

Review

# Transformations of Critical Lithium Ores to Battery-Grade Materials: From Mine to Precursors

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**Abstract:** The escalating demand for lithium has intensified the need to process critical lithium ores into battery-grade materials efficiently. This review paper overviews the transformation processes and cost of converting critical lithium ores, primarily spodumene and brine, into high-purity battery-grade precursors. We systematically examine the study findings on various approaches for lithium recovery from spodumene and brine. Dense media separation (DMS) and froth flotation are the most often used processes for spodumene beneficiation. Magnetic separation (MS) and ore gravity concentration techniques in spodumene processing have also been considered. To produce battery-grade lithium salts, the beneficiated-concentrated spodumene must be treated further, with or without heat, in the presence of acidic or alkaline media. As a result, various pyro and hydrometallurgical techniques have been explored. Moreover, the process of extracting lithium from brine through precipitation, liquid–liquid extraction, and polymer inclusion membrane separation employing different organic, inorganic, and composite polymer sorbents has also been reviewed.

**Keywords:** spodumene; brine; lithium carbonate; lithium hydroxide; lithium chloride



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## 1. Introduction

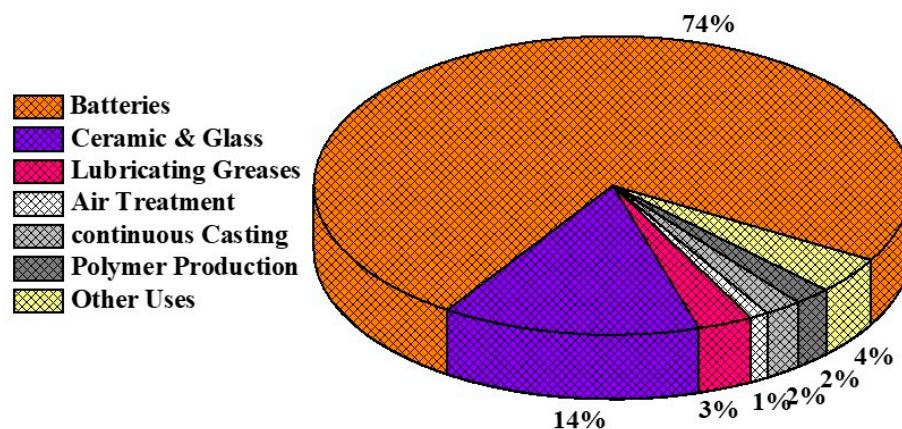
Lithium (Li) was found more than two hundred years ago. It is a silvery-white, soft alkali metal that reacts violently when it comes into contact with water. The Mohs scale of mineral hardness (which ranges from 1 to 10) has a rating of 0.6 for Li [1]. Lithium is listed as a strategic mineral in many countries. Because of its significance to strategically important developing sectors, such as new energy vehicles, it has been regarded as a new sort of ‘gold’ in the modern era [2]. In recent years, lithium has become increasingly prevalent as a novel energy source for fueling electric vehicles (EVs) [3–5]. When discussing lithium, people often first think of its application in batteries, as the battery market has grown significantly in the past few years. Nowadays, it accounts for 74% of the global end-use market for lithium batteries, as shown in Figure 1.

However, lithium was used in various other fields even before the rise of portable batteries. These include the manufacturing of glass materials and ceramics, where the process’s viscosity and melting point are reduced by the addition of lithium. Li is also used in the electrolytic refining process of aluminum to create aluminum alloys compatible with aircraft use. Additionally, many high-performance lubricants and greases contain a percentage of lithium. Other lesser-known uses of lithium include its use in systems for air-conditioning to absorb humidity, its utilization as an additive in polymer manufacturing, and its role in treating bipolar illness. Furthermore, when lithium is transformed into its isotope tritium, it can be utilized as fuel for reactors powered by nuclear energy [6].

### 1.1. Battery Grade Lithium Materials

The minerals required for batteries contain ten critical elements used for Li-ion battery technology. These elements include lithium, iron, manganese, cobalt, aluminum, natural

graphite, copper, phosphorus, nickel, and titanium. These elements have been chosen because they are essential for the development of battery technology and the overall energy transition. At least one of the mentioned elements is found in either the cathode or anode, or they serve as a current collector in the battery cell [7,8]. Battery-grade lithium compounds are high-purity substances suitable for manufacturing cathode materials for lithium-ion batteries. The global production of cathode materials includes  $\text{LiFePO}_4$ ,  $\text{Li}_2\text{MnO}_4$ , and  $\text{LiCoO}_2$ , among others. Usually, the starting raw material is  $\text{Li}_2\text{CO}_3$ , followed by lithium hydroxide monohydrate  $\text{LiOH}\cdot\text{H}_2\text{O}$  and  $\text{LiCl}$  [9].



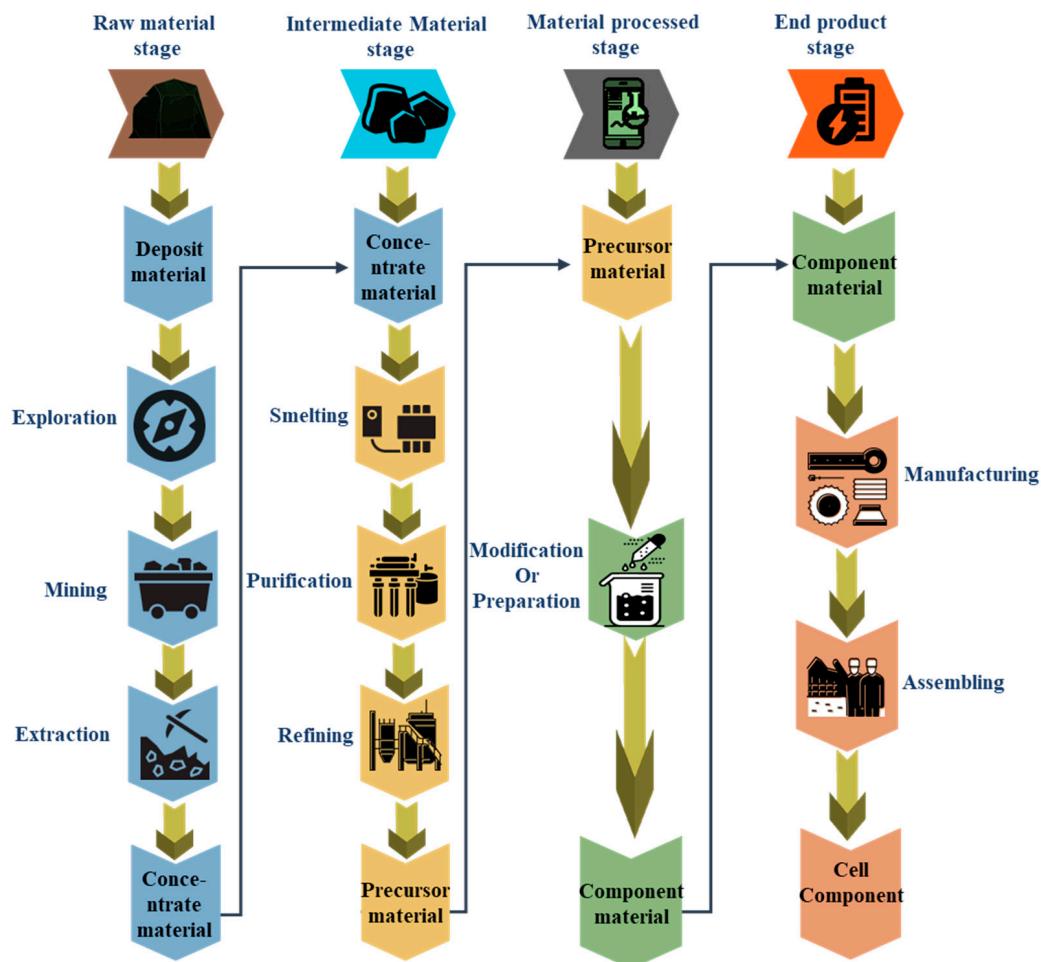
**Figure 1.** The global end-user market size of lithium for various sectors.

The value chain for producing battery-grade materials comprises four key stages or phases, as depicted in Figure 2. These stages function independently of the initial raw material and the final product. Initially, the Raw Material Stage involves various activities related to mining operations, such as exploration, extraction, and beneficiation. Subsequently, the Intermediate Material Stage focuses on chemically altering the material and generating precursors that meet the necessary quality and compositional standards for the third step, typically referred to as refinery production. The third phase, known as the Product Material Stage, deals with producing the specific material required for its designated application. This stage often involves forming the correct physical and chemical properties, with possible blending and combination. Finally, the Tier-n Stage represents the last phase of the value chain and is not associated with a material product. The definition of the Tier-n Stage can be tailored according to the perspective of manufacturers, such as those in the battery or automobile industries [10–16].

### 1.2. Extraction of Lithium

Lithium extraction from natural resources is necessary to fulfill the growing industrial demands that depend on Li-ion batteries. There are three main types of lithium occurrences in nature: pegmatite, brine, and clay. The industrial recovery of lithium mainly centers on brines and pegmatites, with more abundant natural brine sources. Brine deposits provide around 60% of the world's lithium, and the remaining 40% comes from hard-rock lithium deposits. Brine is the main source of lithium production in Chile and Argentina, while Portugal, Brazil, Zimbabwe, Australia, and Canada depend on hard-rock ores for lithium [17].

In recent years, many researchers have thoroughly reviewed the processing features and chemistry of the existing techniques for extracting Li from brines and lithium-bearing rocks. Notable progress, ranging from the laboratory to the pilot and commercial level, has also been achieved in lithium-recovery technologies. However, existing procedures are well-established for typical lithium ore resources but unsuitable for exploiting new resources. Additionally, with the sharp rise in lithium usage and intensifying environmental concerns, there is an urgent requirement for the sustainable utilization of resources [18,19].



**Figure 2.** Overview of defined value chain in different stages.

Several methodologies are used for extracting lithium, including ion-exchange resins, electrochemical processes, solvent extraction, nanofiltration, selective adsorption, and electro-membrane processes. These methods show promise but face environmental challenges, cost, renewability, and long-term stability issues. The newest approach in lithium recovery from spodumene and brine, direct lithium extraction (DLE), allows for faster extraction processes and has demonstrated outstanding proficiency. Yet, these processes need more extensive testing carried out over long periods to determine their financial viability and operational steadiness [20–23]. Despite the significant amount of lithium present in unconventional water sources such as brines from seawater desalination, seawater, geothermal brines, and gas-produced water, extracting lithium from these sources faces challenges in scaling up to meet long-term demands [24,25]. Some recent research results indicate that the methods for extracting lithium vary depending on the mineral phases of different clay-lithium ores. Typically, roasting and extraction processes are necessary [26].

## 2. Lithium Resources

Lithium on Earth occurs in many kinds of forms. It is mainly present as a mineral compound in igneous rocks, subsurface lithium brines, and lithium clays and as a dissolved solid in seawater. Although no significant lithium-extraction projects from seawater have been implemented, only 3 out of over 100 lithium minerals are mined commercially today. The most common spodumene-bearing pegmatite deposits add up to one-third of the world's lithium production [27,28]. Recent developments in mineral processing have made possible the extraction and recovery of lithium from what was then considered waste, such as lithium-bearing micas, generally left as tailings [29]. Approximately 66% of the world's

lithium comes from continental brine deposits located in saline lithium-rich waters. These deposits are mainly located in Chile and Argentina as salt flats, where roughly half of the world's lithium reserves are placed [30].

### 2.1. Spodumene

Spodumene is a lithium-bearing mineral that has an aluminosilicate crystal structure [31]. The color of the pure spodumene crystal in nature ranges from colorless to transparent and includes yellowish, purple, pink, and green hues. These attractive hues are caused by a variety of impurities, primarily Fe, Mn, and Cr, which are present in the spodumene crystal as lattice substitutions [32]. Theoretically, spodumene contains 8.03% Li<sub>2</sub>O, but most of the concentrated spodumene contains Li<sub>2</sub>O between 2.9% and 7.6% [33]. The mineral spodumene occurs naturally in the  $\alpha$ -spodumene configuration, also known as monoclinic spodumene. However, because of its high density (3.27 g/cm<sup>3</sup>) and resistance to extraction chemicals, this allotrope is not appropriate for the effective extraction of lithium [34]. The sites M1 and M2 in spodumene hold different types of cations. The larger Li<sup>+</sup> ion occupies the M2 site, and the smaller Al<sup>3+</sup> ion occupies the M1 site. Aluminum is coordinated with six oxygen atoms from the silicate tetrahedra in an octahedral arrangement. Due to its small size, lithium is arranged irregularly in an octahedral coordination with six oxygen atoms. According to Pauling's electro-neutrality principle, the electrostatic bond strengths are allocated as 1/6 for lithium in octahedral coordination with oxygen, 1/2 for aluminum in octahedral coordination with oxygen, and 1 for silicon in the center of the silicate tetrahedra [35].

### 2.2. Brine

A brine is a solution that contains more than 3.5% total dissolved salts at concentrations higher than saltwater [36]. Its salinity ranges from 1.7 to 24 times that of seawater. Lithium brines are predominantly hypersaline, containing dissolved ions in concentrations that are close to the saturation point for various salts [37]. However, Li-brines are often associated with large concentrations of cations, which may be hundreds or thousands of times more concentrated, such as Mg<sup>2+</sup>, Na<sup>+</sup>, K<sup>+</sup>, and Ca<sup>2+</sup> [38,39]. These positive ions, particularly Mg<sup>2+</sup>, have comparable properties to Li<sup>+</sup> [40]. The chemical compositions of important main salt-lake brines are shown in Table 1.

**Table 1.** Chemical composition of the main salt-lake brine resources (reproduced with permission from [41]).

Country	Salt-Lake Brine	Li <sup>+</sup> (g/L)	Mg <sup>2+</sup> (g/L)	K <sup>+</sup> (g/L)	Na <sup>+</sup> (g/L)	Ca <sup>2+</sup> (g/L)	Mg/Li
China	Qarhan	0.08	115.0	3.73	87.72	0.27	1437.5
	Zabuye	1.53	0.0196	21.56	103.0	0.0	0.013
	West Taijinar	0.26	15.36	8.44	102.4	0.19	59.1
	Longmucuo	0.865	75.41	15.59	11.1	0.12	87.12
	East Taijinar	0.14	5.64	3.79	117.03	0.43	40.3
Chile	Atacama Salar	3.02	17.6	28.2	61.9	0.41	5.8
Bolivia	Uyuni Salar Brine	0.84	17.6	15.7	105.4	3.33	21.0
Argentina	Salar de Olaroz	0.66	2.67	7.9	106.0	0.98	4.0
	Salar del Hombre Muerto	0.773	1.062	8.153	98.055	0.566	1.37
USA	Great Salt Lake	0.04	9.38	5.5	100.8	0.35	234.5

### 2.3. Other Resources

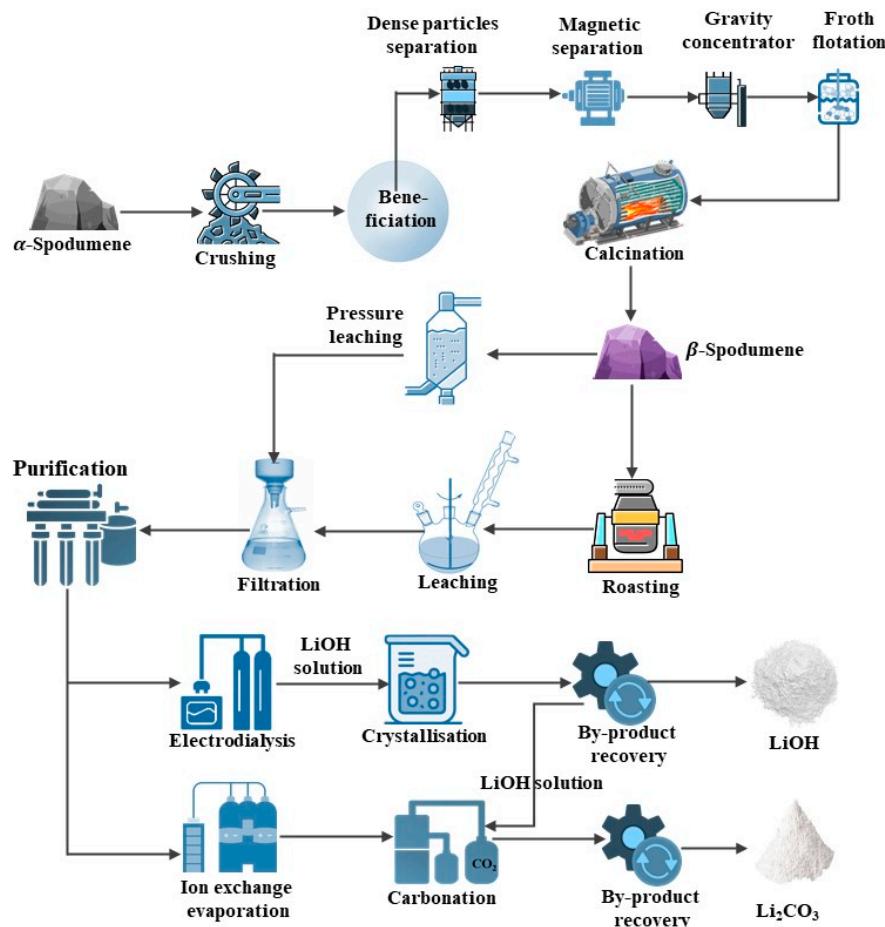
Petalite is a type of tectosilicate in which the silicate framework is defined by all the oxygens in the SiO<sub>4</sub> tetrahedron connecting with adjacent tetrahedra [42]. It is often found

along with other pegmatites including spodumene, eucryptite, and lepidolite. Theoretical lithium percentage in petalite is 2.27% (4.88% Li<sub>2</sub>O), although the actual lithium level in different occurrences ranges from 1.4 to 2.2% Li (3.0–4.7% Li<sub>2</sub>O). Petalite deposits of significant size are found in Brazil, Canada, Australia, and Zimbabwe. Eucryptite is a somewhat uncommon lithium mineral that is mostly found in association with petalite. Pure petalite undergoes a transformation into β-spodumene at elevated temperatures in order to facilitate the process of leaching [43,44]. Eucryptite mineral deposits were once a crucial lithium resource, with an average lithium content ranging from 2.1% to 3.0% (equivalent to 4.5% to 6.5% lithium oxide). Additionally, it is used in the production of glass. The Bikita deposit in Zimbabwe has an average lithium grade of 2.34%, which is equivalent to 5.0% lithium oxide (Li<sub>2</sub>O). Nevertheless, eucryptite deposits are exceedingly infrequent and often occur in modest quantities. Eucryptite may undergo direct leaching by strong acids, eliminating the requirement for roasting [44]. Lepidolite, a kind of mica, has a composition that is intricate and may vary. It is used in the manufacturing of glasses and ceramics. The lithium percentage of the material may range from 1.39% (equivalent to 3.0% Li<sub>2</sub>O) to 3.58% Li (equivalent to 7.7% Li<sub>2</sub>O). Lepidolite has a less extensive occurrence in pegmatites than spodumene. Lepidolite resources of commercial value are located in Zimbabwe, Canada, Namibia, Brazil, Portugal, and Argentina [45]. Lepidolites are valuable sources of rubidium, in addition to lithium, since they contain substantial levels of this element [43]. The primary gangue minerals often associated with lepidolite are calcite, muscovite, feldspar, and quartz. These minerals must be removed in order to concentrate lepidolite. Flotation is a method that may be used to remove calcite, muscovite, feldspar, and/or quartz from lepidolite. One approach for extracting Li from lepidolite involves using sulphuric acid (H<sub>2</sub>SO<sub>4</sub>) digestion at temperatures over 250 °C [46]. Amblygonite is the terminal member of a lithium alumino phosphate group that is rich in fluorine. The theoretical lithium percentage of the substance is 4.76% (equivalent to 10.2% Li<sub>2</sub>O), but most economically viable ores typically have a lithium content ranging from 3.5% to 4.4% (equivalent to 7.5% to 9.5% Li<sub>2</sub>O). The mining of this resource takes place in Canada, Brazil, Surinam, Zimbabwe, Rwanda, Mozambique, Namibia, and South Africa [44]. Dense media separation and flotation are commonly employed to differentiate amblygonite from other lithium-bearing minerals and silicate gangue [47]. When both amblygonite and spodumene coexist in the same ore, amblygonite is typically pre-floated to prevent the contamination of spodumene with phosphate and fluorine [44]. The presence of fluorine in lithium ores is problematic, as it can lead to the production of LiF and the hazardous H<sub>2</sub>F<sub>2</sub> during downstream processing. Compared to other silicates, amblygonite exhibits a higher solubility in acidic conditions. Zinnwaldite, often regarded as an impure form of lepidolite, contains significant levels of iron (up to 11.5% Fe as FeO) and manganese oxide (MnO at 3.2%). Due to its relatively high iron content and low concentration of Li<sub>2</sub>O, zinnwaldite is generally considered less desirable as a lithium source. However, its notable magnetic properties, attributable to its iron content, allow for enrichment using magnetic separation (MS). Following MS, water leaching and precipitation can yield a Li<sub>2</sub>CO<sub>3</sub> concentrate with a purity greater than 99% [48].

