

A review of lithium extraction from natural resources

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Invited Review

A review of lithium extraction from natural resources

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Abstract: Lithium is considered to be the most important energy metal of the 21st century. Because of the development trend of global electrification, the consumption of lithium has increased significantly over the last decade, and it is foreseeable that its demand will continue to increase for a long time. Limited by the total amount of lithium on the market, lithium extraction from natural resources is still the first choice for the rapid development of emerging industries. This paper reviews the recent technological developments in the extraction of lithium from natural resources. Existing methods are summarized by the main resources, such as spodumene, lepidolite, and brine. The advantages and disadvantages of each method are compared. Finally, reasonable suggestions are proposed for the development of lithium extraction from natural resources based on the understanding of existing methods. This review provides a reference for the research, development, optimization, and industrial application of future processes.

Keywords: lithium; extraction; spodumene; lepidolite; brine

1. Introduction

Lithium is the lightest natural metal element, with a density of only 0.534 g/cm³ [1]. The chemical properties of lithium are active [2], and it is silvery white and soft enough to be cut with a knife [3]. Lithium is usually present in the Earth's crust as compounds, with a content of approximately 0.0065wt%. Three main types of lithium resource are found in nature: brine (chloride-sulfate, carbonate, chloride, and nitrate types), pegmatite (spodumene, lepidolite, zinnwaldite, etc.), and sedimentary (bauxite, coal, kaolin, etc.) [4]. Additionally, clay type resource and lacustrine evaporite type resource have potential significance [5]. Global lithium resources are mainly distributed in South America, North America, Australia, and China (Fig. 1(a)) [6]. Brines in Bolivia, Argentina, and Chile contain more than 55% of the world's lithium resources, and the region is known as the "lithium triangle" [7]. The lithium resources in Australia are dominated by spodumene, which are the largest and best in the world [8]. Both brine and lepidolite resources are relatively abundant in China [4].

Lithium is mainly used as an additive in ceramics and glass industries to improve the properties of products in the early days [9]. With the development trend of global electrification, lithium is widely used in the energy industry as an important raw material in new battery technologies [10–14]. According to the Mineral Commodity Summaries 2022 of the U.S. Geological Survey [6], the global consumption of

lithium jumped from 20000 to 93000 tons from 2010 to 2021 (Fig. 1(b)). The proportion of lithium consumption in the battery field increased from 23% (Fig. 1(c)) to 74% (Fig. 1(d)). Batteries surpassed ceramics and glass to become the largest consumer of lithium. In addition, lithium is currently used in lubricating greases, continuous casting, polymer production, air treatment, and other fields. Lithium has been called the most important energy metal of the 21st century not only for batteries but also for controllable nuclear fusion [15–16]. Controlled nuclear fusion, known as "artificial sun", is considered a key technology to fundamentally solve the energy problems. Nuclear fusion is the reaction between deuterium and tritium [17]. Deuterium is abundant and easy to extract in natural seawater, while tritium is nearly absent in nature. Lithium is an indispensable raw material for the production of tritium [18], playing an irreplaceable role in controllable nuclear fusion.

In the past three years, the price of lithium carbonate in the Chinese market has soared nearly tenfold, driven by surging demand and the impact of COVID-19. With the popularity of global electrification and the development of controllable nuclear fusion, the demand for lithium will continue to rise. Although many researchers have focused on the recycling of spent lithium batteries [19–21], lithium extraction from natural resources is still the first choice for the rapid development of emerging industries because of the limited amounts of lithium circulating in the market. This paper provides an overview of the development of lithium extraction from nat-

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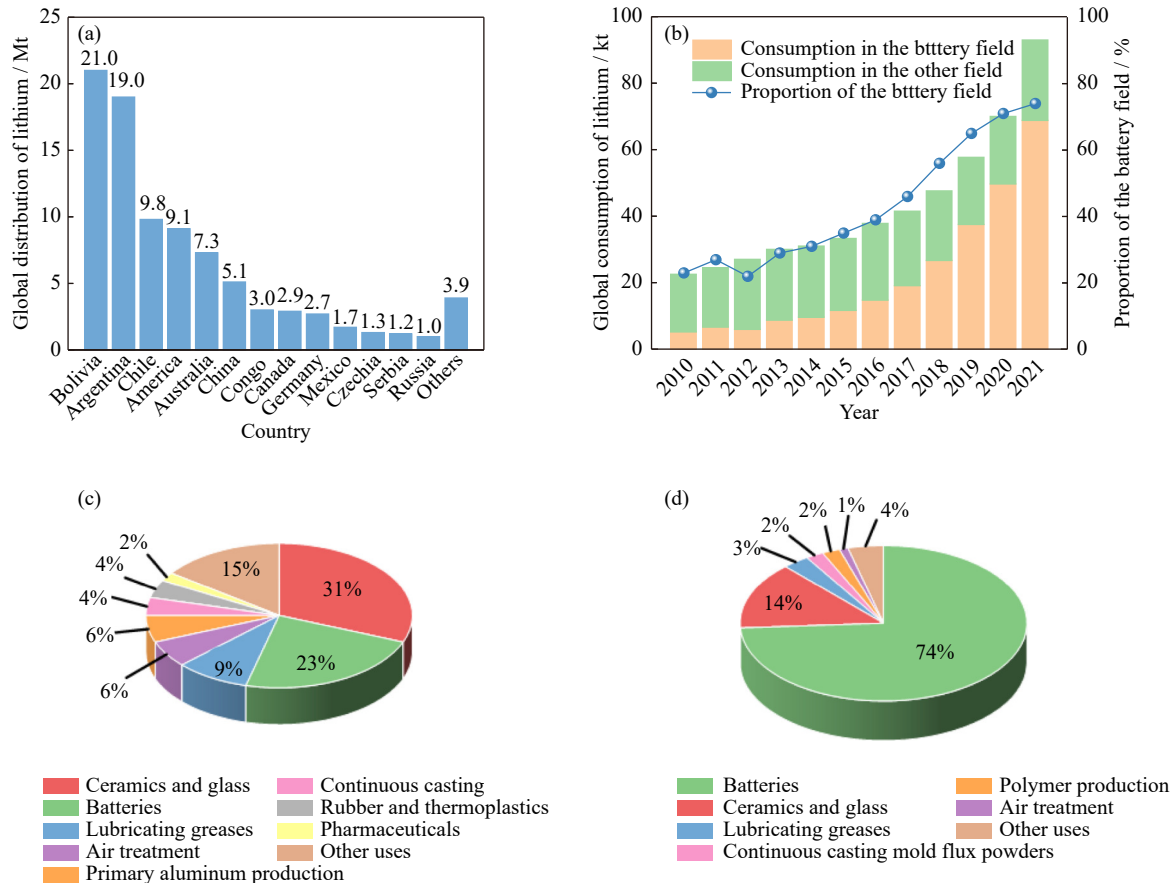


Fig. 1. (a) Global distribution of lithium in 2021. (b) Global consumption of lithium and proportion of the battery field in 2010–2021. Proportion of lithium consumption in various fields in (c) 2010 and (d) 2021 [6].

ural resources in recent years.

