added fields or fundamental research.
Crown Ether	"Size-matching" host-guest recognition	Theoretically highest selectivity based on cavity size, especially suitable for Li^+/Mg^{2+} separation	Extremely expensive; relatively high-water solubility; complex synthesis.	Low (Fundamental Research Stage), farthest from large-scale industrial application; near-term goal is to validate its high-selectivity value via methods like immobilization.
Amides	Synergy of multiple mechanisms	Good selectivity for Li^+; some systems can avoid strong acid/base conditions.	Insufficient research on comprehensive performance; lack of long-term industrial validation data.	Low to Medium (Technology Validation Stage), reported applications in specific fields (e.g., battery recycling leachate), but universality and maturity need improvement.

7. Conclusions and Prospects

Facing the huge demand for lithium resources under the global energy transition strategy, and the severe challenge of high dependence on foreign sources due to the inherent disadvantages such as high magnesium-to-lithium ratio and low grade of salt lake lithium resources in China, the development of efficient and economic key technologies to enhance the comprehensive utilization rate of lithium resources has become a major strategic requirement for ensuring national energy security and industrial development. The efficient recovery of lithium from the large amount of lithium precipitation mother liquor generated during the production of lithium products is one of the key links to make up for the supply gap of primary resources and realize the circular economy. This paper systematically reviews the research progress and technical principles of the solvent extraction method for recovering lithium ions from lithium precipitation mother liquor. The study shows that there are significant differences in the applicability of different types of extractants in the lithium precipitate mother liquor system.

Organic phosphorus, neutral phosphorus extractants (such as TBP, TOPO) have poor selectivity for Li^+ under alkaline conditions and are prone to competing with Na^+ for coordination, while their strong electron-donating ability enables them to be excellent synergistic extractants. Acidic phosphorus extractants have extremely high selectivity for divalent ions like Mg^{2+} and Ca^{2+} under acidic conditions via the cation exchange mechanism, but their efficiency is low and their separation requires significant pH adjustment when separating monovalent Li^+ and Na^+ from alkaline lithium precipitate mother liquor, resulting in poor economic performance.

Diketone extractants (such as HBTA, LIX54) with their ketone-eneolide interconversion characteristics can form stable hexavalent chelate rings with Li^+, exhibiting inherent selectivity for Li^+. However, their standalone use is prone to emulsification, and demonstrates limited extraction efficiency. It confirmed that constructing synergistic extractants with organic phosphorus (such as TOPO, TBP) is the most efficient strategy, which not only overcome the emulsification problem, but also achieve extremely high lithium extraction percentage (>90%). In addition, the lithium-sodium separation coefficient reaches as high as several thousand to 160,000, making it the most widely adopted technological solution for industrial applications.

Extraction systems such ionic liquids extractants, crownextractants, phenolic extractants, and deep eutectic solvents (DESs) can achieve the extraction and separation of Li^+ to a certain extent, but compared with organic phosphine and diketone extractants, their production costs are generally higher than those of β-diketone and organophosphorus extractants, which limits their large-scale application in industrial settings.

At present, solvent extraction still faces several limitations. For example, the high volatility of organic solvents can result in air pollution and pose risks to both the environment and human health. In addition, solvent recovery processes often entail non-negligible losses. In multi-component systems, interactions among different substances may also influence extraction performance. To facilitate the large-scale application of solvent extraction in recovering lithium resources from lithium-containing mother liquors, future research should focus on the following directions:

(1) Rational design and low-cost synthesis of novel extractants-particularly green extractants with high selectivity, strong stability, low toxicity, and economic viability—to reduce environmental risks and treatment costs at the source.
(2) Overcoming the limitations of conventional single-process configurations by promoting the in-depth coupling and systematic integration of multiple technologies, and actively introducing external field-assisted intensification methods to address

engineering challenges such as emulsification and enhance separation efficiency in lithium recovery.

Through coordinated progress in both extractant design and process integration, the economic competitiveness and feasibility of this technology can be significantly improved, thereby providing key technical support for the efficient recovery of lithium resources and accelerating the industrialization of research achievements.

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