### 3. Recovery of Lithium from Spodumene

The starting point in lithium ore processing is the crushing of raw materials. Beneficiation through procedures such as dense media separation, magnetic separation, gravity concentration, and flotation follows this stage. This results in concentrates with a lithium oxide (Li<sub>2</sub>O) content between 4% and 6%. These concentrates can later be used in the process of roasting and leaching in order to extract lithium into a solution. During thermal treatment, metal hydroxides, salts, or acids are combined with the concentrates to produce leachable lithium compounds such as sulfate, carbonate, or chloride. The next stage is purification, generally by precipitation, to remove significant impurities such as Ca, Mg, Al, and Fe. The concentration of lithium ions is attained by ion-exchange or evaporation. In the end, methods such as crystallization, carbonation, or electrodialysis are used to produce

lithium compounds ( $\text{Li}_2\text{CO}_3$ ,  $\text{LiCl}$ ,  $\text{LiOH}$ ) of chemical or battery grade or to extract lithium metal from these precursors. A schematic depicting the transformation of lithium ores is shown in Figure 3 [49].

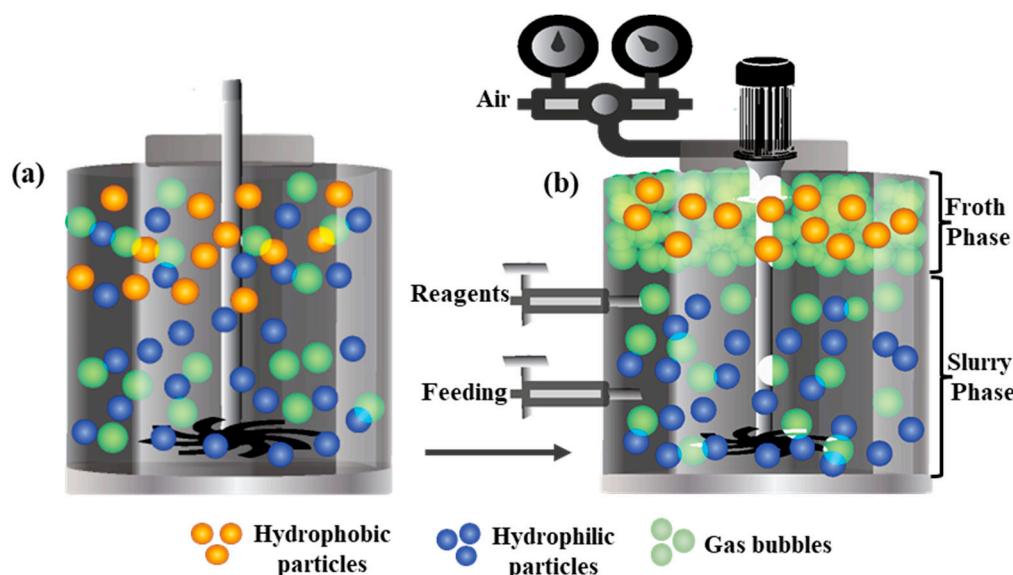


**Figure 3.** General flowchart for lithium extraction from spodumene.

### 3.1. Beneficiation

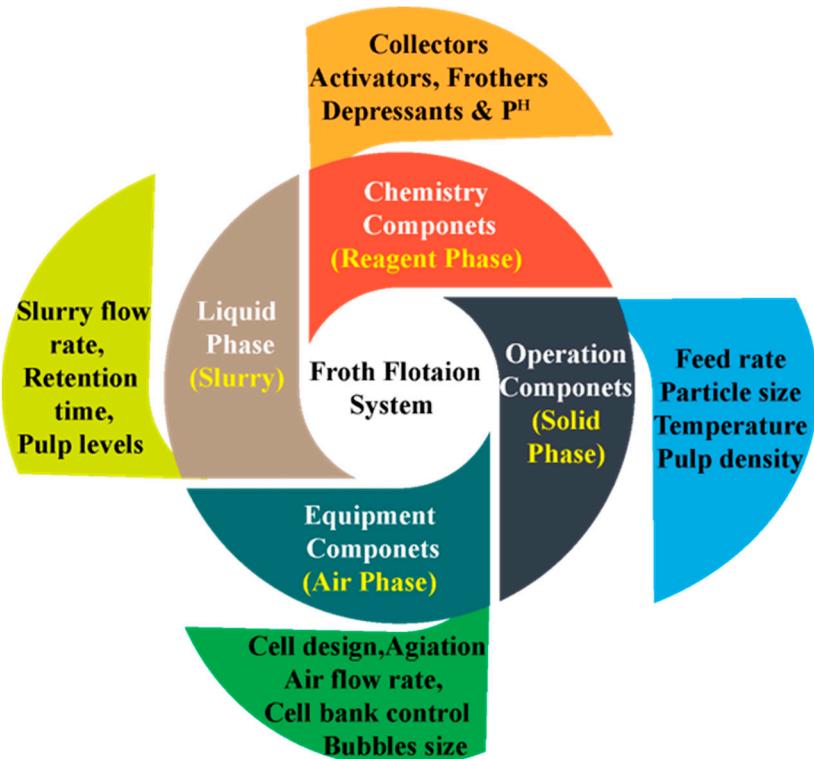
#### 3.1.1. Froth Flotation

Froth flotation is a highly versatile method that physically separates particles by taking advantage of differences in the ability of air bubbles to selectively adhere to specific mineral surfaces within a mixture of minerals and water. Froth flotation is a physicochemical method of separating a combination of fine mineral particles by mixing it with water in a large tank. In this process, little air bubbles, measuring several millimeters in size, are produced at the bottom of the tank and allowed to flow constantly through the slurry. As the bubbles rotate and collide with the particles in the mixture, certain mineral particles adhere to the bubbles and rise to the surface of the slurry, forming a stable froth concentrate. Simultaneously, mineral particles that cannot stick to the bubbles stay scattered in the slurry and are expelled from the operation as tailings (also commonly known as gangue minerals). The process of the froth flotation mechanism before and after can be depicted schematically as illustrated in Figure 4a,b [50].



**Figure 4.** Mechanism of froth flotation, showing the process before (a) and after (b).

Froth flotation is a widely recognized and established method for improving the quality of lithium-containing spodumene. The effectiveness of this unit operation lies in its ability to treat fine particles with minimal variation in specific gravity between the valuable and rejected materials. Traditional gravity concentration procedures are unable to recover such particles. Froth flotation exemplifies an engineering system where the significant parameters are intricately interconnected and changes in one area will produce compensating effects in other areas as depicted in Figure 5. Collectors are surfactants that primarily function by adsorbing at the interface between minerals and water, making mineral surfaces hydrophobic. They are the primary chemicals used in flotation. Frothers predominantly adhere to the interface between air and water, specifically on the surfaces of gas bubbles. Their primary role is to help disperse air into numerous small bubbles and prevent the merging of bubbles into larger ones within the slurry phase. Activators enhance the process of collectors attaching to mineral surfaces. In some cases, a collector may not adsorb onto a mineral unless the mineral is activated beforehand. Activation is a procedure that modifies the surface to improve interactions between minerals and collectors. Dispersants are used to inhibit the agglomeration of mineral particles. pH is a crucial factor in determining surface charging mechanisms, the processes of surfactant and ion adsorption, and the phenomena of interparticle aggregation and dispersion [50].



**Figure 5.** Froth flotation system consists of interconnected components, where any change in one part will cause corresponding adjustments in other areas.

Spodumene usually accompanies gangue minerals such as feldspar and mica and shows poor responsiveness in flotation separation because of the similarity of their mineral surfaces' active sites, which are collector-reactive. It constitutes 45% of the true lithium ore chemistry [51,52]. One of the results showed that the activated form of ions, such as  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{Fe}^{3+}$ , can enhance the capability of sodium oleate to adsorb onto the spodumene surface. In fact, this can boost and intensify the spodumene flotation process. In a way, it is not good enough; the presence of activating metal ions activates not only the gangue minerals, like quartz and feldspar, but also spodumene, making the separation process difficult during flotation. The system that has the closest balance between the two species of  $\text{R}^+$  and  $\text{R}^-$  (where  $\text{R}^+$  is the long-chain cation and  $\text{R}^-$  is the long-chain anion) brings up the situation closer to electrical neutrality. Therefore,  $\text{R}^+$  and  $\text{R}^-$  has the most active surface, and this results in the highest adsorption level onto the mineral surface [53].

K. Shu et al. [54] conducted a study on the impact of mixed collectors with different alkyl chain lengths and ligand types on the hydrophobicity of the spodumene–feldspar flotation system. The study found that the combination of OHA (octanohydroxamic acid) and DDA (dodecylamine), as well as NaOL (sodium oleate) and DDA, effectively separates spodumene and feldspar. For NaOL and DDA, the optimal molar ratio was found to be 6:1 at pH 8–9, resulting in high spodumene recovery (81.19%) and low feldspar recovery (<4.5%). Conversely, OHA and DDA favored reverse flotation, achieving high feldspar recovery (>98%) and significant spodumene depression (>75%). The study also observed a shift in OHA's adsorption behavior, from monodentate chemisorption at pH 4–5 to bidentate chemisorption at pH 8–9, influencing the flotation process's effectiveness. Similarly, the study noted that the adsorption sequence of NaOL with DDA changes with pH, impacting separation efficiency [54].

In another study, K. Shu et al. [55] illustrated that employing a mixed collector system consisting of benzohydroxamic acid (BHA) and dodecylamine (DDA) in a 6:1 molar ratio notably enhances the separation of spodumene from feldspar in flotation processes. The research revealed that the surface of spodumene exhibits a higher number of active sites than

feldspar, leading to improved adsorption of the mixed collector complex on spodumene. At a pH range of 8–9, the spodumene recovery rate reaches 88.31%, while feldspar recovery is reduced to approximately 24%, demonstrating effective selective flotation. Furthermore, thermodynamic investigations indicated that the BHA/DDA collector generates more heat during adsorption compared to individual collectors, suggesting a stronger interaction with spodumene [55].

Ma et al. [56] studied the impact of NaOH as a modifier on the mineral surface. NaOH can change the surface characteristics of minerals and upgrade the floatability difference between feldspar and spodumene. The flotation grade of Li<sub>2</sub>O in spodumene concentrates had a 1.11% rise, while the recovery of Li<sub>2</sub>O improved by 6.99% after undergoing NaOH pretreatment [56]. In another experiment a mixture of anionic-cationic reagents sodium oleate (NaOL) and N-lauryl-1,3-propylene diamine ND13 used, at a molar ratio of 5:1, to achieve selective flotation separation with respect to spodumene from feldspar. At pH 8.0, this hybrid collector worked particularly selectively, by practically excluding the recovery of feldspar from mixed minerals, yet preserving the recovery of spodumene at 80.45%. The flotation results indicated the concentration of Li<sub>2</sub>O in the concentrate increases by using NaOL/ND13 and individual collectors together with improving the overall Li<sub>2</sub>O recovery. This reflects the increased selectivity and efficacy of NaOL in combination with ND13 and the other collectors. The improvement of the efficiency of flotation under such conditions could be related to the increased physicochemical strong interactions of the dual collector with the mineral surface. NaOL/ND13 showed greater adsorption on the spodumene surface comparatively to the feldspar surface. The observed variation in adsorption, confirmed by microcalorimetry and zeta potential tests, is indicative of improved flotation separability. More still, XPS and FTIR research confirm that NaOL/ND13 establishes more robust chemical interactions with the Al sites on the spodumene surface. This emphasizes the selectivity and efficiency of NaOL/ND13 in the flotation process [57].

### 3.1.2. Dense Media Separation

DMS, popularly known as heavy medium separation, is a process of separation based on the difference in particle densities in a medium with an intermediate density between that of the targeted minerals and gangue. This process exploits the difference in specific gravity between the desired spodumene mineral and the unwanted gangue silicates for their separation. Spodumene has a specific gravity of 3.1–3.2, which is slightly higher than that of common gangue minerals, including quartz (2.65), albite (2.60), and muscovite (2.8). Since spodumene is heavy, it settles down and the gangue minerals remain floating in a dense media of proper specific gravity, thus separating the two from each other [45].

Historically, the first DMS facility for processing spodumene-rich pegmatites was established in 1949 at the Edison mine in the USA. A media density of 2.70 is prepared to generate a spodumene concentrate with a grade of 5.36% Li<sub>2</sub>O and a recovery rate of 47.4% [58].

Sagzhanov et al. [59] conducted a dense media separation (DMS) test on low-grade spodumene ore from the Akhmetkino deposit in Eastern Kazakhstan to evaluate the potential for lithium recovery through pre-concentration. They used sodium polytungstate solutions with densities ranging from 2.70 to 3.00 g/cm<sup>3</sup>, adjusted in 0.10 g/cm<sup>3</sup> increments to determine the optimal separation point. The feed materials were divided into two size fractions: 1000/+ 850 µm and 850/+ 500 µm. The best DMS results were achieved with the 850/+ 500 µm fraction, yielding a concentrate with 7.05% Li<sub>2</sub>O and approximately 91% spodumene recovery at a specific gravity of 3.00 g/cm<sup>3</sup>. Meanwhile, the 1000/+ 850 µm fraction attained a concentrate grade of 6.72% Li<sub>2</sub>O, equivalent to about 87% spodumene. The decline in lithium grade with lower specific gravity media is attributed to the increased presence of silicate minerals like quartz and feldspar in the sink fraction. This study highlights the importance of particle size and liberation in achieving high-quality spodumene concentrates using DMS [59].

Similarly, a two-stage dense media separation (DMS) system has been employed at the Bikita processes in Zimbabwe for petalite extraction, where petalite, being the lighter product, is separated in the first stage. The sink material from the initial stage is then further processed in the second stage of DMS to produce a concentrated form of spodumene [45]. Another example is the Bernic Lake Lithium Operation in Canada, where DMS is used to produce feldspar and spodumene concentrates free of tantalum [60].

However, the DMS process faces challenges, particularly with spodumene's tendency to fracture into needle-like particles that can float with unwanted minerals. Additionally, when spodumene converts into micaceous and clay minerals, its specific gravity decreases, reducing the difference between it and the gangue minerals. This leads to limited separation efficiency [58]. Despite DMS having several drawbacks, it remains an appealing pre-concentration method for processing spodumene ore with large particle sizes [61]. For finer mineral liberation, MS is less effective, and froth flotation may be necessary [62]. However, in some cases, small particles are also subjected to DMS. At the Greenbushes Lithium Processes in Australia, DMS is used to process fine particles, including flotation concentrate, to produce a spodumene concentrate that is free of cassiterite and tantalite [63].

### 3.1.3. Magnetic Separation

The presence of dispersed magnetic minerals within the spodumene crystal lattice makes effective separation difficult when using gravity or froth flotation methods [45]. Tourmaline and amphibole are the predominant magnetic minerals found in pegmatites [63]. Additionally, spodumene concentrate intended for glass- or ceramic-grade applications should contain no more than 0.5% iron oxide [64]. Magnetic separation is employed to remove iron-bearing gangue impurities associated with spodumene either before or after flotation. At Bernic Lake, a low-intensity magnetic separator is used to remove iron-bearing impurities from the fine fraction [45]. The partially refined spodumene concentrate is then sent to flotation cells for the extraction of amblygonite, quartz, and Na-feldspar. The flotation concentrate is treated with a wet high-intensity magnetic separator to eliminate magnetic impurities, resulting in a spodumene concentrate averaging 7.25% Li<sub>2</sub>O [60]. At the Greenbushes spodumene processing facility, a magnetic separator is used to produce glass-grade spodumene. The fines fraction is further processed through flotation cells and gravity separators to recover cassiterite and tantalite. A wet high-intensity magnetic separator is then used to produce a spodumene concentrate free of tourmaline in the non-magnetic fraction, with a Li<sub>2</sub>O content of 7.5–7.7% and less than 0.1% Fe<sub>2</sub>O<sub>3</sub> [65].

### 3.1.4. Gravity Concentration

Gravity separation represents currently one of the most important and efficient techniques in the mineral treatment, mainly because of economic and ecological advantages. In this technique of separation, it is performed based on differences in particle density by taking advantage of the density contrasts among the various components of an ore, where the effectiveness of the separation deeply depends on specific gravity contrast and on particle size. The most common devices applied are jigs, spirals, and shaking tables; and more advanced devices using centrifugal forces include the Kelsey centrifugal jig, Knelson concentrator, and Falcon concentrator. All of these devices have their best application size ranges and applicability: jigs in coarser material, and shaking tables for finer particles. Gravity separation has played an important role in the beneficiation of heavy minerals and has been extensively used in treatment concerning tin ore, tungsten ore, gold ore, barite ore, iron ore, diamond ore, and artificial rutile. The latest improvements including [66] multistage and compound spirals provide substantial increases in the capabilities of gravity concentration methods with respect to recoveries of fine particles and extend the application areas. Efficiency in gravity concentration is closely connected with meticulous feed preparation, strict control of operating conditions, and effective handling of slimes—all reminders of the importance of precise process control if the highest performance is to be achieved. However, even with challenges in fine particle separation, gravity concentration

remains one of the cornerstones in mineral processing due to constant development that increases efficiency and sustainability [66].

Among all of the heavy liquid separation (HLS) studies conducted on the gravity concentration of spodumene-bearing pegmatites from the Amareswar area in India, including mineral jigging, shaking table, and Falcon concentrator studies, HLS has given the best separation efficiency; Li content increased from 1.10% to the range of 4.0–4.4% Li<sub>2</sub>O in the concentrate. Jigging is also promising, with a Li<sub>2</sub>O content of up to 3.42% and a separation efficiency of 55.97%. By contrast, the shaking table and Falcon concentrator showed poor efficiencies, especially for finer particles, due to their relatively low concentration criteria. The better performance of HLS with coarser particles indicates that HLS may be a potential pre-concentration [67].

### 3.2. Pyro Metallurgy

The final product of the beneficiation process,  $\alpha$ -Spodumene, shows a strong resistance to chemical reactions. Therefore, industrial practices typically use pyrometallurgical techniques to convert it to  $\beta$ -spodumene, usually at temperatures of 1000–1100 °C [68]. As the phase transformation begins, an intermediate  $\gamma$ -phase forms at temperatures between 700 and 900 °C, eventually converting into the  $\beta$ -phase as the temperature rises. To make the process more practical and cost-effective, other pyrometallurgical techniques, along with the addition of suitable additives, can serve as viable alternatives. Lithium salts with high solubility, such as Li<sub>2</sub>SO<sub>4</sub>, Li<sub>2</sub>CO<sub>3</sub>, LiOH, and LiCl, are typically produced by roasting spodumene in the presence of additives at lower temperatures [69]. Table 2 [65,69] provides a summary of some of the recently utilized reagents and techniques for pyrometallurgical roasting.

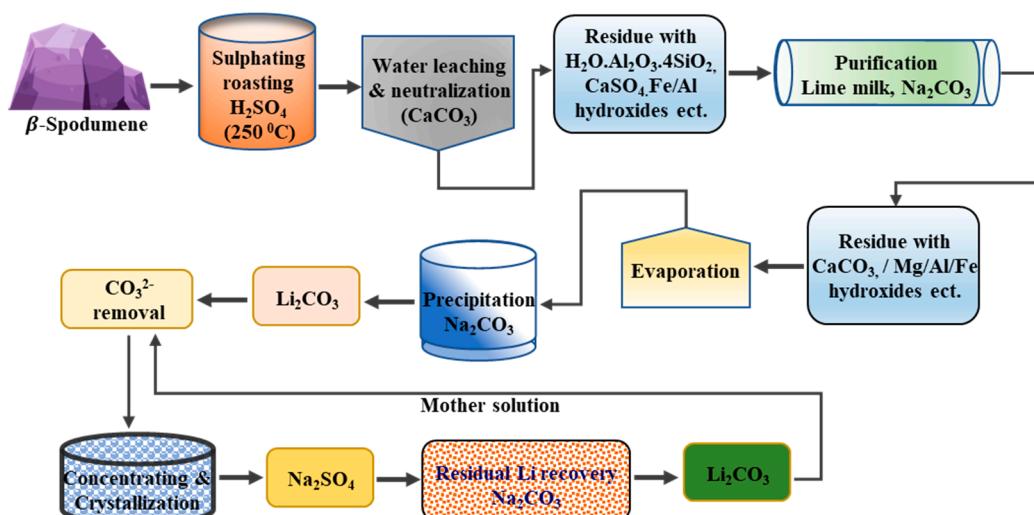
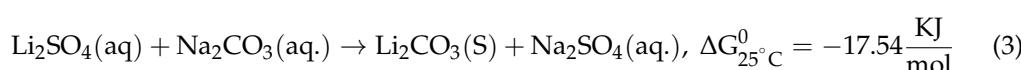
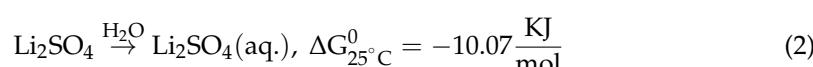
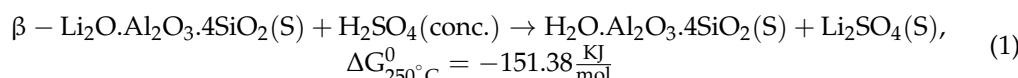
**Table 2.** Some recent examples of roasting techniques adopted for spodumene processing.