2. Extraction of lithium from minerals

Lithium minerals mainly exist in the form of aluminosilicate pegmatites in nature [22]. Pegmatites are formed by slow and sufficient crystallization differentiation of highly volatile magma under specific conditions. Strong metasomatism occurs in pegmatites during the formation process. The metasomatism belt comprises quartz, albite, spodumene, mica, beryl, niobium tantalite, cesium garnet, apatite, and uranium minerals, and they became important deposits of rare metals. Spodumene and lepidolite are the most typical lithium minerals among them. The main methods for lithium extraction from spodumene and lepidolite, as well as methods for other minerals, are summarized.

2.1. Extraction of lithium from spodumene

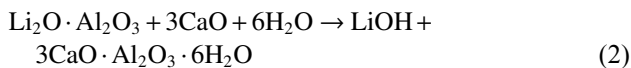
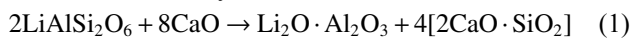
Spodumene ($\text{LiAlSi}_2\text{O}_6$) is typically grayish white with a yellowish or greenish tinge [23] and commonly associated with quartz, feldspar, and mica, with a specific gravity of 3.1–3.2 [24]. Theoretically, the chemical composition (mass fraction) of spodumene is 8.07% Li_2O , 27.44% Al_2O_3 , and 64.49% SiO_2 . A small amount of iron and manganese can replace the six-coordinated aluminum in the form of isomorphism [25]. The position of lithium can also be replaced by sodium. Therefore, the actual content of Li_2O in spodumene is

2.9wt%–7.6wt%. Spodumene is currently the most important resource for lithium extraction processes [26]. The most common methods include “lime roasting”, “phase transition and sulfuric acid digestion”, “direct acid leaching”, “high-pressure alkaline leaching”, and “salt roasting”.

2.1.1. Lime roasting method

The lime roasting method is the earliest method used to extract lithium from spodumene [27]. Spodumene is mixed with lime or limestone for roasting. Sufficient amount of CaO destroys the mineral structure at high temperatures over 1100°C [28–29]. The roasting reaction is shown in reaction (1). The calcine is leached to obtain the LiOH solution. However, it is difficult to extract by water leaching because of the extremely low solubility of $\text{Li}_2\text{O}\cdot\text{Al}_2\text{O}_3$. Excessive CaO is necessary to convert aluminum to insoluble $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 6\text{H}_2\text{O}$ during the leaching process [30]. Lithium reacts to form soluble LiOH , enabling the separation of lithium and aluminum. The leaching reaction is shown in reaction (2). The $\text{LiOH}\cdot\text{H}_2\text{O}$ product can be obtained by evaporation, concentration, and crystallization of leach liquor. The lime roasting method has wide applicability and low requirements of lithium content for spodumene. Excipients (lime or limestone) are inexpensive and easy to obtain, and no other reagents are needed. However, excess CaO eventually enters the leaching residues, producing a large volume of solid waste. Meanwhile, the extraction yield of lithium is relatively low compared with other methods. The lime roasting

method is now mostly obsolete.



2.1.2. Phase transition and sulfuric acid digestion method

The phase transition and sulfuric acid digestion method is the most mainstream spodumene treatment method [31]. Firstly, spodumene is calcined at a high temperature greater than 1000°C to transform it from the α -type monoclinic system to the β -type tetragonal system [32–33]. The transformed spodumene needs to be ground to less than 74 μm . Generally, spodumene is mixed with concentrated sulfuric acid at a theoretical dosage of 140wt% and then digested at approximately 250°C. The reactions are shown in reactions (3)–(4). The acid solution containing Li_2SO_4 can be obtained by water leaching of digestion products, and lithium extraction yield generally approaches 98% [30]. After neutralization and purification, Li_2SO_4 can be converted into a slightly soluble Li_2CO_3 product with a saturated Na_2CO_3 solution. The main flow is shown in Fig. 2.

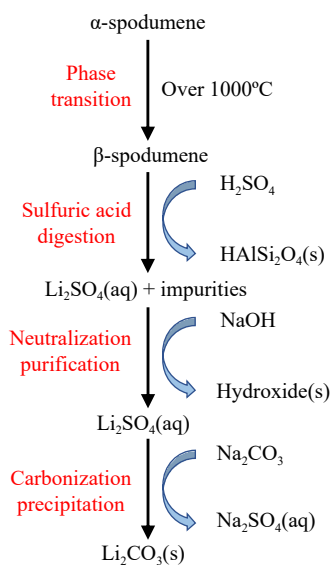
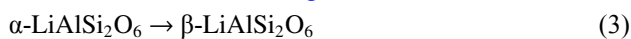


Fig. 2. Main flow for the phase transition and sulfuric acid digestion method.

Dessemond *et al.* [34] conducted a detailed study on the α - β - γ three-phase transition process in the high-temperature roasting of spodumene. γ -spodumene was formed between α -type and β -type at 800–1000°C. The transition of γ -spodumene to β -spodumene was kinetically much easier than the direct transition of α -spodumene. Therefore, the high-temperature transition process of spodumene was summarized as α - γ - β . However, γ -spodumene affected the extraction yield of lithium. The formation of γ -spodumene should be avoided as much as possible in the process of high-temperature transition. Lajoie-Leroux *et al.* [35] studied the effect of impurities on the extraction of lithium in the digestion process. The factorial design experiments proved that the leaching rates of

the impurities were low, and the excessive sulfuric acid did not further improve the extraction yield of lithium. Therefore, the decrease in lithium extraction yield was not caused by acid consumption of the impurities but by physical factors like impurity encapsulation, which prevents spodumene particles from contacting and reacting with sulfuric acid.

In the process of β -spodumene sulfation, only H^+ occupies the original position of Li^+ [36]. The structure of the minerals is not damaged, so few impurities, such as aluminum, silicon, and iron, are leached during the leaching process. The subsequent purification process is simple. The phase transition and sulfuric acid digestion method is the most widely used process. However, there are also problems of high consumption of energy and sulfuric acid. Researches have been conducted to reduce energy consumption. Gasafi and Pardemann [37] explored an energy-efficient fluidized bed technology to replace conventional rotary kilns for high-temperature transition. The temperature and residence time required were investigated at the laboratory and large experimental scale (feed rates 20–500 kg/h). At a temperature of 1050–1070°C and time of 25–40 min, a transition rate greater than 90% was achieved, which indicates that there are advantages in both energy consumption and product quality for development prospects. Kotsupalo *et al.* [38] performed pre-mechanical activation of α -spodumene in a solid ball mill. The Li–O bonds and Al–O bonds in the minerals were broken, and the structures were transformed to amorphous states after 30 min of activation. The activated α -spodumene could be transitioned into β -spodumene at only 900–950°C. The temperature required was effectively reduced, providing the possibility of reducing energy consumption. Salakjani *et al.* [39] used microwave heating instead of traditional heating for the sulfuric acid digestion process. The effect of traditional heating at 250°C for 1 h could be achieved with microwave irradiation for 20 s. The amount of sulfuric acid in excess of 80wt% could also be reduced to 15wt% by pre-grinding. Instead, the extraction yield of lithium decreased as the irradiation time continued to increase. From the analysis of X-ray diffraction (XRD) patterns of leaching residues, the trend may be caused by Li^+ re-entering the mineral phase structures, generating β -spodumene again. Microwave heating only requires 15.4 kJ of energy, much less than the 10.4 MJ required by traditional heating.

Although researchers have been trying to solve the issues of high consumption of energy and sulfuric acid, the high temperature greater than 1000°C and excess concentrated sulfuric acid are still necessary. The directions of the phase transition and sulfuric acid digestion method focus on the development of spodumene low temperature transition technologies and the recycling and cascade use of residual acid.