Type of Roasting	Roasting Additive(s)	Temp (°C)	Time (min)	Efficiency (%)	Leaching Reagent	Product
Sulfation	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	150–370	-	-	NH <sub>3</sub> (aq.)	Li <sub>2</sub> SO <sub>4</sub>
	CaSO <sub>4</sub> + CaCO <sub>3</sub>	1000–1150	120–180	85–90	H <sub>2</sub> O	Li <sub>2</sub> SO <sub>4</sub>
	Na <sub>2</sub> SO <sub>4</sub> + CaO	-	-	93.3	Na <sub>2</sub> SO <sub>4</sub> + CaO	Li <sub>2</sub> SO <sub>4</sub>
	Na <sub>2</sub> SO <sub>4</sub> + NaOH	200–300	-	90.7	Na <sub>2</sub> SO <sub>4</sub> + NaOH	Li <sub>2</sub> SO <sub>4</sub>
Carbonation	CaO + H <sub>2</sub> O	100–205	60	~97	H <sub>2</sub> O	LiOH
	CaO + H <sub>2</sub> O	1000–1230	-	80	H <sub>2</sub> O	LiOH
	Na <sub>2</sub> CO <sub>3</sub>	150–250	10–120	~94	H <sub>2</sub> O	Li <sub>2</sub> CO <sub>3</sub>
	Na <sub>2</sub> CO <sub>3</sub> + NaCl	~923	120	70	H <sub>2</sub> O	Li <sub>2</sub> CO <sub>3</sub>
Chlorination	Cl <sub>2</sub>	1100	150	-	-	LiCl
	CaCl <sub>2</sub>	900	120	90.2	H <sub>2</sub> O	LiCl
	MgCl <sub>2</sub> –CaCl <sub>2</sub> ·12H <sub>2</sub> O	550–1200	120	50–90	H <sub>2</sub> O, HCl	LiCl
	KCl, NaCl	1000–1050	15–60	85–97.5	H <sub>2</sub> O/HCl	LiCl
	CaCl <sub>2</sub>	800–1200	180–720	96.5–98.5	Alcohol	LiCl
	NH <sub>4</sub> Cl	250–750	-	97–98	Cold water	LiCl
Fluorination	NaF	600	120	90	HF	LiF
Microwave	-	570 @ 2 kW	20 s	~97	-	-

#### 3.2.1. Sulfation

The sulfation process consists of introducing alkali metal sulfates, sulfuric acid, and SO<sub>3</sub> gas upon heating to form extremely stable and water-soluble complexes of lithium sulfate. It has been said that lithium sulfate is characterized by a reverse solubility in aqueous solutions, and practically no change in solubility has been noticed for lithium sulfate with the variation in temperature [70]. Roasting through sulfation using H<sub>2</sub>SO<sub>4</sub> was the first method used since the mid-20th century for recovering lithium from  $\beta$ -spodumene concentrate [34,71]. Sulfuric acid roasting is supposed to be successful even for lower-

quality spodumene and yields 85% to 90% of the extraction from fine  $\alpha$ -spodumene [72]. For this reason, this commercially viable process has seen very little change since it was first developed. In 2012, Galaxy Resources commissioned the first continuous facility in China to produce lithium carbonate from spodumene. It includes processes such as calcination, roasting calcine with  $H_2SO_4$ , and water leaching. The calcine is reacted with sulfuric acid, fired at  $250\text{ }^\circ C$ , and then leached with water for one hour to achieve a lithium sulfate solution [73]. By purifying the solution from this method, followed by evaporation and finally the addition of sodium carbonate, it is very easy to prepare lithium carbonate. The schematic representation of the reaction (1 to 3) of  $\beta$ -spodumene with  $H_2SO_4$  is as in the section shown in Figure 6 [74,75].



**Figure 6.** Li recovery procedure from  $\beta$ -spodumene by using the  $H_2SO_4$  method.

The process uses  $H_2SO_4$  and allows for the recovery of 90–95% of lithium with a stoichiometric excess of  $H_2SO_4$  ranging from 30 to 140% [34]. The use of more  $H_2SO_4$  than the stoichiometric amount is necessary due to the presence of impurities. A factorial design of experiments analyzing the impact of  $H_2SO_4$  stoichiometric excess, temperature, duration, and mechanical stirring revealed that these four operational factors significantly influence lithium extraction. The optimal lithium-extraction rate of 97.1%, nearing the maximum of 98.0%, was achieved with a 30%  $H_2SO_4$  excess, a roasting temperature of  $225\text{ }^\circ C$ , and a roasting duration of 30 min. Mechanical stirring has a significant impact and could enhance lithium recovery by 0.3% [76].

Salakjani et al. [77] described a process where a mixture of  $SO_2$ ,  $O_2$ , and  $SO_3$  gases is used at about  $800\text{ }^\circ C$  for lithium extraction. Lithium is obtained as lithium sulfate. The remaining materials consist of mullite and cristobalite. The reactions are temperature-dependent. They mentioned the process can achieve 60–93% lithium extraction, especially with  $\beta$ -spodumene, and it can handle  $\alpha$ -spodumene with particle sizes under 30 mm. Higher temperatures generally improve lithium recovery, but above  $880\text{ }^\circ C$ , recovery decreases due to the melting of lithium sulfate and sintering of particles. Nearly 99.7% lithium extraction is possible between  $225\text{ }^\circ C$  and  $425\text{ }^\circ C$  under pressure (7.5–44 psi) with

counter-current  $\text{SO}_3$  flow. In this method, monitoring  $\text{SO}_2$  emissions is essential due to their toxicity [77].

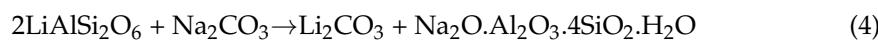
In a recent study, Qiu et al. [78] roasted  $\alpha\text{-LiAlSi}_2\text{O}_6$  concentrate with  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ,  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ , and  $\text{Na}_2\text{SO}_4$  separately. After that, they leached Li from the roasted product with water. The researchers discovered that while  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  did not significantly promote phase transformation or react with  $\alpha$ -spodumene,  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  and  $\text{Na}_2\text{SO}_4$  successfully produced water-soluble  $\text{Li}_2\text{Mg}_2(\text{SO}_4)_3$  and  $\text{LiNaSO}_4$ , respectively. In particular, roasting with  $\text{Na}_2\text{SO}_4$  at 1000 °C for 60 min, using an ore/ $\text{Na}_2\text{SO}_4$  mass ratio of 1:0.7, converted 93.8% of the lithium into  $\text{LiNaSO}_4$ . They also proposed a low-temperature roasting method involving  $\text{Na}_2\text{SO}_4$  and  $\text{CaO}$ , which generated  $\text{LiNaSO}_4$  at 850–875 °C over 60 min, with ore/ $\text{Na}_2\text{SO}_4$ / $\text{CaO}$  mass ratios of 1:0.7:(0.05 to 0.1), achieving lithium-extraction efficiencies of around 86% [78].

### 3.2.2. Chlorination

Chlorination roasting is a less frequently used but efficient option. While being heated, spodumene and chlorinating agents, such as calcium chloride, interact to produce lithium chloride, which can later be extracted [79]. Ni et al. [80] introduced a selective and efficient lithium-extraction method from  $\alpha$ -spodumene by combining mechanical activation and chlorination roasting with water leaching. The method demonstrated a lithium-extraction efficiency of 91.34%. Mechanical activation played a crucial role in lowering the phase transition temperature, allowing the complete chlorination reaction to occur at 900 °C instead of the higher temperatures typically required for spodumene roasting. The optimized conditions for the process were identified as a spodumene/ $\text{CaCl}_2$  mass ratio of 1:1, mechanical activation for 3 h, roasting temperature of 900 °C for 1 h, and leaching at 50 °C for 30 min, yielding an efficient lithium recovery [80]. In another study,  $\beta$ -spodumene was heated with calcium chloride ( $\text{CaCl}_2$ ) to extract lithium. The molar ratio of mineral and  $\text{CaCl}_2$  was 1:2, and the reaction began at approximately 700 °C. The most effective conditions for lithium recovery were 900 °C and 120 min of roasting, resulting in a 90.2% conversion rate. The reaction produced lithium chloride, anorthite, and silica as products [81]. Directly chlorinating alpha-spodumene with calcium chloride, followed by water leaching of the residue to recover lithium reduces both the energy requirement and the number of process steps. If not properly regulated, temperature and time can cause the evaporation of lithium chloride. Lithium recovery into the leach solution generally increases with higher molar ratios, temperatures, and durations, reaching optimal levels with a molar ratio of 2.0, a temperature of 1000 °C, and a duration of 60 min. Under these conditions, approximately 90% of the lithium was extracted, with 85% recovered in the solution and the remainder lost in the gas phase [82].

### 3.2.3. Carbonate Roasting

In the carbonate roasting process, alkali carbonates are added while heating the spodumene ore to form soluble lithium complexes, which can be readily leached out [83–86]. Conventionally, the roasting process begins by adding sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) to spodumene, followed by subjecting the mixture to carbonation at a high temperature for a set period, resulting in the production of lithium carbonate. The introduction of  $\text{CO}_2$  further converts the lithium carbonate into lithium bicarbonate ( $\text{LiHCO}_3$ ), which is highly soluble and can be efficiently leached using  $\text{H}_2\text{SO}_4$  or  $\text{HCl}$  [87]. The carbonation reaction proceeds according to the following Equations (4) and (5) [30].



Chen et al. [87] studied the sodium carbonate autoclave processing of spodumene to produce high-purity lithium carbonate, an alternative to the conventional sulfuric acid roast, suffering from sulfate contamination and cumbersome sodium sulfate recovery. The

process comprises the reaction of the  $\beta$ -spodumene obtained from roasting  $\alpha$ -spodumene with sodium carbonate in an autoclave to produce a lithium carbonate and analcime slurry. With a liquid-to-solid ratio of 4, Na/Li ratio of 1.25, stirring speed at 300 r/min, and a reaction temperature of 225 °C, the conversion efficiency is approximately 96%. While, the reaction time fixed at 60 min secured a conversion efficiency of at least 94% or more. They found a final product purity of 99.6% Li<sub>2</sub>CO<sub>3</sub> in their study, better than the product derived from the sulfuric acid process owing to the absence of sulfate impurities [87]. Lithium could be extracted from the  $\beta$ -spodumene structure through sodium aluminosilicate phases formation under an air atmosphere. This allows the substitution of lithium with sodium. The interaction between Na<sub>2</sub>CO<sub>3</sub> and  $\beta$ -spodumene results in sodium aluminosilicate phases. Dehydrated analcime (NaAlSi<sub>2</sub>O<sub>6</sub>) forms at 400 °C, and sodium aluminosilicate (NaAlSiO<sub>4</sub>) forms at higher temperatures. A molar ratio 2:1 for LiAlSi<sub>2</sub>O<sub>6</sub> to Na<sub>2</sub>CO<sub>3</sub> was optimal for lithium extraction. The yields reached 70% after 10 h of heating at 400 °C. This approach offers an eco-friendlier alternative to conventional extraction procedures by eliminating the use of organic solvents and yielding analcime, a by-product with potential uses in pollutant adsorption [88].

Zhou et al. [89] showed that Li and Rb can be extracted from spodumene by using sodium carbonate roasting, water quenching, and strengthening leaching. The roasting of  $\alpha$ -spodumene concentrate in the presence of Na<sub>2</sub>CO<sub>3</sub> at high temperatures yielded Li<sub>2</sub>SiO<sub>3</sub>, NaAlSiO<sub>4</sub>, and Na<sub>2</sub>SiO<sub>3</sub>. They found the optimum conditions at a temperature of 1100 °C, with 30 min of roasting time, and a 45% dosage of Na<sub>2</sub>CO<sub>3</sub>. They also identified that the dosage of Na<sub>2</sub>CO<sub>3</sub> was the most influential component in relation to the extraction efficiency, and the mineral structure is further broken by rapid water quenching which enhances the extraction. This method avoids the use of toxic additives and allows for the leaching residues to be applied as adsorbents, giving an altogether very efficient, eco-friendly, and low-cost means of obtaining Li and Rb [89].

### 3.3. Hydrometallurgy

Hydrometallurgy has been investigated using acidic and alkaline leaching techniques. The key discoveries from these studies are outlined under the subsequent headings.

#### 3.3.1. Acid Method

H. Zhou et al. [90] investigated lithium recovery from spodumene by nitric acid pressure leaching. It was observed, during pressure leaching, the aluminum–silicate structure of  $\beta$ -spodumene remained unchanged while at the same time freely exchanging H<sup>+</sup> and Li<sup>+</sup> within this structure to form HALSi<sub>2</sub>O<sub>6</sub>. A yield of 95% Li was obtained, and the extraction of the other impurity elements was low under the optimum leaching conditions. It may also be noted that the nitric acid used in the process is recyclable which ensures low acid consumption [90].

In a recent study on extracting lithium from  $\beta$ -spodumene, the leaching agent was phosphoric acid. The maximum lithium extraction in the study was 48%, and optimal conditions involved an 8 M concentration of phosphoric acid, temperature at 100 °C, residence time for 24 h, and a liquid-to-solid ratio of 10 mL/g. This extraction rate is lower than the traditional H<sub>2</sub>SO<sub>4</sub> methods, which exceed 95%. The phosphoric acid process offers a less energy-intensive and safer option. The leaching process preferred lithium, with minimal extraction of aluminum and silicon, and displayed enhanced lithium extraction with a higher temperature and residence time. The lower operating temperatures and acid concentrations of the phosphoric acid process also suggest environmental advantages [91].

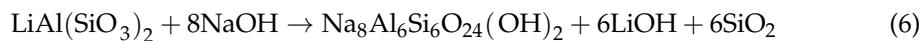
The combination of hydrofluoric acid and sulfuric acid in the acidic mixture avoids the usual necessity of a phase transformation at high temperatures over 1000 °C upon the dissolution of  $\alpha$ -spodumene. In this respect, considerable Li leaching can take place at a much lower temperature, that is, about 100 °C. Under the optimized conditions defined by the ratio of ore/HF/H<sub>2</sub>SO<sub>4</sub> as 1:3:2 (g/mL/mL) and a leaching time of 3 h, a lithium leaching efficiency as high as 96% was realized. The concentration of dissolved lithium

and other elements in the obtained lixivium reached about 1.5 g/L. This process selectively dissolved lithium-bearing minerals, including  $\alpha$ -spodumene and albite, while quartz was left largely undissolved, which will maximize lithium recovery in this process with very minimum dissolution of undesired mineral components. Furthermore, the formation of insoluble fluorides, such as  $\text{AlF}_3$ , cryolite, and cryolithionite  $\text{Na}_3\text{Li}_3\text{Al}_2\text{F}_{12}$ , was observed, and these could be occasionally re-dissolved by  $\text{H}_2\text{SO}_4$  to improve the overall Li recovery. The thermodynamic feasibility for HF/ $\text{H}_2\text{SO}_4$  leaching was examined; the results indicate that all reactions are able to occur spontaneously [92]. Leaching kinetics was evaluated under the optimal leaching conditions. The ratio between the ore and HF, with leaching temperature, has a giant influence on the distribution of HF molecules in Li, Al, and Si leaching. This forms the key to selectivity for Li from Al and Si using this fluoride-based chemical method [93].

Another study showed that leaching with hydrofluoric acid could give an extraction of over 90% of lithium under certain conditions. These conditions were a solid-to-liquid ratio of 1.82% (*w/v*), temperature 75 °C, HF 7% by volume, stirring speed 330 rpm, and reaction time of 10 min. The paper focused on the optimization of operational factors such as particle size, temperature of leaching, and stirring speed, which are essential parameters affecting efficiency in lithium extraction. In parallel, aluminum and silicon are precipitated in the process as  $\text{Na}_3\text{AlF}_6$  and  $\text{Na}_2\text{SiF}_6$ , respectively, to form valuable industrial by-products with a recovery rate of 92%. In addition, lithium is recovered as high-purity lithium carbonate  $\text{Li}_2\text{CO}_3$  with a recovery rate of about 90%. This shows the industrial viability of the process by improving lithium recoveries while producing valuable by-products [94].

### 3.3.2. Alkali Method

Various alkali reagents, such as lime, sodium, or potassium hydroxide, have been used for breaking down spodumene to extract lithium [65]. In 1928 Edison heated Spodumene fine particles in a milk of lime at temperatures between 77 °C and 82 °C for 40 to 60 days. Another method introduced by Nicholson (1946) involved using hot water and lime to achieve over 90% extraction. An industrial method patented by Anovitz, Blencoe, and Palmer in 2006 utilized sodium or potassium hydroxide at temperatures ranging from 200 °C to 300 °C to dissolve spodumene according to the following reaction (6) [77]:



Using a NaOH solution, a study successfully achieved an impressive 87.3% efficiency in lithium extraction, with 79.7% of  $\text{Li}_2\text{O}$  being transformed into  $\text{Li}_2\text{SiO}_3$ . The process was fine-tuned under specific parameters, including a leaching temperature of 250 °C and an initial NaOH concentration of 25 wt%. Significantly, the method displayed stability over multiple cycles, consistently maintaining efficiency and circumventing the environmental and economic disadvantages associated with conventional methods. This hydrothermal alkaline treatment provides reduced energy consumption and environmental impact while upholding high efficiency [95].

Alhadad et al. [96] conducted research on the extraction of lithium from spodumene using NaCl alone and NaCl with NaOH via both analcime and keatite processes. They identified the optimal temperature to be 200 °C and pressures up to 15.8 bar. The study systematically varied parameters such as leaching time, temperature, NaCl/ $\beta$ -spodumene mass ratio, solution pH, and agitation speed to maximize lithium recovery. Both processes achieved high lithium-recovery rates of at least 92.9%. The analcime process demonstrated superiority due to its faster reaction rates, higher lithium concentrations in the leachate, and better impurity management. Despite the keatite process being highly selective, it necessitates a significant excess of NaCl, resulting in slower kinetics and lower lithium concentrations [96].

The use of NaOH in the hydrothermal alkaline treatment process for extracting lithium from  $\alpha$ -spodumene and producing hydroxysodalite zeolite offers an eco-friendly and energy-efficient approach. The process demonstrates a lithium-extraction efficiency of

95.8% under specific conditions, including a temperature of 250 °C, NaOH concentration of 600 g/L, liquid/solid ratio of 5:1, reaction time of 2 h, and stirring speed of 500 rpm. Subjecting  $\alpha$ -spodumene to hydrothermal conversion in an alkaline solution effectively converts it into hydroxysodalite at temperatures exceeding 200 °C, with almost complete conversion at 250 °C. This method not only effectively creates hydroxysodalite, a valuable zeolite, adding commercial value, but also highlights the influence of various parameters such as temperature, NaOH concentration, and reaction time on lithium-extraction efficiency and synthesized zeolite properties. While the addition of the surfactant CTAB (cetyltrimethylammonium bromide) had minimal impact on lithium extraction, it enhanced the surface area of the hydroxysodalite particles, resulting in more uniform and nearly spherical particles. It also stresses the importance of a sustainable desilication process to purify the lithium-containing solution, ensuring the production of high-purity lithium suitable for industrial applications [97].

Using sodium sulfate ( $\text{Na}_2\text{SO}_4$ ) solution in a closed-loop process, achieved high lithium-extraction efficiencies of 93.30% with the addition of CaO and 90.70% with NaOH under optimal conditions, which include a  $\text{Na}_2\text{SO}_4$ /additive (CaO or NaOH)/ore mass ratio of 9:0.4:20, a leaching temperature of 230 °C, a leaching time of 3 h, a liquid-to-solid ratio of 7.5 mL/g, and a particle size (D90) of 39.233  $\mu\text{m}$ . While comparing the effects of CaO and NaOH as additives, it has been founded that CaO resulted in slightly higher lithium-extraction efficiency, while significant agglomerations around ore particles when using NaOH likely contributed to its lower efficiency. The extraction process operates on an ion-exchange mechanism, where  $\text{Li}^+$  in  $\beta$ -spodumene is replaced by  $\text{Na}^+$  from the  $\text{Na}_2\text{SO}_4$  solution, converting  $\beta$ -spodumene into analcime ( $\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$ ). Furthermore, the leaching residue, primarily composed of analcime, can be recycled for applications in environmental protection and the ceramic industry, enhancing the process's sustainability. The proposed method offers a simplified, eco-friendly, and potentially cost-effective approach for industrial lithium extraction from  $\beta$ -spodumene [98].

### 3.4. Direct Lithium Extraction from Spodumene

S. Wang et al. [99] reported an alternative method to extract Li directly from  $\alpha$ -spodumene, which is performed at lower temperatures and avoids the use of acids. In their study, lithium carbonate ( $\text{Li}_2\text{CO}_3$ ) is produced with a yield greater than 90% by reacting  $\alpha$ -spodumene with sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) and aluminum oxide ( $\text{Al}_2\text{O}_3$ ) at 750 °C for 4 h. This method avoids the formation of lithium silicate ( $\text{Li}_2\text{SiO}_3$ ) by trapping silicate anions in nepheline ( $\text{NaAlSi}_4\text{O}_8$ ), with the addition of  $\text{Al}_2\text{O}_3$  being critical as it enhances the thermodynamic driving force for the formation of  $\text{Li}_2\text{CO}_3$  according to the following reaction (7) and reduces the competing formation of  $\text{Li}_2\text{SiO}_3$ , thereby improving lithium recovery.

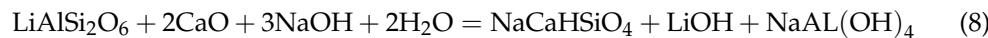


The authors find that this reaction is most effective at 4 h, after which volatility limits the yield. Following its extraction,  $\text{Li}_2\text{CO}_3$  can be isolated by washing the sample using deionized water. The process operates at a relatively low temperature of 750 °C compared to the traditional method, which requires temperatures above 1000 °C. This significantly reduces energy consumption and associated costs [99].

Zhang et al. [100] applied an electrochemical process to direct lithium extraction. The experimental results showed that hydrogen peroxide promoters reduce the leaching potential by facilitating electron transfer and thus shifting reaction pathways. The  $\text{H}_2\text{O}_2$  optimal concentration is 0.5 wt% in 0.5 M  $\text{H}_2\text{SO}_4$  aqueous electrolyte, reaching about 0.95 V vs. SCE. This balance minimizes side reactions, such as oxygen evolution, and maximizes Faradaic efficiency. During leaching,  $\beta$ -phase spodumene undergoes a typical phase transformation to  $\text{HAlSi}_2\text{O}_6$ , while the leached  $\alpha$ -phase retains its original crystal structure, exhibiting lattice shrinkage. To explore the scale-up potential of electrochemical leaching, a catalyst-modified high-throughput current collector was developed to accommodate a

high loading of suspended spodumene. This development resulted in a leaching current of 18 mA and a leaching efficiency of 92.2% [100].

The primary structures of spodumene and illite contain both tetrahedral  $[\text{SiO}_4]$  and octahedral  $[\text{AlO}_6]$  geometries. In the  $[\text{SiO}_4]$  structure, some  $\text{Si}^{4+}$  cations are replaced by  $\text{Al}^{3+}$ , enabling  $\text{Li}^+$  or  $\text{K}^+$  cations to enter the mineral structure to maintain overall charge neutrality. Considering how spodumene and illite are related, Song et al. [101] used the Bayer method to extract lithium directly from  $\alpha$ -spodumene. Initially, when  $\text{NaOH}$  was added solely at a concentration of 400 g/L, with a  $\text{NaOH}$  to ore ratio of 7 mL/g and leached for 4 h, only 24% of  $\alpha$ -spodumene was directly decomposed by the alkali. The addition of  $\text{CaO}$ , along with increased temperature and alkalinity, significantly impacted the decomposition reaction. Under optimal conditions, the lithium leaching efficiency reached 93%. The primary reaction for the decomposition of spodumene is represented in Equation (8) [101].



In the above, the primary connection between  $\alpha$ -spodumene and illite involves the overall idea of alkali substitution to maintain charge equilibrium, but their structural frameworks exhibit significant differences.  $\alpha$ -Spodumene is categorized as a chain silicate, whereas illite is classified as a sheet silicate, leading to distinct physical properties and ion-exchange behaviors [102].

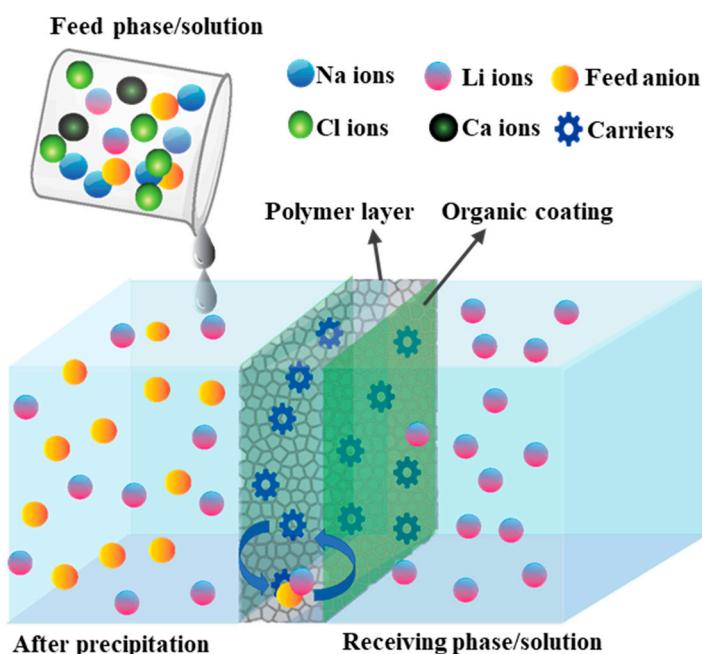
#### 4. Recovery of Lithium from Brine

Brine is a crucial source for extracting lithium. While recovering lithium from brine, it is essential to consider factors such as the availability of land for evaporation ponds, the area's suitability for solar evaporation, lithium concentration levels, and the ratio of other metals like alkali and alkaline earth metals to lithium. Lithium brines can generally be divided into three categories: evaporative, geothermal, and oil field brines. During the evaporation process, roughly 50% of the lithium remains trapped in the leftover brine, as it is held by the salts that precipitate. This remaining brine is often rich in magnesium compared to sodium and potassium, making lithium extraction more difficult. It is important to note that no single method is universally applicable to all brines, as each method must be tailored to the specific composition of the brine being processed [103]. This section primarily focuses on techniques such as polymer inclusion membranes, electrodialysis, and direct lithium extraction to recover lithium from brine.

##### 4.1. Polymer Inclusion Membrane Process

There are several different membrane technologies available, including supporting liquid membrane (SLM), membrane extraction (ME), ion-imprinted membranes (IIM), and others, in addition to the widely used pressure-driven and electricity-driven nanofiltration membranes [104]. The polymer inclusion membrane (PIM) is a new alternative that is spontaneously becoming vibrant and apparent. It originates from the supported liquid membrane and harbors remarkable potential [105]. The main polymer plays an important role in the PIM since it provides the reliability of the long-term work of the membrane. This requires that the material have the required mechanical strength as well as thermal and chemical stability, including the ability to withstand acids and alkalis. Different polymers, such as, cellulose triacetate, poly(vinylidene fluoride-cohexafluoropropylene), and poly(vinyl chloride) have been identified as the fundamental matrix of polymer-integrated membranes (PIMs). The molecular weight and chain length of the polymers play a big role in the performance of the membrane. The carriers in the PIMs are significant in determining the selectivity of the membrane for the removal of certain ions. Carriers are classified into four types according to the reagents used for solvent extraction: basic, neutral or solvating, acidic, and chelating or macrocyclic and macromolecular carriers. The specificity in separating the metal ions can be gained from the specificity in extraction that will result from the carriers' structural and physical difference. The process of penetration

through the PIM will be divided into three distinctive stages. In the first step, the target species are transferred as an adduct—in other words, an ion-pair or complex—with the extractant across the membrane–feed solution interface. In the second step, the adduct is transported across the membrane. In the third step, the target species is transported into the receiving solution across the interface between the membrane and receiving solution. This is performed when the adduct with the extractant is dissociated. Essentially, this process is the reverse of the ones taking place at the interface, on the membrane side of the feed solution interface [106]. The mechanism is schematically shown in Figure 7.



**Figure 7.** Illustration of the lithium-extraction mechanism through a polymer inclusion membrane.

There are several studies supporting the potential of TBP in extraction processes as a significant component, which works toward increasing the efficiency and selectivity of extraction. TBP exhibits a high selectivity for lithium ions compared to other ions, notably magnesium ions, which may often be found in their brines at high concentrations. However, the specific details differ when additional components and operational variables are considered. Zhou et al. [107] used a hydroxyl-functionalized ionic liquid ([OHEMIM][NTf<sub>2</sub>]) combined with TBP to increase the extraction of lithium from brine having a higher Mg/Li ratio. Under the optimized condition, this resulted in a Li-ion extraction efficiency of 94.2% and hence a lithium–magnesium separation factor of 539. Almost perfect efficiencies for washing out Mg<sup>2+</sup> and K<sup>+</sup> ions were obtained with both the washing solutions, 0.6 mol/L LiCl and 1.8 mol/L NaCl. About 98% of the Li<sup>+</sup> ions were taken out with a 1.0 mol/L HCl solution. Their method showed stability in the case of reusability because it showed only a decrease of 4.4% for Li<sup>+</sup> extraction efficiency after seven cycles [107]. Ionic liquids such as [C4mim][PF<sub>6</sub>] are very good reagents for TBP co-extraction in the lithium-extraction process from magnesium-rich brine. Still, they are expensive and may contaminate the aqueous phase. Sodium hexafluorophosphate (NaPF<sub>6</sub>) is a more cost-effective and greener reagent that has shown similarities in performance and extraction processes. Zhou et al. [108] studied the effect of the NaPF<sub>6</sub> concentration, phase ratio, pH, temperature, and MgCl<sub>2</sub> concentration on Li<sup>+</sup> extraction by TBP. The performance of NaPF<sub>6</sub> was found to be similar to that of [C4mim][PF<sub>6</sub>]. Among the other studied Li<sup>+</sup> ions complexation reagents, HCl presented good results compared to Na<sub>2</sub>CO<sub>3</sub>. However, the addition of Na<sub>2</sub>CO<sub>3</sub> increased the extract system recoverability due to the elimination of the organic phase regeneration steps [108]. The work by Meng et al. [109] reports the fabrication of a polymer inclusion membrane in Li<sup>+</sup> electromembrane extraction, or EME, using bis(2-ethylhexyl)

phosphate, or di-2-ethylhexyl phosphoric acid (D2EHPA) and tributylphosphate, or TBP. The researchers optimized the composition, thickness, voltage, and solution environment of the membranes. The established fact indicated that  $\text{Li}^+$  ions' transport was facilitated by an alkaline feed phase and the acidic stripping phases through the membrane over the  $\text{Na}^+$  and  $\text{K}^+$  ions. The D2EHPA functionality in the carrier favored ion transport and showed a synergistic effect in a 1:1 ratio with TBP. The optimized mass of the carrier composition was 70.6% of the PIM mass. The process imparted an acceleration of mass transfer and low selectivity because the mass transfer coefficient of  $\text{Li}^+$  obtained was  $12.9 \mu\text{m}/\text{s}$  for an inflow of  $\text{Li}^+$  at  $249 \text{ mg/m}^2/\text{s}$  at 20 V. Moreover, the separation factor of  $\text{Li}^+$  for the abundant ion,  $\text{Na}^+$ , under 10 V application was 6.41; for  $\text{K}^+$ , this factor was 5.64. Then, the separation factor of  $\text{Li}^+$  in relation to  $\text{Na}^+$  and  $\text{K}^+$  at 20 V was 2.56 and 2.51, respectively. Here, a  $\text{Li}^+$  enrichment factor of about 9.02 was obtained, indicating that the system was stable for 120 h of continuous transfer [109]. However, the PIM which was made using tri-n-butyl phosphate (TBP) and ferric trichloride ( $\text{FeCl}_3$ ) faces major drawbacks like a high  $\text{Cl}^-$  concentration, loss of  $\text{Fe}^{3+}$ , and a complicated method of synthesis. A PVC-[OHEMIM][NTf<sub>2</sub>]-based PIM was synthesized by Zhou et al. [110] to overcome these problems. The analysis showed enhanced extraction of  $\text{Li}^+$  and the efficiency to separate  $\text{Li}^+/\text{Mg}^{2+}$  with a 13.3% and 24.8% increase, respectively.  $\text{Li}^+$  extraction dropped from 17.0% to 13.6% after the 10th cycle, showing stability with minor changes in extraction efficiency. The  $\text{Li}^+$  flux initially was  $1.6 \times 10^{-3} \text{ mol}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ , and the separation factor with  $\text{Li}^+$  and  $\text{Mg}^{2+}$  ions was 184. The study introduces the efficient and selective separation of  $\text{Li}^+$  ions without needing high concentrations of the  $\text{Cl}^-$  ions in the stripping phase and suggests the use of PIMs to extract  $\text{Li}^+$  ions from brine with a high Mg/Li ratio [110]. Xu et al. [111] used 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([C4mim][NTf<sub>2</sub>]) with tributylphosphate (TBP) to separate  $\text{Li}^+$  ions from  $\text{Mg}^{2+}$  ions. The matrix polymer was cellulose triacetate (CTA), a polymer compatible with both PIM and [C4mim][NTf<sub>2</sub>]. This molecule exuded membrane stability, and there was no significant leakage through the extraction process. The lithium selectivity of PIMs was decreased by just <10% in extraction after five cycles. However, during permeation studies in a feed solution of 7.2 mmol/L of  $\text{Li}^+$  and 2.06 mmol/L of  $\text{Mg}^{2+}$ , the membrane containing 40 wt% of TBP-[C4mim] achieved a separation factor of 2.24 and a high  $\text{Li}^+/\text{Mg}^{2+}$  selectivity of 23.87 when extracting  $\text{Li}^+$  from simulated salt-lake brines [111].

Polymer inclusion membranes (PIMs) are limited by slow mass transfer. Shen et al. [112] developed a PIM with tributyl phosphate (TBP) and sodium tetraphenylborate ( $\text{NaBPh}_4$ ) as carriers and cellulose triacetate (CTA) as the polymer skeleton, achieving an initial flux 3–20 times higher than other PIMs. SEM-EDS, XRD, and PALS analyses revealed that a moderate TBP content improves the polymer chain distance and flux, while excessive TBP reduces permeability. This study highlights the compatibility effect on mass transfer in PIMs, enhancing metal separation applications [112]. In another study, crown ether is used as an extractant in polymer inclusion membranes to extract lithium ions selectively. This approach focuses on the highly selective nature of crown ethers for lithium ions due to their specific cavity sizes that preferentially bind lithium ions. This approach uses the incorporation of dibenzo-18-crown-6 for  $\text{Li}^+$  selectivity and Tröger's Base units to create free volume for  $\text{Li}^+$  transport. This combination enables the PIM-DB18C6-TB membrane to effectively separate  $\text{Li}^+$  from  $\text{Mg}^{2+}$  in both static diffusion and electrodialysis, with  $\text{Li}^+/\text{Mg}^{2+}$  selectivities of 35.80 and 24.35, respectively. The  $\text{Li}^+$  permeation rate correlates with the size of free volume elements in the membrane, while selective transport is primarily due to the binding of  $\text{Li}^+$  to the crown ether units [113]. A specific supported ionic liquid membrane prepared using a crown ether functionalized polyimide (Poly(DAB14C4-6FDA)) and a TBP-[C4mim][NTf<sub>2</sub>] mixture achieved a  $\text{Li}^+$  penetration rate of  $0.354 \mu\text{m}/\text{s}$ , an initial flux of  $0.128 \text{ mol}/\text{m}^2\cdot\text{h}$ , and a Li/Mg selectivity of 19.1. Molecular dynamics simulations and DFT calculations confirmed strong interactions and high binding energies with  $\text{Li}^+$ , resulting in stable structures and efficient  $\text{Li}^+$  transfer channels [114].

#### 4.2. Electrodialysis

Electrodialysis is a technique that uses ion-exchange membranes to separate salt ions from a solution under the influence of an electric field [115]. It is commonly applied in water purification, desalination, and the recovery of metals from industrial waste streams [116,117]. The process works by passing the brine solution through selective, permeable membrane pairs that are designed to target and separate specific ions [118], using a two-step coating process with polydopamine (PDA) and polyethyleneimine (PEI) along with 2-hydroxymethyl-15-crown-5 ether (15CE) to enhance the preferential transport of lithium ions ( $\text{Li}^+$ ) over other ions like magnesium ( $\text{Mg}^{2+}$ ) and sodium ( $\text{Na}^+$ ) in brine solutions. The modified membranes, especially the 15CE/PEI-PDA-CR671 membrane (where 15CE represents 2-hydroxymethyl-15-crown-5 ether, PEI stands for polyethyleneimine, PDA denotes polydopamine, and CR671 is the base cation-exchange membrane), showed a significant 39-fold improvement in lithium selectivity and a 55-fold increase in lithium flux for  $\text{Mg}^{2+}/\text{Li}^+$  solutions when compared to unmodified membranes. Small-scale tests demonstrated that these membranes could recover up to 80% of the lithium from  $\text{Mg}^{2+}/\text{Li}^+$  mixtures and 90% from  $\text{Na}^+/\text{Li}^+$  mixtures, indicating their strong potential for industrial use [119].

Guo et al. [120] present a method for separating magnesium from lithium using reaction-coupled separation technology. The process involves the formation of a solid MgAl-layered double hydroxide (MgAl-LDH) through a nucleation crystallization process, resulting in the efficient separation of magnesium while retaining lithium in the solution. This approach enables the nearly complete extraction of magnesium, leading to a significant reduction in the Mg/Li ratio in the filtrate. The technology demonstrates high separation efficiency, with lithium loss minimized to less than 8% under optimum conditions [120]. An ionic liquid (RTIL) is utilized to extract lithium from high Mg/Li ratio brines at room temperature. The RTIL is positioned between two cation-exchange membranes (CEMs) to achieve strong selectivity for lithium, effectively reducing the Mg/Li ratio from 50:1 in the original brine to 0.5:1 in the resulting solution. In addition, it achieves a higher current efficiency (65%) and lower specific energy usage (16 Wh/g Li) compared to traditional electrodialysis methods. Practical viability was also demonstrated through testing with natural brine from West Tairjinair salt lake, successfully reducing the Mg/Li ratio from 53:1 to 0.26:1 and effectively preventing the migration of other cations such as  $\text{K}^+$  and  $\text{Ca}^{2+}$  [121]. Selective-electrodialysis (S-ED) is gaining popularity as a highly effective method for extracting lithium from sources like salt-lake brines and concentrated seawater, especially in brines with a high  $\text{Mg}^{2+}/\text{Li}^+$  ratio. The process can be influenced by other ions present, including potassium ( $\text{K}^+$ ) and calcium ( $\text{Ca}^{2+}$ ), which may impact the migration of lithium and magnesium. Monovalent cations, in particular, have a more pronounced effect on the movement of lithium than on magnesium. Conversely, the anions in the solution mainly influence the migration of magnesium ions first, followed by lithium [122,123].