2.1.3. Direct acid leaching method

To avoid energy consumption during the phase transition, researchers have used the strong corrosiveness of hydrofluoric acid and sulfuric acid to directly leach α -spodumene [40]. The main flow is shown in Fig. 3. Destruction of the mineral structures was achieved at low temperatures. The op-

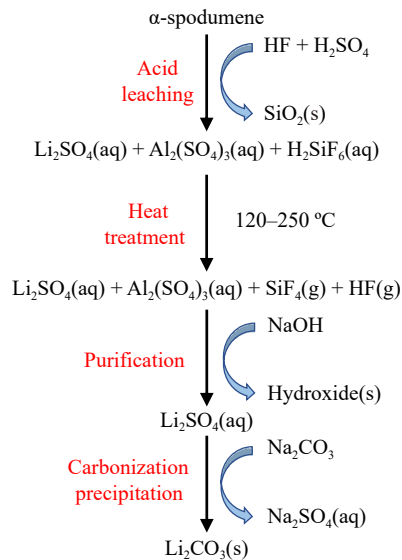
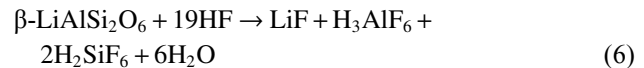
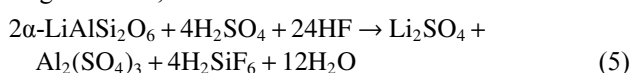


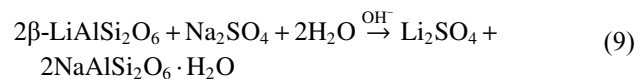
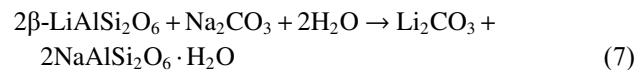
Fig. 3. Main flow for the direct acid leaching method.

timal acid dosage was 1:3:2 (g : mL : mL) for spodumene/HF/H₂SO₄, and 96% lithium was successfully extracted after leaching at 100°C for 3 h. The leaching reaction is shown in reaction (5). In addition, they also investigated the kinetics of mixed acid leaching [41]. The extraction of lithium conformed to the shrinking core model, and it was controlled by both the chemical reaction and product layer diffusion. The apparent activation energy E_a was 32.68 kJ/mol. Insoluble products, such as cryolite and aluminum fluoride, forms a product layer on the surface of the particles, resulting in limited kinetics of the leaching process. The direct acid leaching method can directly process α -spodumene, which greatly reduces energy consumption. However, a large amount of acid (greater than 500wt%) is used from the above research results. The amount of acid is extremely large, and the introduction of F⁻ also increases the difficulty of the subsequent treatment. As a result, Guo *et al.* [42] proposed a two-stage heat treatment method to remove F⁻ and excess SO₄²⁻ in leach liquor according to the difference in the boiling points of hydrofluoric acid and sulfuric acid systems. Only 2.03wt% fluorine remained after each heat treatment of leach liquor at 120 and 250°C for 3 h. The removal of excess SO₄²⁻ was not systematically studied. The extraction yield of silicon decreased from 82.0% to 0.5%, which may be attributed to the volatilization of SiF₄. Although the removal of silicon can be omitted, plenty of fluorine is lost in the unrecoverable form. The amount of hydrofluoric acid and sulfuric acid is not effectively reduced, and recycling is still a problem, which is worthy of further research. Rosales *et al.* [43–44] studied the leaching of β -spodumene with hydrofluoric acid, as shown in reaction (6). At a solid–liquid ratio of 1.82% (w/v) and hydrofluoric acid concentration of 7% (v/v), a lithium extraction yield greater than 90% was achieved. Here, w/v means weight/volume, and v/v means volume/volume.



2.1.4. Direct high-pressure alkaline leaching method

Over the last few years, researchers have turned their attention to the alkaline process. The principle of the alkaline process is generally to replace Li⁺ in spodumene with Na⁺ under high-pressure conditions. Chen *et al.* [45] leached β -spodumene with sodium carbonate. The reaction was conducted in an autoclave at 225°C for 1 h to obtain a suspension of lithium carbonate. The extraction yield of lithium during the process exceeded 94%, and the reactions are shown in reactions (7)–(8). Kuang *et al.* [46] selected sodium sulfate as the main ingredient, supplemented by CaO or NaOH as additives to leaching β -spodumene under high pressure. Under the optimal conditions (45wt% sodium sulfate, 2wt% alkaline additive, 230°C, 3 h), the extraction yield of lithium was greater than 90%. The reaction is shown in reaction (9). It was worth noting that alkaline additives were required.



The high-pressure alkaline leaching process mentioned above are aimed at β -spodumene, and the high-temperature transition process is still inevitable. Researchers attempted to directly high-pressure alkaline leaching α -spodumene, and also achieved good results. The main flow is shown in Fig. 4. Song *et al.* [47] leached α -spodumene at 250°C for 6 h with 400 g/L NaOH and 50wt% CaO. The extraction yield of lithium reached 93%, and the reaction is shown in reaction (10). To enrich the concentration of lithium in leach liquor, the possibility of cyclic leaching was explored, and the extraction yield greater than 90% could still be achieved after ten cycles. Xing *et al.* [48] also achieved a lithium extraction yield of 95% using single NaOH high-pressure leaching (600 g/L NaOH, 250°C, 2 h). The reaction was shown in reaction (11), and the leaching residue under optimal conditions mainly comprised hydroxysodalite with a porous structure.

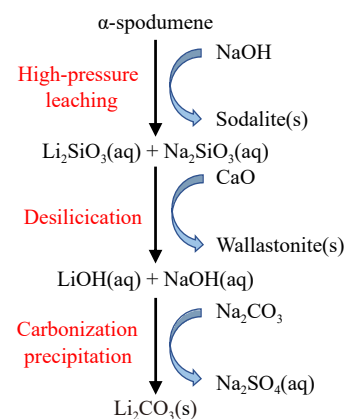
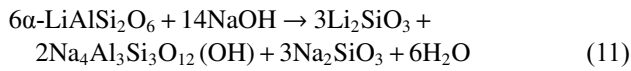
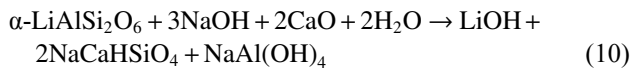


Fig. 4. Main flow for the direct high-pressure alkaline leaching method.

Although more expensive NaOH is used in this process, high-value utilization of residue is realized by synthesizing zeolite, which provides a new direction for the comprehensive utilization of spodumene leaching residue.