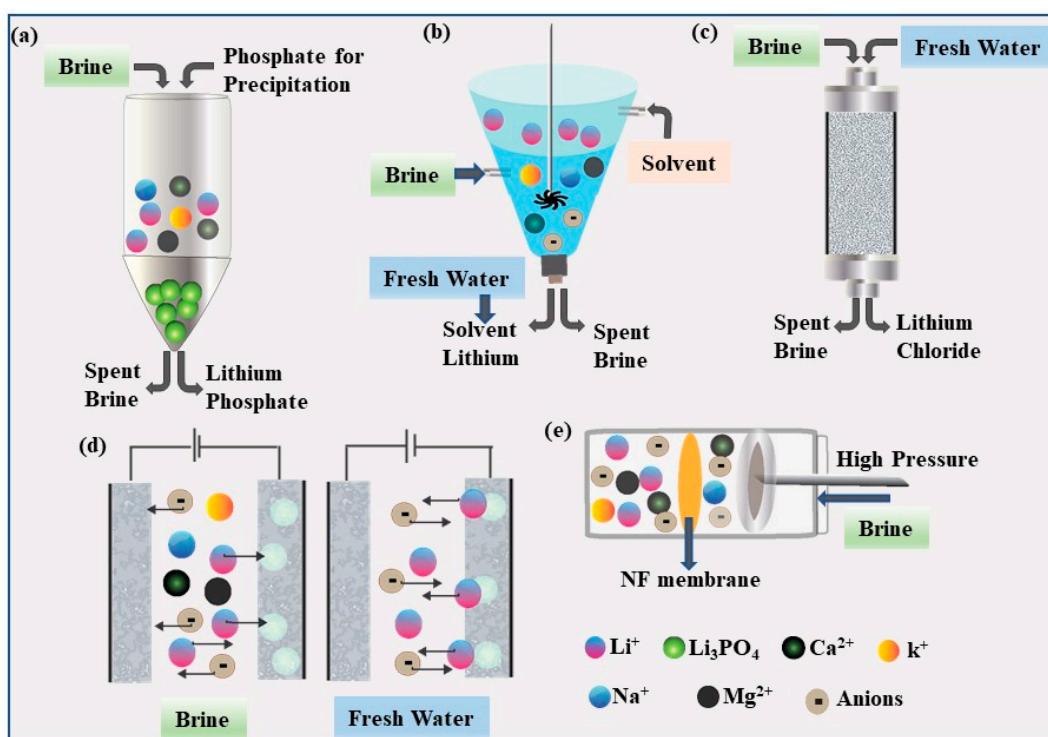
#### 4.3. Direct Lithium Extraction from Brine

##### 4.3.1. Precipitation Method

The precipitation technique is widely employed in large-scale industrial processes to extract lithium from brine, particularly when the brine has a low Mg/Li mass ratio [124]. When the Mg/Li ratio is below 6, separating lithium and magnesium using precipitation is effective. However, when the Mg/Li ratio exceeds 6, this technique becomes significantly less efficient, making lithium extraction more challenging. Unfortunately, most brine resources worldwide have a high Mg/Li ratio [125]. However, the primary challenge of lithium precipitation is the concurrent precipitation of magnesium. To address this, researchers have developed various precipitation techniques tailored to different Mg/Li ratios in brine [18].

Li can be precipitated as  $\text{Li}_2\text{CO}_3$  from brine by a multistage process. When this Mg/Li ratio is small, that is, below 10, the usual method for precipitation is carbonate precipitation. The process initially involves the precipitation of Mg with  $\text{CaO}$  then the addition of  $\text{Na}_2\text{CO}_3$

in order to effect the precipitation of Li as  $\text{Li}_2\text{CO}_3$ . A carbonation precipitation method is used to precipitate Li as  $\text{LiHCO}_3$  when using impure  $\text{Li}_2\text{CO}_3$  with a low Mg/Li ratio. High-purity  $\text{Li}_2\text{CO}_3$  can be obtained by using a combination of carbonate and carbonation precipitation methods [126]. The phosphate precipitation method can be used in alkaline salt-lake brines with a high lithium content and low magnesium and calcium levels. The basis of this kind of selective precipitation (Figure 8a) is lithium phosphate's very low water solubility ( $\text{Li}_3\text{PO}_4$ ). Lithium can often be efficiently extracted from brines by introducing different phosphates, as long as the brine has been depleted of multivalent ions beforehand [127]. Lithium phosphate has a solubility of 0.031 g/100 g  $\text{H}_2\text{O}$ . Additionally, around 96.5% of lithium can be removed at a pH of 11 [128]. Brine deposits usually have a large amount of magnesium or lithium, leading to the need for processes to extract lithium such as the precipitation of aluminate and magnesium. The reaction of sodium hydroxide and aluminum chloride yields aluminum hydroxide  $\text{Al}(\text{OH})_3$  through aluminate precipitation, resulting in the specific formation of  $\text{AlLiO}_2$ . This method has shown excellent outcomes in lithium retrieval, even when dealing with high brine concentrations of magnesium or lithium, making it an environmentally preferable approach [129].



**Figure 8.** Schematic diagram of (a) phosphate precipitation, (b) liquid–liquid extraction, (c) ion-exchange resins, (d) electrochemical ion pumping, and (e) a nanofiltration membrane.

Liu et al. [130] studied the interaction between aluminum and brine by combining aluminum powder with  $\text{NaCl}$  at a mass ratio of 3:7. The mixture was ground using a ball crusher for 30 min. The primary focus of the study was to analyze the lithium-precipitation process and its effect on both the rate of lithium precipitation and the Mg/Li mass ratio. Their results indicated that when the aluminum-based compound directly reacted with the brine, it promoted the removal of the coating from the raw material's surface, significantly increasing the lithium precipitation rate. Furthermore, the aluminum-based compounds demonstrated high efficiency in separating lithium from magnesium. Under optimal conditions, lithium precipitation reached 78.3%, and the Mg/Li mass ratio in the resulting precipitate was as low as 0.02. This research provided valuable insights into improving lithium and magnesium separation from salt-lake brines [131]. Additionally, another study

showed that aluminum–calcium alloys can recover up to 94% of lithium from brines with a high Mg/Li ratio [130].

Lai et al. [132] introduced the crystallization–precipitation process to extract lithium from salt-lake brine with a high Mg/Li mass ratio (>40). In this approach, a closed-loop method for the crystallization of carnallite is designed to efficiently eliminate magnesium by forming  $MgHPO_4(S)$ , based on thermodynamic analysis and experimental results. Initially, the addition of KCl to the brine removes around 50% of the magnesium as carnallite. By using 55.9% of the required amount of KCl and evaporating the solution to 17.6%, the total magnesium removal efficiency reaches 53.1%, with a lithium loss of only 5.4%. In the next step, the remaining magnesium in the brine is removed by precipitating it as  $MgHPO_4(S)$ . This step requires  $Na_2HPO_4$ , a reaction temperature of 40 °C, a reaction time of 30 min, and an aging period of 3 h. Under these conditions, 99.2% of the remaining magnesium is removed, and 98.5% of the residual lithium is recovered. Overall, the process achieves a magnesium removal efficiency of 99.6% and a lithium-recovery rate of 93.2%. Additionally, this method allows for the recycling of KCl and  $Na_2HPO_4$ , making it cost-effective [132].

Studies have demonstrated that multi-step and integrated methods are highly effective for removing and precipitating 99% of the magnesium from brines with elevated Mg/Li ratios. It involves the calcium hydroxide and sodium oxalate usage in a two-step precipitation method. This eliminates magnesium, along with other impurities such as boron and sulfur [133]. According to a proposed double-drop technique, deionized water was combined with  $AlCl_3 \cdot 6H_2O$  and introduced into the brine. Then, a solution of sodium carbonate and sodium hydroxide was gradually added while keeping the pH at 10. This method facilitated the efficient separation of magnesium, and then boron was extracted using LSC-800 boron adsorbent resin. Following this, carbonate ions were removed by acidifying with HCl, and sulfate was precipitated by adding barium chloride after concentrating the brine. Finally, lithium carbonate was obtained from the lithium-enriched brine by using sodium carbonate, resulting in a yield of over 91% lithium carbonate with a purity of 99.70%. This demonstrates the process's effectiveness in recovering magnesium and lithium from brines with a high Mg/Li ratio [134]. Another method to address a high Mg/Li ratio is by using Mg precipitation, which can reduce the Mg/Li ratio to facilitate Li recovery. Under optimal reaction conditions, it was discovered that both ammonium oxalate and sodium carbonate are efficient in precipitating 98% of Mg [135]. Oxalic acid was discovered to effectively precipitate over 95% of magnesium as magnesium oxalate in brine, even at a high magnesium-to-lithium ratio of 21 [124].

#### 4.3.2. Liquid–Liquid Extraction

Liquid–liquid extraction, often called solvent extraction, is highly effective for lithium recovery and has a good selectivity. The extractants include neutral organic phosphorus compounds,  $\beta$ -diketones, crown ethers, and ionic liquids. TBP/ $FeCl_3$  is a commonly used extractant that provides a separation order of  $H^+ > Li^+ > Na^+ > K^+ \gg Mg^{2+}$  [136]. When brine interacts with these solvents, most of the lithium ions transfer to the organic or ionic liquid phase. This lithium-loaded phase is then combined with an aqueous phase to free the lithium ions. Adjusting the pH is usually necessary to promote the transfer of lithium ions between phases (Figure 8b). In a study focusing on TBP (tributyl phosphate),  $FeCl_3$ , and P507 (2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester), a sustainable method for lithium extraction from salt-lake brine was explored, achieving a 99.8% lithium-recovery rate, even in brines with high magnesium content [91]. The study demonstrated a superior lithium selectivity over magnesium, which is a known challenge in traditional extraction techniques. Replacing corrosive acids with water for lithium stripping makes the process simpler and reduces environmental and operational costs. Additionally, the system's cost-effectiveness and operational efficiency are enhanced by the ability to reuse the organic phase without the need for regeneration. These factors make the TBP/ $FeCl_3$ /P507 system a promising option for large-scale industrial applications [137].

Li et al. [138] studied the temperature-responsive liquid–liquid extraction of Li<sup>+</sup> from high Mg/Li ratio brine. In their research, they introduced an approach that combines efficiency, selectivity, and sustainability. Utilizing a temperature-responsive ionic liquid (IL) system with tributyl phosphate (TBP), the research demonstrates a highly effective method for extracting lithium, achieving an extraction rate exceeding 80%. This system's unique ability to leverage temperature adjustments for phase separation significantly enhances operational simplicity and efficiency, allowing for easy recovery of the lithium-loaded organic phase. Notably, the system exhibits exceptional selectivity for lithium over magnesium, making it particularly well-suited for challenging brines with high magnesium content. The study also underscores the sustainability of the process, with the TBP-IL extraction system maintaining high efficiency over multiple reuse cycles, thereby reducing waste and operational costs. Thermodynamically, the process is identified as exothermic and spontaneous, with the formation of the  $[LiFeCl_4 \cdot 2TBP] +$  complex driving the selective extraction of lithium [138].

Hua et al. [139] enhanced Li<sup>+</sup>/Mg<sup>2+</sup> selectivity and Li<sup>+</sup> recovery by incorporating di(aminobenzo)-14-crown-4 (DAB14C4, a crown ether) into a tributyl phosphate–ionic liquid (TBP-IL) extraction system. Including DAB14C4 as a co-extractant dramatically improved the selectivity of lithium over magnesium and the overall recovery rates, achieving remarkable efficiencies of up to 89.5% and 81.8% in challenging brines. This success was driven by the synergistic interaction between DAB14C4, TBP, and IL, forming a highly stable organic phase complex and ensuring a superior lithium-extraction performance [139].

Sahu et al. [140] investigated the liquid–liquid extraction (LLE) of lithium (Li) using various extractants and conditions to optimize recovery rates. The study found that the highest extraction efficiency (53%) was achieved using the functionalized ionic liquid [Cyphos IL 101][D2EHPA] (triethyl(tetradecyl)phosphonium chloride combined with di-2-ethylhexyl phosphoric acid), while adding lactic acid further enhanced Li extraction to 70% with D2EHPA at an organic-to-aqueous (O/A) phase ratio of 2:1 and pH 6. Extractants such as TOPO (trioctylphosphine oxide), Cyanex 272 (bis-2,4,4-trimethylpentyl phosphinic acid), and D2EHPA demonstrated similar extraction efficiencies of around 30%, while chelating agents like LIX 984 (hydroxyoxime-based extractant) were less effective, with only 15% extraction. D2EHPA showed selectivity for Li over alkali metals such as sodium (Na) and potassium (K), although alkaline-earth metals like magnesium (Mg) and calcium (Ca) exhibited higher extraction rates (77% and 83%, respectively). Complexation of Li with lactic acid significantly improved extraction [140].

In recent years, researchers have been focusing on solvent extraction methods to recover lithium from magnesium-heavy brines, especially from salt lakes. The main goal has been to ensure that lithium is selectively extracted over magnesium for better efficiency. Su et al. (2022) developed a new solvent extraction system using tributyl phosphate (TBP), 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (HL), and ferric chloride (FeCl<sub>3</sub>). This system was able to effectively separate lithium, using water to strip the lithium from the solution. To better understand how this TBP/HL/FeCl<sub>3</sub> system works and to make the extraction process more efficient, a thermodynamic model was created. This model took into account different concentrations of components from various brines and was based on mass balance and equilibrium equations. The model's parameters were refined by comparing calculated results to experimental data. It was found that lithium mainly existed as  $[Li(TBP)_2][FeCl_4]$  in the organic phase, followed by  $[Li(TBP)][FeCl_4]$ . When water was used for stripping, Fe<sup>3+</sup> formed as  $FeCl_2L \cdot HL \cdot 2TBP$  at lower organic-to-aqueous ratios, but at higher ratios, it converted into  $[H(TBP)_2][FeCl_4]$ . This model provides practical insights for improving lithium-extraction processes [141].

In another study, Qiao et al. [142] developed an effective process for the lithium extraction from salt-lake brine with a recovery of more than 96%. Their route showed high selectivity during the removal of impurities like sodium, potassium, and magnesium while keeping the solution of lithium pure with low ratios of impurities. This process involved a 13-step process using TBP-ethyl benzoate-kerosene-FeCl<sub>3</sub>, which further allowed them

to reach a concentration of 38.87 g/L lithium in the final solution. They also minimized iron losses and sags actuators to make the process even safer and more environmentally friendly with the addition of ethyl benzoate as a diluent in that process as well. The results indicate that the method above can be viable for an extraction process of lithium at an industrial level, especially from high-concentration brines originating from salt lakes [142].

Research on  $\beta$ -diketone systems that can interact with lithium ions and other alkali and alkaline earth metals has been ongoing since the 1960s. Several  $\beta$ -diketone extractants, such as benzoyl-1,1,1-trifluoroacetone (HBTA), 2-thenoyltrifluoroacetone (HTTA), and  $\alpha$ -acetyl-m-dodecylacetophenone (LIX54), have been studied. Researchers have also looked into synergistic extractants like trioctylphosphine oxide (TOPO) and trialkylphosphine oxide (TRPO/Cyanex 923) to improve the effectiveness of these systems. These methods have shown a strong performance in extracting lithium from sodium-rich, lithium-poor brines, and they are also effective at separating lithium from sodium. These extraction techniques have been applied to lithium recovery from diverse sources, including lithium-precipitation mother liquors, low-magnesium brines, alkaline ores, and leach solutions from spent lithium-ion batteries. Nevertheless, in many cases, removing calcium and magnesium first is necessary, requiring substantial amounts of alkaline reagents, which drives up costs [143].

The combination of benzoyl trifluoroacetone (HBTA) and tri-n-octyl phosphine oxide (TOPO) in the HBTA-TOPO synergistic extraction system provides a highly efficient and selective approach for recovering lithium from alkaline brine. This system based on  $\beta$ -diketone demonstrates an impressive lithium (Li)-extraction efficiency of up to 95%, with a separation factor exceeding 2100, indicating exceptional selectivity for Li over sodium (Na). The exothermic nature of the extraction process enhances its efficiency at lower temperatures, although operational convenience led to the selection of room temperature. The stability and reusability of the organic phase are substantial, as it can be regenerated with sodium hydroxide (NaOH) and reused for up to 30 cycles without a significant decrease in efficiency or the formation of emulsions or third phases [144].

In addition to the HBTA-TOPO system, when 4,4,4-Trifluoro-1-phenyl-1,3-butanedione (HBTA) and trialkylphosphine oxide (TRPO) are added to brine with a high ratio of sodium to lithium (Na/Li), an effective solvent extraction system is created, resulting in a significant advancement in lithium (Li) recovery. This system delivers an impressive 99% extraction efficiency and shows exceptional selectivity by isolating Li from other metal ions like sodium (Na), potassium (K), calcium (Ca), and magnesium (Mg). Selectively removing Na and K impurities, using a combination of hydrochloric acid (HCl) and lithium chloride (LiCl) solutions, ensures that lithium is concentrated in the organic phase, enhancing the purity of the final product. Additionally, the organic phase remains stable and can be reused through multiple cycles of extraction, stripping, and regeneration, maintaining high performance and demonstrating the system's suitability for industrial use. This process results in the production of high-purity lithium carbonate ( $\text{Li}_2\text{CO}_3$ ) with a purity of 99.89% [145].

In addition, the use of 3-benzoyl-1,1,1-trifluoroacetone (HBTA) in new solvents enables a significantly effective and environmentally friendly approach to recover lithium ions. A study has shown that HBTA, when dissolved in the ionic liquid [C<sub>2</sub>mim][Tf<sub>2</sub>N] (1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide), can efficiently extract lithium from alkaline aqueous solutions without the need for additional co-extractants such as TOPO, which are typically essential in traditional systems. This extraction method not only operates with high effectiveness but also exhibits exceptional selectivity for lithium over sodium, despite encountering difficulties with calcium, making it suitable for applications where sodium is the primary contaminant. The process involves the creation of a neutral lithium-HBTA complex in the [C<sub>2</sub>mim][Tf<sub>2</sub>N] phase, bypassing the usual cation- or anion-exchange processes observed in other metal extractions, thereby contributing to its efficiency. Furthermore, the system facilitates the efficient removal of lithium using concentrated hydrochloric acid, thus enhancing its practicality by streamlining the recovery process.

Nevertheless, despite their environmental benefits, deep eutectic solvents (DESs) were notably less effective than ionic liquids, particularly at higher pH levels [146].

The TBP–NaBPh<sub>4</sub>–phenethyl isobutyrate system represents a significant advancement in lithium-recovery technology due to its 85.70% single-stage extraction efficiency and a high lithium-to-magnesium separation factor of 1175, making it effective in extracting lithium selectively from brines with challenging high Mg/Li ratios. The use of sodium bicarbonate ( $\text{NaHCO}_3$ ) as a stripping agent simplifies the process and avoids the environmental and operational hazards associated with strong acids and bases, making the process both eco-friendly and safer for industrial applications [147].

#### 4.3.3. Ion-Exchange Resins

Ion-exchange resins (Figure 8c) are materials known for their strong attraction to lithium ( $\text{Li}^+$ ) ions. These ions are adsorbed onto the surface of the resin particles, which are often arranged in columns, even when lithium ions are present in lower concentrations compared to other cations in the brine. To release the adsorbed lithium ions and obtain a relatively pure  $\text{Li}^+$  solution, freshwater or acidic solutions are typically used.

Liu et al. [148] studied usage of granular Polyvinyl Butyral–Hydrogen Titanium Oxide (PVB-HTO) ion-sieves based on the  $\text{Li}^+/\text{H}^+$  ion-exchange mechanism. The traditional method of using ammonia buffer solutions to maintain an optimal pH for lithium adsorption poses environmental concerns due to ammonia nitrogen pollution. The alkaline anion-exchange resins with amine functional groups effectively neutralize the released  $\text{H}^+$  ions without causing harmful precipitation of magnesium and calcium hydroxides. The lithium-recovery efficiency can reach up to 72.96% and the release of ammonium ions is eliminated, making it a promising green technology for practical applications [148].

Bonin et al. [149] presented a method for enhancing magnesium recovery from lithium-rich brines by selectively removing boron using Amberlite IRA743 ion-exchange resin. Notably, the removal of boron prior to magnesium hydroxide ( $\text{Mg(OH)}_2$ ) precipitation significantly improves the purity of the magnesium product, achieving up to 95% purity. Additionally, the process substantially reduces lithium loss during precipitation, with reported decreases from 13.7% to as low as 1.4%, resulting in a lithium-extraction efficiency of approximately 98.6%. Although the initial use of NaOH as an alkalizing agent increases costs compared to CaO, this approach enables the recovery of high-purity magnesium hydroxide [149].

Arroyo et al. [150] demonstrated the effectiveness of specific ion-exchange resins, particularly TP207, for the recovery of lithium (Li) from desalination brines. The study showed that these resins achieve high Li retention yields exceeding 95% in synthetic solutions containing only Li. However, the presence of competing ions, such as sodium (Na), significantly reduced the efficiency of Li retention, with K2629 being the most affected. TP207, a macroporous, weakly acidic cation-exchange resin with imino-diacetate functional groups, emerged as the most effective resin, showing the highest affinity for Li even in the presence of Na. The Li desorption process using 4 M hydrochloric acid (HCl) was efficient, with yields ranging from 73.8% to 89.8%, and the resins maintained high recovery efficiencies after regeneration and reuse. Li retention followed pseudo-second-order kinetics and fitted the Langmuir isotherm model, indicating a monolayer adsorption on homogeneous sites. While real brine applications show lower retention due to competing ions like calcium (Ca) and magnesium (Mg), pretreatment to remove these ions can enhance Li recovery, making these resins promising for practical applications in desalination brine management [150].