2.1.5. Salt roasting method

In addition to leaching using acids and alkalis, salt roasting methods have also been reported, as shown in Table 1 [49–58]. The main flow is shown in Fig. 5. It indicates that the principle of the salt roasting method is similar to that of high-pressure alkaline leaching, mainly replacing Li^+ sites with alkali metal ions such as Na^+ and K^+ . For β -spodumene that has undergone high-temperature transition, the temperature required for salt roasting is less, approximately 600°C . Rosales *et al.* [49] predicted the equilibrium amount of each substance with different NaF dosages via HSC Chemistry 6.0 modeling. Two times the molar amount of NaF was the op-

timal amount. Both thermogravimetric–differential thermal analysis (TG–DTA) analysis and the effect of temperature proved that 600°C was necessary. The reaction is shown in reaction (12). Santos *et al.* [50] and Grasso *et al.* [51] used Na_2CO_3 mixed with NaCl and single Na_2CO_3 to calcine β -spodumene, respectively. The process is similar to the Na_2CO_3 high-pressure leaching [45], as shown in reaction (13). The purpose of adding NaCl is to reduce the dosage of Na_2CO_3 , and it acts like a catalyst and is not lost during calcination, as shown in reactions (14)–(15). The extraction yield of lithium is reduced from 86% to 71% with the method of adding NaCl. However, considering that the dosage of Na_2CO_3 is greatly reduced (only 1/6), the effect of NaCl is obvious. This process provides ideas for the optimization of the subsequent salt roasting method. It may be possible to introduce catalyst-like chemicals to facilitate the reactions. Barbosa *et al.* [52–54] roasted β -spodumene with chlorine gas [52–53] and calcium chloride [54]. Lithium extraction yield of over 90% was obtained. However, the usage of chlorinating agents seriously corroded the equipment, and the economic feasibility should be carefully studied.

Table 1. Experimental details of lithium extraction from spodumene by the salt roasting method

Year	Spodumene	Salt used	Roasting conditions	Leaching solution	Extraction yield of Li	Ref.
2019	β -phase	Ore : NaF = 1:2 (n/n)	600°C , 1 h	H_2SO_4	90%	[49]
2019	β -phase	Ore : Na_2CO_3 = 3:1 (n/n), 5wt% NaCl	650°C , 2 h	Water	71%	[50]
2022	β -phase	Ore : Na_2CO_3 = 1:2 (n/n)	400°C , 10 h	Water	86%	[51]
2013	β -phase	Cl_2 (100 mL/min)	1100°C , 150 min		Nearly 100%	[52–53]
2015	β -phase	Ore : CaCl_2 = 1:2 (n/n)	900°C , 2 h	Water	90%	[54]
2020	α -phase	Ore : NH_4HF_2 = 1:17.5 (n/n)	157°C , 100 min	H_2SO_4	96%	[55–56]
2020	α -phase	Ore : Na_2SO_4 = 1:0.5 (w/w)	1000°C , 1 h	Water	92%	[57]
2021	α -phase	Ore : K_2SO_4 = 1:1 (m/m)	870°C	Water	Over 90%	[58]

Note: n/n and w/w represent molar ratio and weight ratio, respectively.

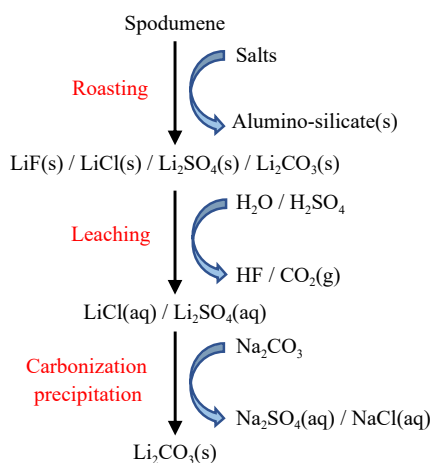
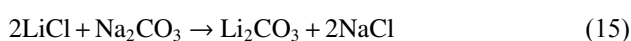
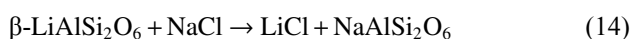
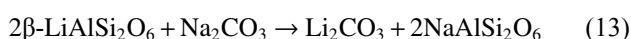
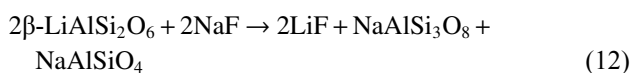
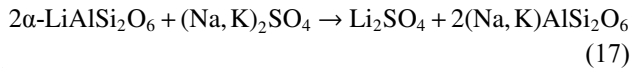
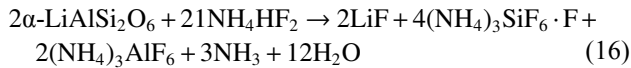


Fig. 5. Main flow for the salt roasting method.



More salt must be used when the more stable α -spodumene is treated with the salt roasting method. For example, 17.5 times the molar amount of NH_4HF_2 was roasted with α -spodumene by Resentera *et al.* [55–56] to achieve 96% lithium extraction yield. The reaction is shown in reaction (16). This process innovatively used NH_4^+ to destroy the structure of α -spodumene and energy-intensive phase transition processes greater than 1000°C were avoided. However, the handling of large quantities of vapors with ammonia needed to be seriously considered. Setoudeh *et al.* [57] and Ncube *et al.* [58] selected Na_2SO_4 and K_2SO_4 , respectively, to be mixed with α -spodumene for roasting, and the reaction process is shown in reaction (17). The addition of a large amount of sulfates is necessary. Even after 5 h of mechanical activation, 50wt% Na_2SO_4 is still required. Overall, large amounts of auxiliary materials are unavoidable when extracting lithium from α -spodumene by the salt roasting method. This step reduces the processing capacity and produces more solid waste. Moreover, a large amount of Na^+ or K^+ enters the leach liquor system, which greatly impacts the quality of lithium products.



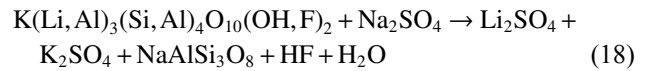
2.2. Extraction of lithium from lepidolite

Lepidolite is the next most important lithium-bearing mineral after spodumene. The molecular formula is typically $\text{K}(\text{Li, Al})_3(\text{Si, Al})_4\text{O}_{10}(\text{OH, F})_2$ [59]. The chemical composition of lepidolite varies greatly because of the different degrees of crystallization differentiation. Generally, the content of Li_2O is 1.2wt%–5.9wt%, K_2O is 4.8wt%–13.8wt%, Al_2O_3 is 11.3wt%–28.8wt%, and SiO_2 is 46.9wt%–60wt%. In addition, lepidolite also contains iron, calcium, magnesium, rubidium, and cesium [60]. Lepidolite has not been commonly investigated because of its complex composition and significantly lower lithium content than spodumene [36,61]. However, lepidolite has gained more attention with the increasing demand for lithium. The main methods include the sulfate roasting, chlorination roasting, sulfuric acid digestion, diluted acid leaching, and high-pressure alkaline leaching.

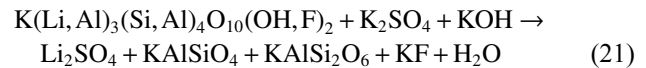
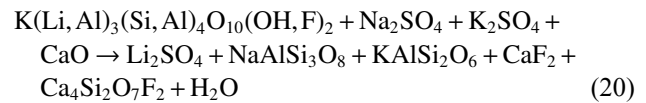
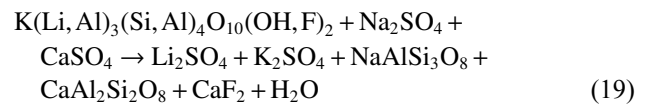
2.2.1. Sulfate roasting method

The sulfate roasting method is currently the most common method for lithium extraction from lepidolite. Lithium is converted into soluble lithium sulfate by adding sulfate roasting with lepidolite. The main flow is shown in Fig. 6. Luong *et al.* [62] roasted lepidolite with Na_2SO_4 at 1000°C for 0.5 h and then immersed it in water to obtain a lithium extraction yield of 90.4%. LiKSO_4 and $\text{Li}_2\text{NaK}(\text{SO}_4)_2$ were the main products containing lithium during the process of roasting. Setoudeh *et al.* [63] mechanically activated lepidolite and Na_2SO_4 in a planetary ball mill for 5 h with zirconia media. Through the investigation of Na_2SO_4 dosage and roasting temperature, it was concluded that the extraction yield of lithium could reach more than 99%. XRD analysis showed that new phases, such as LiKSO_4 , LiNaSO_4 , and $\text{Li}_2\text{NaK}(\text{SO}_4)_2$, were also formed. The temperature required for sulfate roasting was significantly reduced by mechanical activation. The brief summary of the reaction process was shown in reaction (18) due to the variable composition of lepidolite. The formation of HF cannot be avoided during the single Na_2SO_4 roasting process that would otherwise corrode the equipment and

cause additional equipment wear.