#### 4.3.4. Electrochemical Ion Pumping

In addition to electrodialysis, a new electrochemical approach for lithium (Li) recovery, known as battery-type electrochemical ion pumping, has been developed in recent years [41,151]. In this method, electrodes designed for ion extraction selectively capture lithium from the input solution and release it into a collection solution. For these electrodes

to function effectively, they must demonstrate a high selectivity for lithium, a large lithium capacity, low energy usage, and long-term operational stability [152]. This process does not require the addition of chemicals, and no other species are released into the brine. Following this, lithium ions are extracted from the electrode material using recovery solutions that generally involve fresh water (Figure 8d).

The flow electrodes address the challenges of conventional solid-state electrodes, including intermittent operation, limited capacity, and ineffective mass transfer. By improving mass transfer and redox kinetics, the flow electrodes significantly increase the lithium-extraction capacity—up to six times greater in simulated Atacama brine and nineteen times greater in diluted saline solutions. This system also shows potential for large-scale use, achieving a lithium production rate of  $1 \text{ mol m}^{-2} \text{ h}^{-1}$  at a high current density with a purity of 0.97. However, the process does encounter issues related to higher energy consumption compared to solid-state systems, suggesting that further optimization of the materials and system components could improve efficiency. Additionally, the versatile design of the flow electrodes allows for potential applications in other selective electrochemical recovery processes [153].

The use of aluminum phosphate ( $\text{AlPO}_4$ ) coating on lithium manganese oxide (LMO) greatly improves the material's electrochemical performance. This coating enhances not only the release capacity of lithium ions but also the stability of the cycles, resulting in an impressive 93.6% capacity retention after 20 cycles. Additionally, it minimizes the dissolution of manganese, ensuring the long-term integrity of the electrode. Furthermore, the  $\text{AlPO}_4$  coating alters the surface of LMO, making it more hydrophilic and improving the transport of lithium ions, which leads to a 90.4% increase in the lithium-release capacity in the 0.5AP-LMO//Ag system compared to uncoated LMO in simulated brine. Moreover, it demonstrates consistent performance in more complex real brine environments. These enhancements demonstrate the potential of the 0.5AP-LMO//Ag lithium-ion pump as an effective, selective, and scalable solution for industrial-scale lithium recovery, offering promising implications for the future of the lithium-extraction industry [154].

Gas flushing combined with porous electrodes in electrochemical lithium-extraction system allows for continuous and automatic operation, transforming the process of lithium recovery. The system stands out for its capacity to greatly reduce the consumption of ultrapure water, achieving almost 100% lithium purity with just 20 mL of water—merely 1/60th of the amount needed by traditional single flush methods. By modeling lithium-ion concentration distributions, the study emphasizes the effectiveness of the flow-through arrangement in minimizing medium concentration polarization and maintaining high lithium ion concentration on the electrode surface. When tested with simulated Atacama salt lake water, the system not only delivers high-purity lithium extraction but also operates with remarkable energy efficiency, consuming only 0.732 kWh per kilogram of lithium extracted. These results highlight the system's potential as a scalable and environmentally sustainable solution for large-scale lithium recovery from seawater and brine, holding significant implications for addressing the increasing global demand for lithium [155].

Lithium nickel manganese oxide ( $\text{LiNi0.05Mn1.95O}_4$ , LNMO-0.05) showcases a significant leap forward in lithium-recovery technology. This material is specifically designed for the effective and sustainable extraction of lithium from brine and boasts a distinctive truncated octahedral structure and nickel doping, enabling it to function through an electrochemical process like a battery. It exhibits high selectivity for lithium ions compared to other cations commonly present in brine. The LNMO-0.05 electrode delivers an exceptional performance, achieving a high lithium-extraction capacity of 25.87 mg/g, an impressive lithium-recovery efficiency surpassing 90%, excellent ion selectivity, and outstanding stability over multiple cycles, significantly surpassing the 38% observed in traditional LMO electrodes. These enhancements are credited to the suppression of the Jahn–Teller effect and the improved structural stability provided by nickel doping. Additionally, the electrode's low energy consumption and minimal environmental impact highlight its potential for large-scale applications, presenting a more environmentally

friendly and cost-effective alternative to conventional lithium-extraction methods. This research emphasizes the LNMO-0.05 electrode as a promising solution for addressing the increasing demand for lithium across various industries, particularly in environments with high Mg/Li ratios [156].

Zinc has been used as a cost-effective and high-capacity negative electrode, alongside LiMn<sub>2</sub>O<sub>4</sub> as the positive electrode, in the LiMn<sub>2</sub>O<sub>4</sub>-zinc (LMO-Zn) battery system. This setup efficiently recovered lithium from brine with high impurity levels, consuming 6.3 Wh of energy per mole of lithium. The zinc electrode showed remarkable stability, enduring reversible oxidation and reduction processes without any side reactions or potential shifts, even after 100 cycles, while retaining 73% of its initial capacity [157].

When modified LiFePO<sub>4</sub> and FePO<sub>4</sub> electrodes were used in an H-type electrolytic cell, lithium extraction from geothermal water reached 90.65% after eight adsorption-desorption cycles. The electrodes remained stable during the process [158].

#### 4.3.5. Nanofiltration Membrane

Membrane processes used for selectively recovering lithium often rely on mechanical forces (Figure 8e). These forces push brines through nanofiltration membranes, which typically retain multivalent species.

Peng and Zhao (2021) present a nano-heterogeneous membrane modified with di-aminoethimidazole bromide (DAIB) that significantly enhances the separation of lithium (Li<sup>+</sup>) from high magnesium/lithium (Mg<sup>2+</sup>/Li<sup>+</sup>) ratio brines. This innovative membrane design improves hydrophilicity and reduces water transport resistance, resulting in a five-fold increase in water permeability. The DAIB-modified membrane achieves a high lithium flux of 0.7 mol m<sup>-2</sup> h<sup>-1</sup> and demonstrates excellent Mg<sup>2+</sup>/Li<sup>+</sup> selectivity, effectively reducing the Mg<sup>2+</sup>/Li<sup>+</sup> ratio in the permeate to below 2, even at challenging Mg<sup>2+</sup>/Li<sup>+</sup> ratios of 20. The membrane exhibits strong operational stability and reusability, maintaining high performance over a 200 h continuous nanofiltration test and resisting pressures of up to 8 bar. Its versatility across various brine compositions enhances its potential for widespread industrial application, particularly in lithium extraction from salt-lake brines. Additionally, the membrane's production process is scalable and economical, making it a practical solution for large-scale lithium-recovery operations, addressing the growing demand for lithium in high-tech industries [159].

Li et al. [160] demonstrate that the DK nanofiltration (NF) membrane, a commercial membrane designed for the selective separation of ions, is highly effective in separating magnesium (Mg<sup>2+</sup>) and lithium (Li<sup>+</sup>) from sulfate-type salt-lake brine. The membrane achieves a high magnesium retention rate ( $\geq 81\%$ ) and a negative lithium-retention rate ( $\leq -69\%$ ), resulting in a lithium yield of 83%. The DK membrane significantly improves the magnesium-to-lithium separation efficiency, reducing the mass ratio of magnesium to lithium in the permeate by 8.5 times. However, long-term use leads to membrane fouling, which decreases separation performance by causing structural damage, increasing surface roughness, and reducing hydrophilicity, though it also unexpectedly increases membrane flux. The study highlights the critical role of calcium (Ca<sup>2+</sup>) in fouling, with the most severe fouling observed at a calcium concentration of 2 mmol/L, but with a reduction in fouling at higher concentrations due to complexation effects. To enhance lithium-recovery efficiency and membrane longevity, the research suggests reducing calcium and magnesium concentrations in the brine through pretreatment, thereby mitigating fouling and improving the overall performance of the DK membrane in lithium-extraction processes [160].

Zha et al. [161] introduce an advanced polyamide (PA) nanofiltration membrane enhanced with diazo-18-crown-6 (DA18C6) aza-crown ether for efficient lithium (Li<sup>+</sup>) and magnesium (Mg<sup>2+</sup>) separation in salt-lake brines. This innovative membrane design increases the crosslinking degree and reduces the average pore size, resulting in a high pure water permeance of  $10.4 \text{ L} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1}$  and an excellent Li<sup>+</sup>/Mg<sup>2+</sup> separation factor of 11.2. The strong interaction between DA18C6 and Li<sup>+</sup>, confirmed through molecular dynamics simulations, plays a crucial role in this performance. The membrane was effectively

utilized in a three-stage nanofiltration process, drastically reducing the  $Mg^{2+}/Li^+$  ratio in simulated brine from 57 to 0.03, demonstrating its potential for efficient lithium extraction from high  $Mg^{2+}/Li^+$  ratio brines. Moreover, the membrane exhibited excellent operational stability, maintaining consistent performance over time, making it a promising candidate for industrial-scale lithium recovery from salt-lake brines, addressing the growing demand for lithium in various industries [161].

## 5. Cost

The expense of any Li recovery system is split into the ‘capital’ and ‘operational’ expenses. Generally, the capital cost of new lithium-extraction technologies is much higher than that of typical evaporative techniques due to costly materials and equipment [162]. The cost of lithium carbonate, a crucial component used to produce commercial cathode materials, rose by five times in 2021 [163]. The cost of processing lithium from ores like spodumene is significantly influenced by the cost of materials such as fuel and sulfate, making up over 75% of the expenses. Table 3 shows the processing cost of spodumene and brine in different countries. However, this cost varies from mine to mine. For example, the MSB Blanco mine in Chile requires more manpower and energy for processing which leads to higher costs in general [164].

**Table 3.** Processing cost of spodumene and brine in different countries.

Country	Raw Material	Cost/Ton (USD)
Whabouchi, Canada	Spodumene	2785
China	Spodumene	3030
Czech Republic	Spodumene	2914
Canada	Brine	3030–3787
Argentina	Brine	2963–3903
Chile	Brine	2963–3903

The production cost of lithium carbonate fluctuates with the price of lithium concentrate. When spodumene was priced at USD 1000 per ton, producing lithium carbonate cost around USD 12,120 to USD 13,640 per ton. With the price surge of spodumene concentrate to USD 5650 per ton in 2022, the cost skyrocketed to over USD 53,030 per ton, far higher than extracting lithium from brine [165].

The high cost of equipment is a major hurdle in scaling up lithium-recovery methods that rely on membranes. Systems like ion-exchange membranes, electrodialysis (ED), and bipolar membrane electrodialysis (BPMED) need large initial investments, which can be hard to justify given the current lithium market. In addition, membrane fouling is a common problem that reduces performance over time, leading to increased operational costs [18,166]. Before using the brine, it must be pretreated to remove impurities, which adds further costs. These costs can vary depending on the type of brine used [167]. Electrochemical methods face challenges because of low lithium uptake by the electrode materials (~1 mol per 150 g of material), making it difficult to scale up [168]. Albo et al. [169] analyzed the economic viability of these methods and found that many modern lithium-recovery processes are not feasible on a large scale due to high operational costs. These costs are significantly higher than those of traditional evaporation-based methods [169]. Although selective electrodialysis has shown promise, the required capital investment and pretreatment steps are expected to drive up costs even more [170].

## 6. Conclusions

The transformation of critical lithium ores, such as spodumene and brine, into battery-grade materials is a complex and evolving process that plays a crucial role in meeting the growing demand for lithium-ion batteries. This review highlights significant advancements

that have been made in beneficiation, pyrometallurgical, hydrometallurgical, and direct lithium-extraction techniques for the extraction of lithium from spodumene. This review also covers the important research works that have been performed in lithium extraction from brine by using polymer inclusion membrane, electrodialysis, and direct lithium-extraction methods.

Recent studies have shown great progress in Li extraction in spodumene. During beneficiation, associated aluminosilicate minerals, such as feldspar and mica, are regarded as gangue minerals and remain underutilized. This is primarily due to the challenges posed by the flotation separation process. These accumulated gangue minerals, treated as tailings, not only raise management costs but also contribute to various environmental issues. The use of a combination of the anionic collector sodium oleate (NaOL) with cationic collectors such as dodecyl ammonium chloride or tributyl tetradecyl phosphonium chloride can significantly address this issue. Sulfuric acid roasting enables 90% lithium recovery with a stoichiometric excess of  $H_2SO_4$  ranging from 30% to 140%.

Chlorination and carbonate roasting could be good alternatives to sulfuric acid roasting techniques. As using chlorine for roasting has some environmental issues, more research work should focus on mitigating the environmental issues. On the other hand, for hydrometallurgical techniques, different acids and alkalis are used nowadays. Using nitric acid under pressure for leaching lithium from spodumene has shown promising results for lithium extraction. Phosphoric acid and a mixture of hydrofluoric and phosphoric acid is also found as a good alternative leaching agent of sulfuric acid. But though hydrofluoric acid is highly corrosive, new research should focus on finding alternatives to this acid. In the case of direct lithium extraction from spodumene, electrochemical methods, sodium carbonate, and the Bayer process have been used recently.

In the case of lithium extraction from brine, using polymer inclusion membrane (PIMs) has been found to be very useful. Several polymers have been discovered as the base matrices of PIMs, including poly(vinyl chloride), cellulose triacetate, and poly(vinylidene fluoride-cohexafluoropropylene). Tri-n-butyl phosphate (TBP) is being used extensively in many research studies as a significant component for selective Li extraction. In electrodialysis technique, using a two-step coating process with polydopamine (PDA) and polyethyleneimine (PEI) along with 2-hydroxymethyl-15-crown-5 ether (15CE) has been found to be an effective lithium-extraction method. DLE techniques like electrochemical ion pumping are new, and they will need more extensive engineering work before they can be used on an industrial scale. On the other hand, different approaches like precipitation, solvent extraction, and NF filtration have been researched for decades in related industrial separation chemical engineering processes; the difficulty here is tailoring these approaches to the intricacy of brines rich in lithium. Increasing the level of readiness for these technologies requires conducting laboratory tests using real brines or solutions that closely resemble real compositions. The enormous volumes of brine that must be processed every day are a crucial consideration when trying to scale up from the laboratory to the industrial scale. To ensure the sustainability of the above methods for extracting the lithium from ores, we must lower the temperature, as it is currently an intensive operation (1100 °C) that generates significant CO<sub>2</sub> emissions and produces liquid acid effluents. Utilizing hydroelectric or solar energy can help to reduce CO<sub>2</sub> emissions; and by recovering secondary materials from the effluents, we can achieve a zero-waste process.

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## References

- Sterba, J.; Krzemień, A.; Fernández, P.R.; García-Miranda, C.E.; Valverde, G.F. Lithium mining: Accelerating the transition to sustainable energy. *Resour. Policy* **2019**, *62*, 416–426. [CrossRef]
- Liu, D.; Gao, X.; An, H.; Jia, N.; Wang, A. Exploring market instability of global lithium resources based on chaotic dynamics analysis. *Resour. Policy* **2024**, *88*, 104373. [CrossRef]
- Cano, Z.P.; Banham, D.; Ye, S.; Hintennach, A.; Lu, J.; Fowler, M.; Chen, Z. Batteries and fuel cells for emerging electric vehicle markets. *Nat. Energy* **2018**, *3*, 279–289. [CrossRef]
- Tarascon, J.-M. Is lithium the new gold? *Nat. Chem.* **2010**, *2*, 510. [CrossRef]
- Wietelmann, U.; Klett, J. 200 Years of Lithium and 100 Years of Organolithium Chemistry. *Z. Anorg. Allg. Chem.* **2018**, *644*, 194–204. [CrossRef]
- Baudino, L.; Santos, C.; Pirri, C.F.; La Mantia, F.; Lamberti, A. Recent Advances in the Lithium Recovery from Water Resources: From Passive to Electrochemical Methods. *Adv. Sci.* **2022**, *9*, e2201380. [CrossRef]
- Manjong, N.B.; Marinova, S.; Bach, V.; Burheim, O.S.; Finkbeiner, M.; Strømman, A.H. Approaching battery raw material sourcing through a material criticality lens. *Sustain. Prod. Consum.* **2024**, *49*, 289–303. [CrossRef]
- Bouguern, M.D.; Reddy, A.K.M.R.; Li, X.; Deng, S.; Laryea, H.; Zaghib, K. Engineering Dry Electrode Manufacturing for Sustainable Lithium-Ion Batteries. *Batteries* **2024**, *10*, 39. [CrossRef]
- Grágeda, M.; González, A.; Grágeda, M.; Ushak, S. Purification of brines by chemical precipitation and ion-exchange processes for obtaining battery-grade lithium compounds. *Int. J. Energy Res.* **2018**, *42*, 2386–2399. [CrossRef]
- Campagnol, N.; Hoffman, K.; Lala, A.; Ramsbottom, O. The Future of Nickel: A Class Act. 2017. mckinsey.com. Available online: <https://www.mckinsey.com/~media/McKinsey/Industries/Metals%20and%20Mining/Our%20Insights/The%20future%20of%20nickel%20A%20class%20act/The%20future%20of%20nickel%20A%20class%20act.pdf> (accessed on 26 July 2024).
- Gunn, G.; Petavratzi, E. Battery Raw Materials. 2018. Available online: <https://nora.nerc.ac.uk/id/eprint/534463/1/batteryRawMaterial.pdf> (accessed on 26 July 2024).
- Olivetti, E.A.; Ceder, G.; Gaustad, G.G.; Fu, X. Lithium-Ion Battery Supply Chain Considerations: Analysis of Potential Bottlenecks in Critical Metals. *Joule* **2017**, *1*, 229–243. [CrossRef]
- Ahmed, S.; Nelson, P.A.; Gallagher, K.G.; Susarla, N.; Dees, D.W. Cost and energy demand of producing nickel manganese cobalt cathode material for lithium ion batteries. *J. Power Sources* **2017**, *342*, 733–740. [CrossRef]
- Azevedo, M.; Campagnol, N.; Hagenbruch, T.; Hoffman, K.; Lala, A.; Ramsbottom, O. Lithium and Cobalt. mckinsey.com. Available online: <https://www.mckinsey.com/~media/mckinsey/industries/metals%20and%20mining/our%20insights/lithium%20and%20cobalt%20a%20tale%20of%20two%20commodities/lithium-and-cobalt-a-tale-of-two-commodities.pdf> (accessed on 26 July 2024).
- Zheng, C.; Jian, R.H.; Pan, J.L.; Zou, C.; Wang, H.; Sheng, Y.Y.; Zhou, Q.F.; Liu, W.Q. Study on the preparation of battery grade cobalt carbonate from PTA oxidation residue. *Integr. Ferroelectr.* **2018**, *189*, 65–70. [CrossRef]
- Schmidt, T.; Buchert, M.; Schebek, L. Investigation of the primary production routes of nickel and cobalt products used for Li-ion batteries. *Resour. Conserv. Recycl.* **2016**, *112*, 107–122. [CrossRef]
- Jayanthi, K.; Lamichhane, T.N.; Roy, V.; Zhao, F.; Navrotsky, A.; Moyer, B.A.; Paranthaman, M.P. Integrated Circular Economy Model System for Direct Lithium Extraction: From Minerals to Batteries Utilizing Aluminum Hydroxide. *ACS Appl. Mater. Interfaces* **2023**, *15*, 58984–58993. [CrossRef] [PubMed]
- Khalil, A.; Mohammed, S.; Hashaikeh, R.; Hilal, N. Lithium recovery from brine: Recent developments and challenges. *Desalination* **2022**, *528*, 115611. [CrossRef]
- Ni, C.; Liu, C.; Wang, J.; Liang, Y.; Xie, W.; Zhong, H.; He, Z. Advances and promotion strategies of processes for extracting lithium from mineral resources. *J. Ind. Eng. Chem.* **2024**, *in press*. [CrossRef]
- Nie, X.-Y.; Sun, S.-Y.; Sun, Z.; Song, X.; Yu, J.-G. Ion-fractionation of lithium ions from magnesium ions by electrodialysis using monovalent selective ion-exchange membranes. *Desalination* **2017**, *403*, 128–135. [CrossRef]
- Shi, D.; Zhang, L.; Peng, X.; Li, L.; Song, F.; Nie, F.; Ji, L.; Zhang, Y. Extraction of lithium from salt lake brine containing boron using multistage centrifuge extractors. *Desalination* **2018**, *441*, 44–51. [CrossRef]
- Shi, D.; Cui, B.; Li, L.; Peng, X.; Zhang, L.; Zhang, Y. Lithium extraction from low-grade salt lake brine with ultrahigh Mg/Li ratio using TBP—kerosene—FeCl<sub>3</sub> system. *Sep. Purif. Technol.* **2019**, *211*, 303–309. [CrossRef]
- Ryabtsev, A.D. Beneficiation technology for lithium-containing hydrogenic mineral products. *J. Min. Sci.* **2005**, *41*, 573–582. [CrossRef]
- Yan, G.; Wang, M.; Hill, G.T.; Zou, S.; Liu, C. Defining the challenges of Li extraction with olivine host: The roles of competitor and spectator ions. *Proc. Natl. Acad. Sci. USA* **2022**, *119*, e2200751119. [CrossRef]
- Battistel, A.; Palagonia, M.S.; Brogioli, D.; La Mantia, F.; Trócoli, R. Electrochemical Methods for Lithium Recovery: A Comprehensive and Critical Review. *Adv. Mater.* **2020**, *32*, e1905440. [CrossRef] [PubMed]
- Ran, Y.; Qu, G.; Yang, J.; Zhou, S.; Li, B.; Wang, H.; Wei, Y. Efficient separation and extraction of lithium from low-grade claystone by chloride salt-enhanced roasting process. *J. Clean. Prod.* **2024**, *434*, 140156. [CrossRef]
- Sverdrup, H.U. Modelling global extraction, supply, price and depletion of the extractable geological resources with the LITHIUM model. *Resour. Conserv. Recycl.* **2016**, *114*, 112–129. [CrossRef]