In response to this problem, researchers have studied methods of adding calcium salts and alkaline chemicals. Viecelli *et al.* [64] used the mixed sulfates of CaSO_4 and Na_2SO_4 (3:1 mass ratio) for roasting with lepidolite, as shown in reaction (19). More than 90% lithium was extracted under the conditions of mixed sulfates dosage at 60wt%, 875°C, and 1 h. Yan *et al.* [65] roasted lepidolite with 50wt% Na_2SO_4 , 10wt% K_2SO_4 , and 10wt% CaO at 850°C for 0.5 h, and a lithium extraction of 91.6% was obtained. The addition of CaO fixed fluorine in residues as CaF_2 and $\text{Ca}_4\text{Si}_2\text{O}_7\text{F}_2$ according to reaction (20). Su *et al.* [66] selected KOH as the alkaline chemical additive. 92.8% lithium and 81.7% potassium were extracted under optimal conditions. Harmful fluorine was fixed in the residues; however, its form was not mentioned. It is possible that the resulting HF reacted with KOH to form KF , which subsequently entered the solution during the leaching process. The reaction is shown in reaction (21).



Luong *et al.* [67] and Zhang *et al.* [68] innovatively used FeSO_4 as an additive in the roasting with lepidolite. The reaction mechanism of FeSO_4 is different from that of Na_2SO_4 and K_2SO_4 , which mainly produces SO_3 gas, as shown in reactions (22)–(24). CaO was selected as another additive by Luong *et al.* [67] with FeSO_4 (reaction (25)). The effect of the $\text{SO}_4^{2-}/\text{Li}^+$ and $\text{Ca}^{2+}/\text{F}^-$ molar ratio on the sulfur and fluorine content in roasting gas was studied. When the molar ratio of $\text{Ca}^{2+}/\text{F}^-$ was greater than 2:1, the generation of HF was minimized, and fluorine was fixed in the slags in the form of CaF . However, the formation of SO_2 and SO_3 , which are beneficial for lithium extraction, was affected. In the study by Zhang *et al.* [68], fluorine mainly existed as AlF_3 without the addition of CaO . The temperature required for the reaction was greatly reduced, and even the extraction effect at higher temperatures was worse. When the FeSO_4 dosage was 200wt%, the extraction yield of lithium, rubidium, and cesium was 92.7%, 87.1%, and 82.6%, respectively, at 675°C for 1.5 h. The SO_3 produced by FeSO_4 first reacted with the outer layer of lepidolite and albite to form Na_2SO_4 and K_2SO_4 (reactions (26)–(27)). Subsequently, the sulfates continued to combine with SO_3 to form the corresponding pyrosulfates (reactions (28)–(29)). The structure of lepidolite could be destroyed by pyrosulfates (reactions (30)–(31)). The formation of pyrosulfates accelerated the procedure of roasting reactions. Compared with Na_2SO_4 and K_2SO_4 , the SO_3 gas gen-

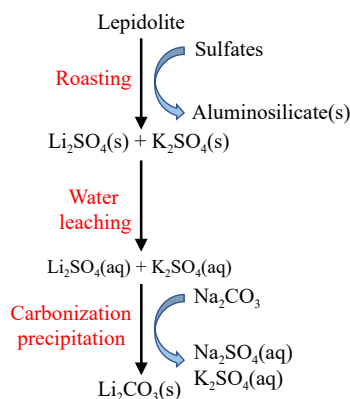
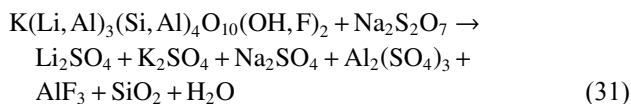
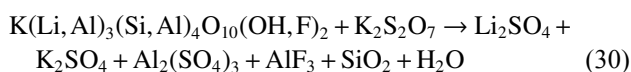
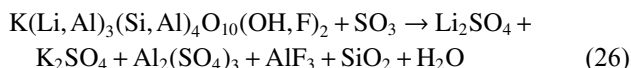
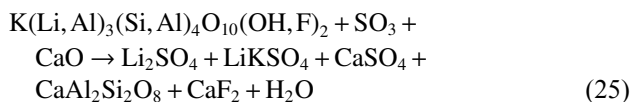
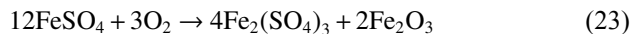


Fig. 6. Main flow for the sulfate roasting method.

erated by the decomposition of FeSO_4 played the role in the roasting process, not Fe^{2+} . This process is therefore more like an acid method, albeit under the cloak of sulfate roasting method.

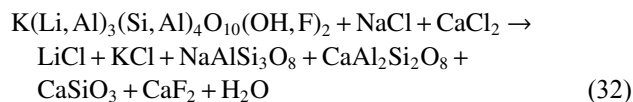


In summary, researchers have conducted research on the process of treating lepidolite by a sulfate roasting method, and the extraction yield of lithium generally exceeded 90%. A few factories have realized the industrial production of sodium sulfate and the potassium sulfate roasting process. However, high-value rubidium and cesium are rarely mentioned at this stage because the sulfate roasting method is not conducive to the extraction of rubidium and cesium, whose yields are generally only about 30%.

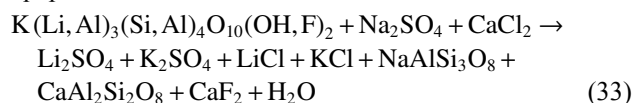
2.2.2. Chlorination roasting method

Researchers have conducted studies on the chlorination roasting method to achieve the purpose of synergistic extraction of high-value elements such as lithium, rubidium, and cesium in lepidolite [69–71]. The extraction of lithium under various excipient ratios was investigated by Yan *et al.* [69]. When the total amount of chlorinating agent was fixed at 100wt%, the extraction yield of lithium showed a trend of first increasing and then decreasing with the amount of NaCl. The maximum value occurred when NaCl and CaCl_2 were 60wt% and 40wt%, respectively. Under the optimal roasting conditions (880°C for 30 min), the extraction yield of lithium, rubidium, and cesium was 92.9%, 93.6%, and 93.0%. Kehinde *et al.* [70] processed lepidolite from Nigeria with the same parameters and achieved 89.9% lithium extraction yield. This study once again confirmed the feasibility of the process; however, the extraction yield of rubidium and cesium was not mentioned. Zhang *et al.* [71] indicated that the extraction yield increased slightly with the increase in CaCl_2 from 30wt% to 50wt%, while the concentration of calcium in leach liquor increased rapidly from 0.8 to 9.0 g/L. The higher concentration of calcium increased the difficulty of the subsequent purification process. In addition, Cl_2 gas was generated during the chlorination roasting process by the detection

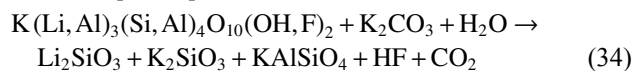
of starch iodide test paper. The distribution of fluorine and calcium in the SEM–EDS images of the leaching residue was consistent, indicating that the fluorine existed in the form of CaF_2 . Therefore, the reaction process of the chlorination roasting method was summarized as shown in reaction (32). The process can realize the synergistic extraction of lithium, rubidium, and cesium. However, many Cl^- inevitably escaped as HCl and Cl_2 because of the large amount of added chloride salts that can seriously corrode the equipment.