28. Meshram, P.; Pandey, B.; Mankhand, T. Extraction of lithium from primary and secondary sources by pre-treatment, leaching and separation: A comprehensive review. *Hydrometallurgy* **2014**, *150*, 192–208. [CrossRef]
29. Johnson, G.D. Recovery Process. WO2016/054683A1, 9 August 2016.
30. Choubey, P.K.; Kim, M.-S.; Srivastava, R.R.; Lee, J.-C.; Lee, J.-Y. Advance review on the exploitation of the prominent energy-storage element: Lithium. Part I: From mineral and brine resources. *Miner. Eng.* **2016**, *89*, 119–137. [CrossRef]
31. Roy, R.; Roy, D.M.; Osborn, E.F. Compositional and Stability Relationships Among the Lithium Aluminosilicates: Eucryptite, Spodumene, and Petalite. *J. Am. Ceram. Soc.* **1950**, *33*, 152–159. [CrossRef]
32. de Lima, A.; Souza, S.; Lalic, M. Electronic and optical properties of spodumene gemstone: A theoretical study. *Opt. Mater.* **2008**, *30*, 1048–1051. [CrossRef]
33. Menéndez, M.; Vidal, A.; Toraño, J.; Gent, M. Optimisation of spodumene flotation. *Eur. J. Miner. Process. Environ. Prot.* **2004**, *4*, 130–135.
34. Ellestad, R.B.; Milne, L.K. Method of Extracting Lithium Values from Spodumene Ores. U.S. Patent 2,516,109, 25 July 1950.
35. Moon, K.S.; Fuerstenau, D.W. Surface crystal chemistry in selective flotation of spodumene ( $\text{LiAl}[\text{SiO}_3]_2$ ) from other aluminosilicates. *Int. J. Miner. Process.* **2003**, *72*, 11–24. [CrossRef]
36. Kharaka, Y.K.; Hanor, J.S. Deep Fluids in the Continents: I. Sedimentary Basins. *TrGeo* **2003**, *5*, 605. [CrossRef]
37. Bowell, R.J.; Lagos, L.; Hoyos, C.R.d.L.; Declercq, J. Classification and Characteristics of Natural Lithium Resources. *Elements* **2020**, *16*, 259–264. [CrossRef]
38. Park, H.; Singhal, N.; Jho, E.H. Lithium sorption properties of  $\text{HMnO}$  in seawater and wastewater. *Water Res.* **2015**, *87*, 320–327. [CrossRef] [PubMed]
39. Sun, K.; Tebyetekerwa, M.; Zeng, X.; Wang, Z.; Duignan, T.T.; Zhang, X. Understanding the Electrochemical Extraction of Lithium from Ultradilute Solutions. *Environ. Sci. Technol.* **2024**, *58*, 3997–4007. [CrossRef] [PubMed]
40. Tansel, B. Significance of thermodynamic and physical characteristics on permeation of ions during membrane separation: Hydrated radius, hydration free energy and viscous effects. *Sep. Purif. Technol.* **2012**, *86*, 119–126. [CrossRef]
41. Luo, G.; Li, X.; Chen, L.; Chao, Y.; Zhu, W. Electrochemical lithium ion pumps for lithium recovery: A systematic review and influencing factors analysis. *Desalination* **2023**, *548*, 116228. [CrossRef]
42. Thibault, Y.; McEvoy, J.G. Alkali-Induced Phase Transition to  $\beta$ -Spodumene along the  $\text{LiAlSi}_2\text{O}_6$ – $\text{LiAlSi}_4\text{O}_{10}$  Join. *Crystals* **2023**, *13*, 1182. [CrossRef]
43. Wietelmann, U.; Bauer, R.J. Lithium and Lithium Compounds. *Ullmann's Encycl. Ind. Chem.* **2000**. [CrossRef]
44. Garret, D.E. *Handbook of Lithium and Natural Calcium Chloride*, Part. 1; Elsevier BV: New York, NY, USA, 2004.
45. Tadesse, B.; Makuei, F.; Albijanic, B.; Dyer, L. The beneficiation of lithium minerals from hard rock ores: A review. *Miner. Eng.* **2019**, *131*, 170–184. [CrossRef]
46. Choi, J.; Kim, W.; Chae, W.; Kim, S.B.; Kim, H. Electrostatically Controlled Enrichment of Lepidolite via Flotation. *Mater. Trans.* **2012**, *53*, 2191–2194. [CrossRef]
47. Bulatovic, S.M. Beneficiation of Barite Ores. In *Handbook of Flotation Reagents: Chemistry, Theory and Practice*; Elsevier: Amsterdam, The Netherlands, 2015; pp. 41–56. [CrossRef]
48. Jandová, J.; Vu, H.N.; Belková, T.; Dvořák, P.; Kondás, J. Obtaining  $\text{Li}_2\text{Co}_3$  from Zinnwaldite Wastes. *Ceram. Silikáty* **2009**, *53*, 108–112.
49. Tran, T.; Luong, V.T. Lithium Production Processes. In *Lithium Process Chemistry: Resources, Extraction, Batteries, and Recycling*; Elsevier Inc.: Amsterdam, The Netherlands, 2015; pp. 81–124. [CrossRef]
50. Pawlik, M. Fundamentals of froth flotation. *ChemTexts* **2022**, *8*, 1–40. [CrossRef]
51. Tian, J.; Xu, L.; Wu, H.; Fang, S.; Deng, W.; Peng, T.; Sun, W.; Hu, Y. A novel approach for flotation recovery of spodumene, mica and feldspar from a lithium pegmatite ore. *J. Clean. Prod.* **2018**, *174*, 625–633. [CrossRef]
52. Rai, B.; Sathish, P.; Tanwar, J.; Pradip; Moon, K.; Fuerstenau, D. A molecular dynamics study of the interaction of oleate and dodecylammonium chloride surfactants with complex aluminosilicate minerals. *J. Colloid Interface Sci.* **2011**, *362*, 510–516. [CrossRef] [PubMed]
53. Lucassen-Reynders, E.; Lucassen, J.; Giles, D. Surface and bulk properties of mixed anionic/cationic surfactant systems i. equilibrium surface tensions. *J. Colloid Interface Sci.* **1981**, *81*, 150–157. [CrossRef]
54. Shu, K.; Xu, L.; Wu, H.; Xu, Y.; Luo, L.; Yang, J.; Tang, Z.; Wang, Z. In Situ Adsorption of Mixed Anionic/Cationic Collectors in a Spodumene–Feldspar Flotation System: Implications for Collector Design. *Langmuir* **2020**, *36*, 8086–8099. [CrossRef]
55. Shu, K.; Xu, L.; Wu, H.; Peng, L.; Xu, Y.; Luo, L.; Yang, J.; Tang, Z. In situ adsorption of mixed collectors BHA/DDA in spodumene–feldspar flotation system. *Sep. Purif. Technol.* **2020**, *251*, 117325. [CrossRef]
56. Ma, Z.; Xu, L.; Guo, W.; Wang, D.; Xue, K. Effects of alkali pretreatment on the flotation of spodumene and feldspar. *Miner. Eng.* **2024**, *210*, 108676. [CrossRef]
57. Ma, Z.; Shi, X.; Xu, L.; Wang, D.; Xue, K.; Jing, L.; Meng, J. Selective flotation separation of spodumene from feldspar using a novel mixed anionic/cationic collector NaOL/ND13. *Miner. Eng.* **2023**, *201*, 108152. [CrossRef]
58. Munson, G.A.; Clarke, F.F. Mining and Concentrating Spodumene in the Black Hills, South Dakota. 911metallurgist.comGA Munson, FF ClarkeAIME Trans, 1955•911metallurgist.com. 1955. Available online: <https://911metallurgist.com/blog/wp-content/uploads/2016/05/Extraction-of-Lithium-from-Its-Ores.pdf> (accessed on 14 August 2024).

59. Sagzhanov, D.; Ito, J.; Altansukh, B.; Godirilwe, L.L.; Jeon, S.; Haga, K.; Shibayama, A. Beneficiation of Low-Grade Lithium Ores from Eastern Kazakhstan by Dense Media Separation (DMS) and Froth Flotation. In *TMS Annual Meeting & Exhibition; Minerals, Metals and Materials Series*; Springer Nature: Cham, Switzerland, 2024; pp. 201–213. [CrossRef]
60. Cerny, P.; Ercit, T.S.; Vanstone, P.T. Petrology and mineralization of the Tanco rare-element pegmatite, Southeastern Manitoba. In *Geological Association of Canada—Mineralogical Association of Canada, Field Trip Guidebook*; Geological Association of Canada, Winnipeg Section: St. John's, NL, Canada, 1996; Volume 63.
61. Aghamirian, M.; Mohns, C.; Grammatikopoulos, T.; Imeson, D.; Pearse, G. An overview of spodumene beneficiation. In Proceedings of the 44th Annual Canadian Mineral Processors Operators' Conference, Ottawa, ON, Canada, 17–19 January 2012; p. 153.
62. Ferguson, W.; Young, S.R.; Deveau, C.; Hazel, W.; Lussier, A.; Copeland, R. Cabot Corp; Tantalum Mining and Corporation of Canada Ltd. Canadian Institute of Mining, Metallurgy and Petroleum: Westmount, QC, Canada, 2000; pp. 225–230.
63. Bale, M.D.; May, A.V. Processing of ores to produce tantalum and lithium. *Miner. Eng.* **1989**, *2*, 299–320. [CrossRef]
64. Banks, M.K.; McDaniel, W.T.; Sales, P.N. *A Method for Concentration of North Carolina Spodumene Ores*; Mining Engineering: Lubumbashi, Congo, 1953; pp. 181–186.
65. Kundu, T.; Rath, S.S.; Das, S.K.; Parhi, P.K.; Angadi, S.I. Recovery of lithium from spodumene-bearing pegmatites: A comprehensive review on geological reserves, beneficiation, and extraction. *Powder Technol.* **2023**, *415*, 118142. [CrossRef]
66. Wills, B.A.; Finch, J.A. Gravity Concentration. In *Wills' Mineral Processing Technology*; Butterworth-Heinemann: Oxford, UK, 2016; pp. 223–244. [CrossRef]
67. Kundu, T.; Das, S.K.; Dash, N.; Parhi, P.K.; Sangurmath, P.; Angadi, S.I. Characterization and gravity concentration studies on spodumene bearing pegmatites of India. *Sep. Sci. Technol.* **2023**, *58*, 2331–2343. [CrossRef]
68. Kulumbegov, R.V.; Delitsyn, L.M.; Belyaev, I.A.; Klimenko, N.N.; Tarasenko, A.B.; Popel, O.S. Extraction of Lithium from  $\beta$ -Spodumene via Ion Exchange in Molten Sodium Salts. *Inorg. Mater.* **2023**, *59*, 912–917. [CrossRef]
69. Asif, A.H.; Li, C.; Lim, H.; Sun, H. Australia's Spodumene: Advances in Lithium Extraction Technologies, Decarbonization, and Circular Economy. *Ind. Eng. Chem. Res.* **2024**, *63*, 2073–2086. [CrossRef]
70. Cartón, A.; Bolado, S.; Marcos, M. Liquid–Liquid Equilibria for Aqueous Solutions of Lithium Sulfate or Lithium Formate and Triethylamine or Diisopropylamine. *J. Chem. Eng. Data* **2000**, *45*, 260–264. [CrossRef]
71. MacEwan, J.U. Method of Producing Lithium Sulphate from Alphaia and Betaspodumene. U.S. Patent US2972517A, 21 February 1961.
72. Robinson, G.P. Recovery of Lithium from Ore. U.S. Patent 2983576, 9 May 1961.
73. Maliachova, K.; Doukas, N.; Tsakiri, D.; Samouhos, M.; Sakellariou, L.; Douni, I.; Taxiarchou, M.; Paspaliaris, I. Li Extraction from a-Spodumene Concentrate via Carbonizing Calcination. *Mater. Proc.* **2023**, *15*, 62. [CrossRef]
74. Rioyo, J.; Tuset, S.; Grau, R. Lithium Extraction from Spodumene by the Traditional Sulfuric Acid Process: A Review. *Miner. Process. Extr. Met. Rev.* **2022**, *43*, 97–106. [CrossRef]
75. Li, H.; Eksteen, J.; Kuang, G. Recovery of lithium from mineral resources: State-of-the-art and perspectives—A review. *Hydrometallurgy* **2019**, *189*, 105129. [CrossRef]
76. Lajoie-Leroux, F.; Dessemont, C.; Soucy, G.; Laroche, N.; Magnan, J.-F. Impact of the impurities on lithium extraction from  $\beta$ -spodumene in the sulfuric acid process. *Miner. Eng.* **2018**, *129*, 1–8. [CrossRef]
77. Salakjani, N.K.; Singh, P.; Nikoloski, A.N. *Production of Lithium—A Literature Review. Part 2. Extraction from Spodumene*; Bellwether Publishing, Ltd.: Minnetonka, MN, USA, 2021. [CrossRef]
78. Qiu, S.; Sun, T.; Zhu, Y.; Liu, C.; Yu, J. Direct Preparation of Water-Soluble Lithium Salts from  $\alpha$ -Spodumene by Roasting with Different Sulfates. *Ind. Eng. Chem. Res.* **2023**, *62*, 685–697. [CrossRef]
79. Medina, L.F.; El-Naggar, M.M.A.A. An alternative method for the recovery of lithium from spodumene. *Met. Trans. B* **1984**, *15*, 725–726. [CrossRef]
80. Ni, C.; Liu, C.; Liu, J.; Wang, J.; Liang, Y.; Sun, W.; Zhong, H.; He, Z. Thermochemically driven crystal phase transfer via mechanical activation-assisted chlorination roasting toward the selective extraction of lithium from spodumene. *J. Ind. Eng. Chem.* **2024**, *138*, 632–640. [CrossRef]
81. Barbosa, L.I.; González, J.A.; Ruiz, M.d.C. Extraction of lithium from  $\beta$ -spodumene using chlorination roasting with calcium chloride. *Thermochim. Acta* **2015**, *605*, 63–67. [CrossRef]
82. Fosu, A.Y.; Kanari, N.; Bartier, D.; Vaughan, J.; Chagnes, A. Novel extraction route of lithium from  $\alpha$ -spodumene by dry chlorination. *RSC Adv.* **2022**, *12*, 21468–21481. [CrossRef]
83. Maurice, A.; Olivier, C.A. Carbonatizing Roast of Lithium Bearing Ores. U.S. Patent US3380802, 30 April 1968.
84. Kroll, A.V. Method of Recovering Lithium Compounds from Lithium Minerals. U.S. Patent US2662809A, 15 December 1953.
85. Archambault, M. Lithium Carbonate Production. U.S. Patent 3112171, 26 November 1963.
86. Zhu, Y.; Zhang, D.; Qiu, S.; Liu, C.; Yu, J. Lithium recovery from pretreated  $\alpha$ -spodumene residue through acid leaching at ambient temperature. *Can. J. Chem. Eng.* **2023**, *101*, 4360–4373. [CrossRef]
87. Chen, Y.; Tian, Q.; Chen, B.; Shi, X.; Liao, T. Preparation of lithium carbonate from spodumene by a sodium carbonate autoclave process. *Hydrometallurgy* **2011**, *109*, 43–46. [CrossRef]
88. Grasso, M.; González, J.; Gennari, F. Lithium extraction from  $\beta$ -LiAlSi<sub>2</sub>O<sub>6</sub> using Na<sub>2</sub>CO<sub>3</sub> through thermal reaction. *Miner. Eng.* **2022**, *176*, 107349. [CrossRef]
89. Zhou, H.; Liu, Y.; Ma, B.; Wang, C.; Chen, Y. Strengthening extraction of lithium and rubidium from activated  $\alpha$ -spodumene concentrate via sodium carbonate roasting. *J. Ind. Eng. Chem.* **2023**, *123*, 248–259. [CrossRef]