Yan *et al.* [72] managed to combine the sulfate roasting and chlorination roasting methods to obtain a more suitable process. Na_2SO_4 and CaCl_2 were used for co-roasting with lepidolite, and the reaction process is shown in reaction (33). Under the same roasting conditions of 880°C and 30 min, the extraction yields of lithium, rubidium, and cesium were 94.8%, 93.5%, and 90.1%, respectively. Compared with the chlorination roasting method, the extraction of lithium increased slightly, while that of rubidium and cesium decreased slightly. Fewer chloride salts greatly reduced the production of HCl and Cl_2 corrosive gases. The operable conditions of the process were optimized without significantly affecting the extractions, providing more possibilities for equipment selection.



Additionally, in addition to the above roasting methods, Kuai *et al.* [73] innovatively proposed the carbonization roasting by K_2CO_3 in the atmosphere of water vapor (reaction (34)). It was speculated that the reactions started at approximately 500°C and the removal of fluorine occurred after 815°C through thermogravimetric–differential scanning calorimeter (TG–DSC) analysis. Under optimal conditions (K_2CO_3 dosage 58.5wt%, 850°C, 2 h), the extraction yields of lithium and the removal of fluorine both reached a maximum of 95.5% and 80.9%, respectively. This method also achieved high-efficiency extraction of lithium; however, the massive leaching of silicon complicated the subsequent purification process. The experimental details on lithium extraction from lepidolite by the roasting method are summarized in Table 2 [62–73].



2.2.3. Diluted acid leaching method

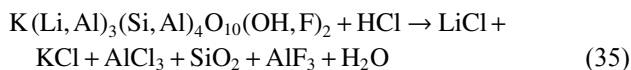
The usage of high-concentration sulfuric acid in the sulfuric acid digestion method was unavoidable, resulting in operational hazards. Considering its susceptibility to acid, researchers attempted to leach lepidolite by dilute acid. Liu *et al.* [74] carried out high temperature and atmospheric pressure leaching in a three-necked flask with the help of a condenser tube. The extraction yield of lithium, rubidium, and cesium was 94.2%, 91.8%, and 89.2%, respectively, after

Table 2. Experimental details on lithium extraction from lepidolite by the roasting method

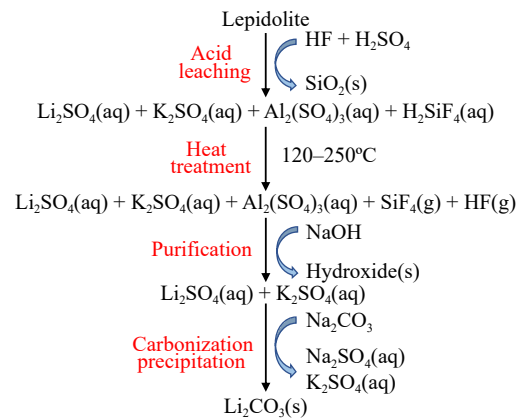
Method	Year	Salt used	Roasting conditions	Extraction yield of Li	Ref.
Sulfate roasting	2013	Li : Na ₂ SO ₄ = 1:2 (n/n)	1000°C, 0.5 h	90.4%	[62]
	2019	Ore : Na ₂ SO ₄ = 1:1 (w/w)	800°C, 1 h	99%	[63]
	2017	Ore : CaSO ₄ : Na ₂ SO ₄ = 1:0.45:0.15 (w/w/w)	875°C, 1 h	90%	[64]
	2012	Ore : Na ₂ SO ₄ : K ₂ SO ₄ : CaO = 1:0.5:0.1:0.1 (w/w/w/w)	850°C, 0.5 h	91.6%	[65]
	2020	Ore : K ₂ SO ₄ : KOH = 1:1:0.5 (w/w/w)	900°C, 2 h	92.8%	[66]
	2014	Li : FeSO ₄ = 1:3 (n/n); F : CaO = 1:1 (n/n)	850°C, 1.5 h	93%	[67]
	2022	Ore : FeSO ₄ = 1:2 (w/w)	675°C, 1.5 h	92.7%	[68]
Chlorination roasting	2012	Ore : CaCl ₂ : NaCl = 1:0.4:0.6 (w/w/w)	880°C, 30 min	92.9%	[69]
	2020	Ore : CaCl ₂ : NaCl = 1:0.4:0.6 (w/w/w)	880°C, 30 min	89.9%	[70]
	2020	Ore : CaCl ₂ : NaCl = 1:0.3:0.2 (w/w/w)	750°C, 45 min	94.5%	[71]
Salt roasting	2012	Ore : Na ₂ SO ₄ : CaCl ₂ = 1:0.5:0.3 (w/w/w)	880°C, 30 min	94.8%	[72]
Carbonate roasting	2021	Ore : K ₂ CO ₃ = 1:0.585 (w/w)	850°C, 2 h	95.5%	[73]

Note: The leaching solutions in these methods are all water.

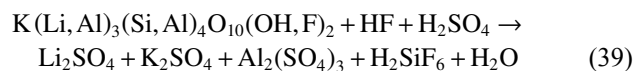
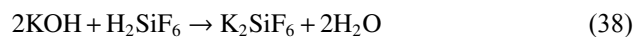
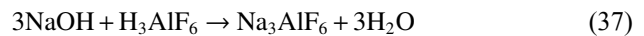
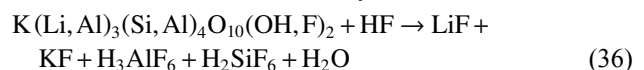
10 h continuous leaching at 138°C. In addition, Liu *et al.* [75] also tried two-stage leaching with 6.21 mol/L hydrochloric acid. 95.7% lithium was extracted with 8 h leaching at 108°C and the reaction is shown in reaction (35). Rentsch *et al.* [76] proposed the direct carbonization leaching of lepidolite after heat treatment at 950°C. The extraction yield of lithium reached 71% at 230°C and 10 MPa CO₂ pressure for 3 h. Liu *et al.* [2] proposed a process combining thermal activation and sulfuric acid leaching. The thermal shrinkage behavior of the samples indicated that the hemispherical melting point of lepidolite was 1345°C. The mineral structure was nearly completely destroyed at this temperature, and the minerals were in a highly active molten state. After water quenching and forced transformation, the theoretical amount of acid dosage could achieve the thorough extraction of lithium and rubidium.



Studies on leaching lepidolite with fluorine have been reported based on the strong erosive effect of fluoride ions on aluminosilicates. Rosales *et al.* [77] achieved a lithium extraction yield of more than 90% by single HF (concentration 7vol%) at 123°C. Lithium, aluminum, and silicon were subsequently recovered in the form of LiF, Na₃AlF₆, and K₂SiF₆ by precipitation and evaporation, as shown in reactions (36)–(38). Guo *et al.* [78] and Wang *et al.* [79] selected mixed acids of HF and H₂SO₄ for synergistically processing lepidolite. The main flow and reaction occurred are shown in Fig. 7 and reaction (39). The addition of H₂SO₄ accelerated the leaching reaction procedure. Over 98% lithium and 90% rubidium and cesium were converted into sulfates and entered the leach liquor under optimal conditions. The kinetic data were consistent with the shrinking core model. In the initial stage, the process was controlled by interfacial chemical reactions and internal diffusion. As the reaction proceeded, internal diffusion gradually became the dominant limiting factor. For the treatment of leach liquor, a step-wise heating method was proposed to remove fluorine [80]. Only 0.68wt% fluorine remained in the solution after heat treat-

**Fig. 7. Main flow for the diluted acid leaching method.**

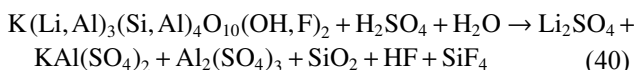
ment at 120°C for 3 h and 200°C for 6 h. At this time, the extraction yield of lithium could still be maintained at 94.3%. Guo *et al.* [81] also attempted to replace HF with H₂SiF₆, the by-product of the hydrofluoric acid production process, and also achieved a lithium extraction yield of 97%.



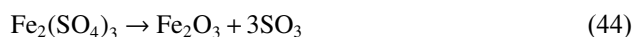
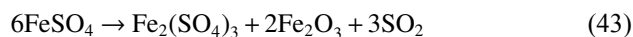
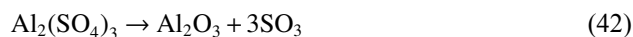
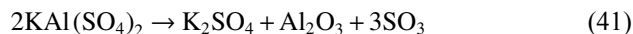
2.2.4. Sulfuric acid digestion method

Researchers have proposed the sulfuric acid digestion method of lepidolite, imitating the traditional method of β-spodumene. Vieceli *et al.* [82] destroyed the mineral structure of lepidolite by mechanical activation, leaving it in a highly reactive amorphous state. The lithium extraction yield of approximately 85% was obtained by digesting at 165°C for 4 h with 65wt% dosage of concentrated sulfuric acid. In addition, the response surface method was also used to simulate and optimize the process parameters [83]. The optimal parameters were 130wt% dosage of concentrated sulfuric acid, 190°C, and 15 min. Subsequently, they conducted a de-

tailed study on the water leaching process after digestion [84]. Only the leaching temperature had a significant effect, which is caused by the large change in the solubility of rubidium and potassium alum with temperature. Zhang *et al.* [85] focused on the effect of the sulfuric acid concentration on the basis of the above research. The extraction yield of lithium, rubidium, and cesium showed a trend of first increasing and then decreasing with the increase of sulfuric acid concentration. In particular, the lepidolite hardly reacts with concentrated sulfuric acid, which is different from the results of Vieceli *et al.* [82–84]. This may be caused by the no dissociation of H⁺ in concentrated sulfuric acid. The digestion reaction is shown in reaction (40).

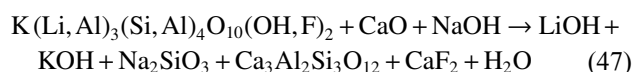
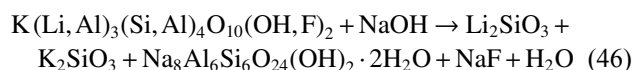
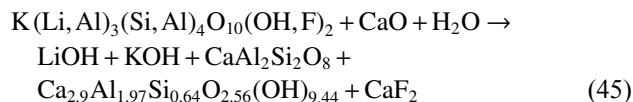


The sulfuric acid digestion of β-spodumene was only the replacement of Li⁺ by H⁺, and the structure of aluminosilicate was not destroyed. Little aluminum was extracted during the leaching process. However, during the sulfuric acid digestion for lepidolite, the structure of the minerals was destroyed, and large amounts of aluminum and iron were leached into the solution. Liu *et al.* [86] found that a large amount of lithium was lost with the removal of impurities during the subsequent purification process. The XRD pattern of the purification residue showed that the stable phase of Li-Al₂(OH)₇·H₂O was formed, which explains the loss of lithium. In response to this problem, they proposed sulfuric acid digestion and a decomposition method (Fig. 8). Soluble impurity sulfates were converted into insoluble impurity oxide by the decomposition of sulfates. Under the optimal conditions (800°C, 2 h), the extraction yield of aluminum and iron could be reduced to 0.08% and 0.02%, respectively. The extraction of impurities was successfully suppressed from the source, and the selective extraction of lithium, rubidium, and cesium was realized. Meanwhile, 90.4wt% of the sulfate radicals were decomposed into SO_x gas, and the acid could be recycled in the acid-making process. The reactions are shown in reactions (41)–(44).



2.2.5. High-pressure alkaline leaching method

The high-pressure alkaline leaching method was also used for the comprehensive utilization of lepidolite. Yan *et al.* [87] performed high-pressure leaching at 150°C for 60 min with 100wt% CaO, and the extraction of lithium reached 98.9%. The reaction is shown in reaction (45). Lv *et al.* [88] selected NaOH as the leaching agent, and the reaction process is shown in reaction (46). The main flow is shown in Fig. 9. The concentration of NaOH had a significant effect and the XRD pattern described that the leaching residue was sodalite with high purity under optimal conditions. Zeolite NaA was successfully prepared by hydrothermal synthesis, the zeolite had adsorption properties for Pb²⁺ and Cd²⁺, and the maximum adsorption capacities were 487.8 and 193.8 mg/g, respectively [89]. Mulwanda *et al.* [90] combined the above two processes, using NaOH and Ca(OH)₂ as co-leaching agents, as shown in reaction (47). The extraction yield of lithium, rubidium, and cesium reached 94%, 96%, and 90%, respectively, under the conditions of 320 g/L NaOH, 30 g/L Ca(OH)₂, 250°C, and 2 h. The advantage of the alkaline process is that the residue might be re-produced into products with high value; however, high pressure and high concentration of alkali cannot be avoided during the operation.



Various efforts have been made to extract lithium from spodumene and lepidolite. A comparison of the advantages and disadvantages of the different methods is summarized in Table 3.

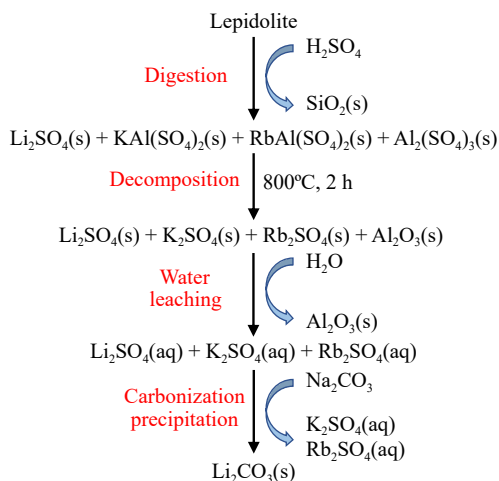


Fig. 8. Main flow for the sulfuric acid digestion and decomposition method.