90. Zhou, H.; Cao, Z.; Ma, B.; Wang, C.; Chen, Y. Selective and efficient extraction of lithium from spodumene via nitric acid pressure leaching. *Chem. Eng. Sci.* **2024**, *287*, 119736. [[CrossRef](#)]
91. Paris, J.; Mohammadi-Jam, S.; Li, R.; Liang, J.; Oh, H.J.; Kökkiliç, O.; Omelon, S.; Waters, K.E. Preliminary investigation into lithium extraction by phosphoric acid leaching of spodumene. *Miner. Eng.* **2024**, *209*, 108613. [[CrossRef](#)]
92. Guo, H.; Kuang, G.; Wang, H.; Yu, H.; Zhao, X. Investigation of Enhanced Leaching of Lithium from  $\alpha$ -Spodumene Using Hydrofluoric and Sulfuric Acid. *Minerals* **2017**, *7*, 205. [[CrossRef](#)]
93. Guo, H.; Yu, H.-Z.; Zhou, A.-A.; Lü, M.-H.; Wang, Q.; Kuang, G.; Wang, H.-D. Kinetics of leaching lithium from  $\alpha$ -spodumene in enhanced acid treatment using HF/H<sub>2</sub>SO<sub>4</sub> as medium. *Trans. Nonferrous Met. Soc. China* **2019**, *29*, 407–415. [[CrossRef](#)]
94. Rosales, G.D.; Ruiz, M.d.C.; Rodriguez, M.H. Novel process for the extraction of lithium from  $\beta$ -spodumene by leaching with HF. *Hydrometallurgy* **2014**, *147–148*, 1–6. [[CrossRef](#)]
95. Qiu, S.; Liu, C.; Yu, J. Conversion from  $\alpha$ -spodumene to intermediate product Li<sub>2</sub>SiO<sub>3</sub> by hydrothermal alkaline treatment in the lithium extraction process. *Miner. Eng.* **2022**, *183*, 107599. [[CrossRef](#)]
96. Alhadad, M.F.; Oskierski, H.C.; Chischi, J.; Senanayake, G.; Dlugogorski, B.Z. Lithium extraction from  $\beta$ -spodumene: A comparison of keatite and analcime processes. *Hydrometallurgy* **2023**, *215*, 105985. [[CrossRef](#)]
97. Xing, P.; Wang, C.; Zeng, L.; Ma, B.; Wang, L.; Chen, Y.; Yang, C. Lithium Extraction and Hydroxysodalite Zeolite Synthesis by Hydrothermal Conversion of  $\alpha$ -Spodumene. *ACS Sustain. Chem. Eng.* **2019**, *7*, 9498–9505. [[CrossRef](#)]
98. Kuang, G.; Liu, Y.; Li, H.; Xing, S.; Li, F.; Guo, H. Extraction of lithium from  $\beta$ -spodumene using sodium sulfate solution. *Hydrometallurgy* **2018**, *177*, 49–56. [[CrossRef](#)]
99. Wang, S.; Szymanski, N.J.; Fei, Y.; Dong, W.; Christensen, J.N.; Zeng, Y.; Whittaker, M.; Ceder, G. Direct Lithium Extraction from  $\alpha$ -Spodumene through Solid-State Reactions for Sustainable Li<sub>2</sub>CO<sub>3</sub> Production. *Inorg. Chem.* **2024**, *63*, 13576–13584. [[CrossRef](#)] [[PubMed](#)]
100. Zhang, H.; Han, Y.; Lai, J.; Wolf, J.; Lei, Z.; Yang, Y.; Shi, F. Direct extraction of lithium from ores by electrochemical leaching. *Nat. Commun.* **2024**, *15*, 5066. [[CrossRef](#)]
101. Song, Y.; Zhao, T.; He, L.; Zhao, Z.; Liu, X. A promising approach for directly extracting lithium from  $\alpha$ -spodumene by alkaline digestion and precipitation as phosphate. *Hydrometallurgy* **2019**, *189*, 105141. [[CrossRef](#)]
102. Li, J.; Gao, Z.R.; Lin, Q.-F.; Liu, C.; Gao, F.; Lin, C.; Zhang, S.; Deng, H.; Mayoral, A.; Fan, W.; et al. A 3D Extra-Large-Pore Zeolite Enabled by 1D-to-3D Topotactic Condensation of a Chain Silicate. Available online: <https://www.science.org> (accessed on 15 October 2024).
103. Swain, B. Recovery and recycling of lithium: A review. *Sep. Purif. Technol.* **2017**, *172*, 388–403. [[CrossRef](#)]
104. Zhang, Y.-N.; Yu, D.-H.; Jia, C.-Y.; Sun, L.-Y.; Tong, A.; Wang, Y.; Wang, Y.-X.; Huang, L.-J.; Tang, J.-G. Advances and promotion strategies of membrane-based methods for extracting lithium from brine. *Desalination* **2023**, *566*, 116891. [[CrossRef](#)]
105. Nghiem, L.D.; Mornane, P.; Potter, I.D.; Perera, J.M.; Catrall, R.W.; Kolev, S.D. Extraction and transport of metal ions and small organic compounds using polymer inclusion membranes (PIMs). *J. Membr. Sci.* **2006**, *281*, 7–41. [[CrossRef](#)]
106. Zhao, S.; Samadi, A.; Wang, Z.; Pringle, J.M.; Zhang, Y.; Kolev, S.D. Ionic liquid-based polymer inclusion membranes for metal ions extraction and recovery: Fundamentals, considerations, and prospects. *Chem. Eng. J.* **2024**, *481*, 148792. [[CrossRef](#)]
107. Zhou, W.; Xu, S.; Li, Z. Recovery of Lithium from Brine with a High Mg/Li Ratio Using Hydroxyl-Functionalized Ionic Liquid and Tri-n-butyl Phosphate. *J. Sustain. Met.* **2021**, *7*, 256–265. [[CrossRef](#)]
108. Zhou, W.; Li, Z.; Xu, S. Extraction of Lithium from Magnesium-Rich Solution Using Tri-n-butyl Phosphate and Sodium Hexafluorophosphate. *J. Sustain. Met.* **2021**, *7*, 1368–1378. [[CrossRef](#)]
109. Meng, X.; Long, Y.; Tian, Y.; Li, W.; Liu, T.; Huo, S. Electro-membrane extraction of lithium with D2EHPA/TBP compound extractant. *Hydrometallurgy* **2021**, *202*, 105615. [[CrossRef](#)]
110. Zhou, W.; Li, Z.; Bi, Q.; Ma, L.; Xu, S. Extraction of Lithium from Brine with a High Mg/Li Ratio Using Polymer Inclusion Membrane Containing Tri-n-butyl Phosphate and Ionic Liquid. *J. Sustain. Met.* **2022**, *8*, 1639–1649. [[CrossRef](#)]
111. Xu, L.; Zeng, X.; He, Q.; Deng, T.; Zhang, C.; Zhang, W. Stable ionic liquid-based polymer inclusion membranes for lithium and magnesium separation. *Sep. Purif. Technol.* **2022**, *288*, 120626. [[CrossRef](#)]
112. Shen, W.; Wang, D.; Tian, Y.; Zhou, F.; Lin, Y.; Zhang, Z.; Xu, J.; Yang, C. Highly permeable and selective polymer inclusion membrane for Li<sup>+</sup> recovery and underlying enhanced mechanism. *J. Membr. Sci.* **2024**, *699*, 122671. [[CrossRef](#)]
113. Dong, Y.; Liu, Y.; Li, H.; Zhu, Q.; Luo, M.; Zhang, H.; Ye, B.; Yang, Z.; Xu, T. Crown ether-based Tröger's base membranes for efficient Li<sup>+</sup>/Mg<sup>2+</sup> separation. *J. Membr. Sci.* **2023**, *665*, 121113. [[CrossRef](#)]
114. Hua, J.; He, J.; Pei, H.; Ma, X.; Wickramasinghe, S.R.; Li, J. Supported ionic liquid membrane contactor with crown ether functionalized polyimide membrane for high-efficient Li<sup>+</sup>/Mg<sup>2+</sup> selective separation. *J. Membr. Sci.* **2023**, *687*, 122038. [[CrossRef](#)]
115. Xu, X.; He, Q.; Ma, G.; Wang, H.; Nirmalakhandan, N.; Xu, P. Pilot Demonstration of Reclaiming Municipal Wastewater for Irrigation Using Electrodialysis Reversal: Effect of Operational Parameters on Water Quality. *Membranes* **2021**, *11*, 333. [[CrossRef](#)] [[PubMed](#)]
116. Ying, J.; Luo, M.; Jin, Y.; Yu, J. Selective separation of lithium from high Mg/Li ratio brine using single-stage and multi-stage selective electrodialysis processes. *Desalination* **2020**, *492*, 114621. [[CrossRef](#)]
117. Jiang, W.; Lin, L.; Xu, X.; Wang, H.; Xu, P. Physicochemical and electrochemical characterization of cation-exchange membranes modified with polyethylenimine for elucidating enhanced monovalent permselectivity of electrodialysis. *J. Membr. Sci.* **2019**, *572*, 545–556. [[CrossRef](#)]

118. Xu, X.; Lin, L.; Ma, G.; Wang, H.; Jiang, W.; He, Q.; Nirmalakhandan, N.; Xu, P. Study of polyethyleneimine coating on membrane permselectivity and desalination performance during pilot-scale electrodialysis of reverse osmosis concentrate. *Sep. Purif. Technol.* **2018**, *207*, 396–405. [[CrossRef](#)]
119. Yin, X.; Xu, P.; Wang, H. Modification of cation exchange membranes for enhanced extraction of lithium from magnesium and sodium brine solutions via selective electrodialysis. *J. Membr. Sci.* **2024**, *701*, 122705. [[CrossRef](#)]
120. Guo, X.; Hu, S.; Wang, C.; Duan, H.; Xiang, X. Highly Efficient Separation of Magnesium and Lithium and High-Valued Utilization of Magnesium from Salt Lake Brine by a Reaction-Coupled Separation Technology. *Ind. Eng. Chem. Res.* **2018**, *57*, 6618–6626. [[CrossRef](#)]
121. Liu, G.; Zhao, Z.; He, L. Highly selective lithium recovery from high Mg/Li ratio brines. *Desalination* **2020**, *474*, 114185. [[CrossRef](#)]
122. Ji, P.-Y.; Ji, Z.-Y.; Chen, Q.-B.; Liu, J.; Zhao, Y.-Y.; Wang, S.-Z.; Li, F.; Yuan, J.-S. Effect of coexisting ions on recovering lithium from high  $Mg^{2+}/Li^+$  ratio brines by selective-electrodialysis. *Sep. Purif. Technol.* **2018**, *207*, 1–11. [[CrossRef](#)]
123. Xu, S.; Song, J.; Bi, Q.; Chen, Q.; Zhang, W.-M.; Qian, Z.; Zhang, L.; Xu, S.; Tang, N.; He, T. Extraction of lithium from Chinese salt-lake brines by membranes: Design and practice. *J. Membr. Sci.* **2021**, *635*, 119441. [[CrossRef](#)]
124. Tran, K.T.; Van Luong, T.; An, J.-W.; Kang, D.-J.; Kim, M.-J.; Tran, T. Recovery of magnesium from Uyuni salar brine as high purity magnesium oxalate. *Hydrometallurgy* **2013**, *138*, 93–99. [[CrossRef](#)]
125. Zhao, Z.; Si, X.; Liu, X.; He, L.; Liang, X. Li extraction from high Mg/Li ratio brine with  $LiFePO_4/FePO_4$  as electrode materials. *Hydrometallurgy* **2013**, *133*, 75–83. [[CrossRef](#)]
126. Mojid, M.R.; Lee, K.J.; You, J. A review on advances in direct lithium extraction from continental brines: Ion-sieve adsorption and electrochemical methods for varied Mg/Li ratios. *Sustain. Mater. Technol.* **2024**, *40*, e00923. [[CrossRef](#)]
127. Vera, M.L.; Torres, W.R.; Galli, C.I.; Chagnes, A.; Flexer, V. Environmental impact of direct lithium extraction from brines. *Nat. Rev. Earth Environ.* **2023**, *4*, 149–165. [[CrossRef](#)]
128. Zhang, Y.; Hu, Y.; Wang, L.; Sun, W. Systematic review of lithium extraction from salt-lake brines via precipitation approaches. *Miner. Eng.* **2019**, *139*, 105868. [[CrossRef](#)]
129. Chang, S.A.; Balouch, A. Abdullah Analytical perspective of lithium extraction from brine waste: Analysis and current progress. *Microchem. J.* **2024**, *200*, 110291. [[CrossRef](#)]
130. Liu, X.; Zhong, M.; Chen, X.; Zhao, Z. Separating lithium and magnesium in brine by aluminum-based materials. *Hydrometallurgy* **2018**, *176*, 73–77. [[CrossRef](#)]
131. Li, Y.-H.; Zhao, Z.-W.; Liu, X.-H.; Chen, X.-Y.; Zhong, M.-L. Extraction of lithium from salt lake brine by aluminum-based alloys. *Trans. Nonferrous Met. Soc. China* **2015**, *25*, 3484–3489. [[CrossRef](#)]
132. Lai, X.; Xiong, P.; Zhong, H. Extraction of lithium from brines with high Mg/Li ratio by the crystallization-precipitation method. *Hydrometallurgy* **2020**, *192*, 105252. [[CrossRef](#)]
133. An, J.W.; Kang, D.J.; Tran, K.T.; Kim, M.J.; Lim, T.; Tran, T. Recovery of lithium from Uyuni salar brine. *Hydrometallurgy* **2012**, *117–118*, 64–70. [[CrossRef](#)]
134. Wang, H.; Zhong, Y.; Du, B.; Zhao, Y.; Wang, M. Recovery of both magnesium and lithium from high Mg/Li ratio brines using a novel process. *Hydrometallurgy* **2018**, *175*, 102–108. [[CrossRef](#)]
135. Hamzaoui, A.; M’Nif, A.; Hammi, H.; Rokbani, R. Contribution to the lithium recovery from brine. *Desalination* **2003**, *158*, 221–224. [[CrossRef](#)]
136. Liu, C.; Lowenstein, T.K.; Wang, A.; Zheng, C.; Yu, J. Annual Review of Environment and Resources Brine: Genesis and Sustainable Resource Recovery Worldwide. *Annu. Rev. Environ. Resour.* **2023**, *48*, 371–394. [[CrossRef](#)]
137. Su, H.; Li, Z.; Zhang, J.; Zhu, Z.; Wang, L.; Qi, T. Recovery of lithium from salt lake brine using a mixed ternary solvent extraction system consisting of TBP,  $FeCl_3$  and P507. *Hydrometallurgy* **2020**, *197*, 105487. [[CrossRef](#)]
138. Li, X.; Chen, W.; Chen, L.; Luo, G.; Sun, J.; Huang, Y.; Bizuneh, K.; Chao, Y.; Zhu, W. Temperature-responsive liquid-liquid extraction of  $Li^+$  from high Mg/Li ratio brine. *Sep. Purif. Technol.* **2023**, *322*, 124309. [[CrossRef](#)]
139. Hua, J.; He, J.; Pei, H.; Du, J.; Ma, X.; Li, J. A remarkable improved  $Li^+/Mg^{2+}$  selectivity and  $Li^+$  recovery simultaneously by adding crown ether to tributyl phosphate-ionic liquid extraction system as co-extractant. *Sep. Purif. Technol.* **2024**, *335*, 126162. [[CrossRef](#)]
140. Sahu, S.; Mohanty, A.; Devi, N. Application of various extractants for liquid-liquid extraction of lithium. *Mater. Today Proc.* **2023**, *76*, 190–193. [[CrossRef](#)]
141. Su, H.; Tan, B.; Zhang, J.; Liu, W.; Wang, L.; Wang, Y.; Zhu, Z.; Qi, T. Modelling of lithium extraction with TBP/P507- $FeCl_3$  system from salt-lake brine. *Sep. Purif. Technol.* **2022**, *282*, 120110. [[CrossRef](#)]
142. Qiao, L.; Chen, H.; Yu, J. Recovery of lithium from salt-lake brine by liquid-liquid extraction using TBP- $FeCl_3$  based mixture solvent. *Can. J. Chem. Eng.* **2023**, *101*, 2139–2147. [[CrossRef](#)]
143. Hu, Y.; Su, H.; Zhu, Z.; Qi, T.; Pang, Q. Environmentally benign techniques of lithium extraction from salt lakes: A review. *Environ. Chem. Lett.* **2024**, *22*, 105–120. [[CrossRef](#)]
144. Zhang, L.; Li, L.; Shi, D.; Li, J.; Peng, X.; Nie, F. Selective extraction of lithium from alkaline brine using HBTA-TOPO synergistic extraction system. *Sep. Purif. Technol.* **2017**, *188*, 167–173. [[CrossRef](#)]
145. Zhang, L.; Li, J.; Liu, R.; Zhou, Y.; Zhang, Y.; Ji, L.; Li, L. Recovery of lithium from salt lake brine with high Na/Li ratio using solvent extraction. *J. Mol. Liq.* **2022**, *362*, 119667. [[CrossRef](#)]

146. Masmoudi, A.; Zante, G.; Trébouet, D.; Barillon, R.; Boltoeva, M. Solvent extraction of lithium ions using benzoyltrifluoroacetone in new solvents. *Sep. Purif. Technol.* **2021**, *255*, 117653. [[CrossRef](#)]
147. Li, R.; Wang, Y.; Duan, W.; Du, C.; Tian, S.; Ren, Z.; Zhou, Z. Selective extraction of lithium ions from salt lake brines using a tributyl phosphate-sodium tetraphenyl boron-phenethyl isobutyrate system. *Desalination* **2023**, *555*, 116543. [[CrossRef](#)]
148. Liu, J.; Zhang, Y.; Miao, Y.; Yang, Y.; Li, P. Alkaline Resins Enhancing  $\text{Li}^+/\text{H}^+$  Ion Exchange for Lithium Recovery from Brines Using Granular Titanium-Type Lithium Ion-Sieves. *Ind. Eng. Chem. Res.* **2021**, *60*, 16457–16468. [[CrossRef](#)]
149. Bonin, L.; Deduytsche, D.; Wolthers, M.; Flexer, V.; Rabaey, K. Boron extraction using selective ion exchange resins enables effective magnesium recovery from lithium rich brines with minimal lithium loss. *Sep. Purif. Technol.* **2021**, *275*, 119177. [[CrossRef](#)]
150. Arroyo, F.; Morillo, J.; Usero, J.; Rosado, D.; El Bakouri, H. Lithium recovery from desalination brines using specific ion-exchange resins. *Desalination* **2019**, *468*, 114073. [[CrossRef](#)]
151. Zavahir, S.; Elmakki, T.; Gulied, M.; Ahmad, Z.; Al-Sulaiti, L.; Shon, H.K.; Chen, Y.; Park, H.; Batchelor, B.; Han, D.S. A review on lithium recovery using electrochemical capturing systems. *Desalination* **2021**, *500*, 114883. [[CrossRef](#)]
152. Wang, J.; Yue, X.; Wang, P.; Yu, T.; Du, X.; Hao, X.; Abudula, A.; Guan, G. Electrochemical technologies for lithium recovery from liquid resources: A review. *Renew. Sustain. Energy Rev.* **2022**, *154*, 111813. [[CrossRef](#)]
153. Zhu, Q.; Yu, X.; Liu, Y.; Wang, Y.; Yang, P.; Liu, K. Electrochemical lithium extraction with continuous flow electrodes. *Desalination* **2024**, *574*, 117250. [[CrossRef](#)]
154. Gu, J.; Chen, L.; Li, X.; Luo, G.; Fan, L.; Chao, Y.; Ji, H.; Zhu, W. Multifunctional  $\text{AlPO}_4$  reconstructed  $\text{LiMn}_2\text{O}_4$  surface for electrochemical lithium extraction from brine. *J. Energy Chem.* **2024**, *89*, 410–421. [[CrossRef](#)]
155. Wang, S.; Yu, X.; Hu, X. Electrochemical Lithium Extraction with Gas Flushing of Porous Electrodes. *Nanomaterials* **2023**, *13*, 1471. [[CrossRef](#)] [[PubMed](#)]
156. Meng, X.; Jing, Y.; Li, J.; Sun, Z.; Wu, Z. Electrochemical recovery of lithium from brine by highly stable truncated octahedral  $\text{LiNi}_{0.05}\text{Mn}_{1.95}\text{O}_4$ . *Chem. Eng. Sci.* **2024**, *283*, 119400. [[CrossRef](#)]
157. Kim, S.; Lee, J.; Kim, S.; Kim, S.; Yoon, J. Electrochemical Lithium Recovery with a  $\text{LiMn}_2\text{O}_4$ -Zinc Battery System using Zinc as a Negative Electrode. *Energy Technol.* **2018**, *6*, 340–344. [[CrossRef](#)]
158. Sun, S.; Yu, X.; Li, M.; Duo, J.; Guo, Y.; Deng, T. Green recovery of lithium from geothermal water based on a novel lithium iron phosphate electrochemical technique. *J. Clean. Prod.* **2020**, *247*, 119178. [[CrossRef](#)]
159. Peng, H.; Zhao, Q. A Nano-Heterogeneous Membrane for Efficient Separation of Lithium from High Magnesium/Lithium Ratio Brine. *Adv. Funct. Mater.* **2021**, *31*, 2009430. [[CrossRef](#)]
160. Li, Y.; Wang, M.; Xiang, X.; Zhao, Y.; Peng, Z. Separation performance and fouling analyses of nanofiltration membrane for lithium extraction from salt lake brine. *J. Water Process. Eng.* **2023**, *54*, 104009. [[CrossRef](#)]
161. Zha, Z.; Li, T.; Hussein, I.; Wang, Y.; Zhao, S. Aza-crown ether-coupled polyamide nanofiltration membrane for efficient  $\text{Li}^+/\text{Mg}^{2+}$  separation. *J. Membr. Sci.* **2024**, *695*, 122484. [[CrossRef](#)]
162. Ryu, J.; Kim, S.; Hong, H.-J.; Hong, J.; Kim, M.; Ryu, T.; Park, I.-S.; Chung, K.-S.; Jang, J.S.; Kim, B.-G. Strontium ion ( $\text{Sr}^{2+}$ ) separation from seawater by hydrothermally structured titanate nanotubes: Removal vs. recovery. *Chem. Eng. J.* **2016**, *304*, 503–510. [[CrossRef](#)]
163. Yang, X.-G.; Liu, T.; Wang, C.-Y. Thermally modulated lithium iron phosphate batteries for mass-market electric vehicles. *Nat. Energy* **2021**, *6*, 176–185. [[CrossRef](#)]
164. Tian-Ming, G.; Na, F.; Wu, C.; Tao, D. Lithium extraction from hard rock lithium ores (spodumene, lepidolite, zinnwaldite, petalite): Technology, resources, environment and cost. *China Geol.* **2023**, *6*, 137–153. [[CrossRef](#)]
165. Hu, Z. Analysis of typical lithium extraction from mines and its economic benefit. *J. Salt Sci. Chem. Ind.* **2019**, *48*, 5–8.
166. Morillo, J.; Usero, J.; Rosado, D.; El Bakouri, H.; Riaza, A.; Bernaola, F.-J. Comparative study of brine management technologies for desalination plants. *Desalination* **2014**, *336*, 32–49. [[CrossRef](#)]
167. McGovern, R.K.; Weiner, A.M.; Sun, L.; Chambers, C.G.; Zubair, S.M.; Lienhard, J.H., V. On the cost of electrodialysis for the desalination of high salinity feeds. *Appl. Energy* **2014**, *136*, 649–661. [[CrossRef](#)]
168. Flexer, V.; Baspineiro, C.F.; Galli, C.I. Lithium recovery from brines: A vital raw material for green energies with a potential environmental impact in its mining and processing. *Sci. Total. Environ.* **2018**, *639*, 1188–1204. [[CrossRef](#)]
169. Ortiz-Albo, P.; Torres-Ortega, S.; Prieto, M.G.; Urtiaga, A.; Ibañez, R. Techno-Economic Feasibility Analysis for Minor Elements Valorization from Desalination Concentrates. *Sep. Purif. Rev.* **2019**, *48*, 220–241. [[CrossRef](#)]
170. Ge, L.; Wu, B.; Li, Q.; Wang, Y.; Yu, D.; Wu, L.; Pan, J.; Miao, J.; Xu, T. Electrodialysis with nanofiltration membrane (EDNF) for high-efficiency cations fractionation. *J. Membr. Sci.* **2016**, *498*, 192–200. [[CrossRef](#)]

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