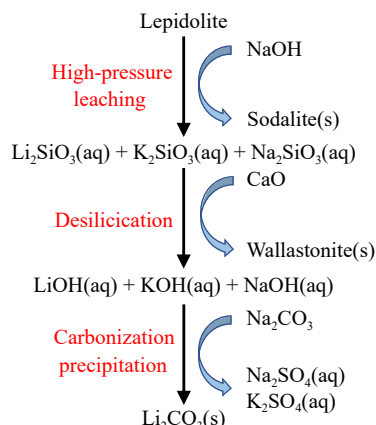


Fig. 9. Main flow for the high-pressure alkaline leaching method.

Table 3. Comparison of different lithium extraction methods from spodumene and lepidolite

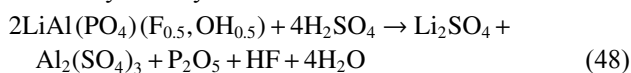
Mineral	Method	Advantages	Disadvantages
Spodumene	Lime roasting	Wide applicability, low requirements of lithium content, inexpensive excipients	Large amount of solid waste, relatively low lithium extraction
	Phase transition and sulfuric acid digestion	Simple purification process, high lithium extraction	High energy consumption, large dosage of sulfuric acid
	Direct acid leaching	Low energy consumption	Extremely large dosage of acid, difficult purification process
	High-pressure alkaline leaching	Low energy consumption, high-value utilization of residues	Harsh reaction conditions, large dosage of leaching agents
	Salt roasting	Simple reaction conditions, high lithium extraction	High energy consumption, large dosage of salts, low processing capacity, difficult purification process
	Sulfate roasting	Simple reaction conditions, high lithium extraction	Low rubidium and cesium extraction, low processing capacity
Lepidolite	Chlorination roasting	Simple reaction conditions, high lithium, rubidium, and cesium extraction	Large dosage of chlorinating agents, environmental pollution, equipment corrosion
	Sulfuric acid digestion	Simple reaction conditions, high lithium, rubidium, and cesium extraction	Difficult purification process, large dosage of sulfuric acid
	Diluted acid leaching	Low energy consumption	Extremely large dosage of acid, difficult purification process
	High-pressure alkaline leaching	Low energy consumption, high-value utilization of residues	Harsh reaction conditions, large dosage of leaching agents

2.3. Extraction of lithium from other minerals

In addition to spodumene and lepidolite, there are also some minerals containing lithium in nature, including montebrasite, petalite, and lithium porcelain stone. However, few studies have been reported on lithium extraction from these minerals because of their lower lithium content or poorer reserves. This section selects relatively common minerals and introduces their lithium extraction methods.

2.3.1. Montebrasite

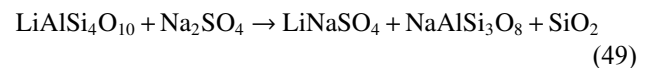
Montebrasite ($\text{LiAl}(\text{PO}_4)(\text{F},\text{OH})$) is commonly found in granite pegmatite, combined with spodumene and lepidolite. Fluorine and hydroxide in the chemical formula can be replaced completely by isomorphism to form amblygonite and montebrasite, respectively. The theoretical content of Li_2O is approximately 10wt%, which is much greater than that of spodumene and lepidolite. It is a kind of high-quality mineral which can extract lithium when enriched in large quantities. However, because there are few independent deposits, the corresponding research is limited. Braga *et al.* [91] conducted a study on montebrasite in northern Portugal. Dilute sulfuric acid was used to mix with montebrasite and roasted, as shown in reaction (48). A lithium extraction yield of more than 95% was achieved at 800°C for 15 min. The main phases in leaching residue were aluminum phosphate and unreacted gangue. Aluminum phosphate was produced as a by-product, improving the economics of the process. Montebrasite has extremely low fluorine content, making it an environmentally friendly resource for lithium extraction.



2.3.2. Petalite

Petalite ($\text{LiAlSi}_4\text{O}_{10}$) is also produced in granite pegmatite. Industrially, petalite with low iron content is commonly used as high-grade ceramics and special glass. Its theoretical Li_2O

content is 4.88wt%. Petalite decomposes into β -spodumene and quartz when heated to 1100°C. Thus, the conventional phase transition and sulfuric acid digestion method is also effective for petalite. In addition, Setoudeh *et al.* [92] mixed 100wt% Na_2SO_4 with petalite and milled them in a planetary ball mill. After heat treatment at 1000°C for 1 h, a lithium extraction greater than 99% was achieved. The reaction is shown in reaction (49).



2.3.3. Lithium porcelain stone

The lithium content of lithium porcelain stone is relatively low (average Li_2O is only 1wt%), and it is mainly concentrated in the Jiangxi Province in China. Lithium porcelain stone has been used as a raw material for ordinary ceramics and glass for long periods of time because of its low price [93]. A small amount of lithium porcelain stone is used to select lepidolite for lithium production by mineral processing. Wang *et al.* [94–95] used a mixed additive of 20wt% Na_2SO_4 and 20wt% CaCl_2 to selectively extract lithium, rubidium, and cesium. After roasting at 850°C for 1 h, the extraction yield reached more than 95% by water leaching.

2.3.4. Clay

The reserves of clay-type lithium minerals account for approximately 7% of the world's total lithium reserves. However, they have not been developed yet and are potential resources for lithium extraction. Gu *et al.* [96] and Li *et al.* [5] proposed roasting combined with a leaching process for lithium-rich bauxitic clay using dilute sulfuric acid and ferric sulfate solution as leaching agents, respectively. The extraction of lithium was greater only after roasting at 500–800°C. Temperatures that were too high or too low were ineffective, potentially because the clay minerals generally began to remove structural hydroxyl groups after 500°C. The structures

changed and the interlayer cations escaped. The clay was fired into the corresponding stable structures, such as spinel and cordierite, when the temperature was too high. The roasted clay could be leached to obtain a lithium extraction yield of approximately 73%.

2.3.5. Geothermal mud

The geothermal mud on the Indonesian island of East Java has been erupting for decades. Mubarok *et al.* [97] have attempted to extract lithium from the mud. The solid phase of the geothermal mud was leached with 6 mol/L hydrochloric acid. The average lithium extraction was 98.3%, while plenty of iron and aluminum were also leached. More research is needed on the enrichment and purification of leach liquor because of its extremely low content of lithium.

3. Extraction of lithium from brines

More than 60% of the world's lithium is stored in brines [15], and they are one of the most important resources for lithium extraction. However, the process flow is complicated and variable because of their complex composition containing various elements such as Mg, Na, K, Ca, and B. In particular, the presence of Mg impurity significantly affects the extraction of lithium [98–99]. The mass ratio of Mg/Li has always been an important indicator for evaluating the feasibility of lithium extraction from salt lakes. Most brines in China have a relatively high Mg/Li mass ratio, generally greater than 50 [100–101]. The separation of magnesium and lithium in traditional methods is difficult, which limits the development of lithium extraction from brines with a high Mg/Li mass ratio.

3.1. Electrochemistry method

The electrochemistry method is a newly emerging method [102] that simulates the charging and discharging process of lithium batteries [103]. A battery system was constructed with brine as an electrolyte. By controlling the potential, the charging process of the battery is simulated, such that the lithium in brines enters the negative electrode that does not contain lithium, and the selective extraction of lithium is realized. The most common electrodes used are $\text{LiFePO}_4/\text{FePO}_4$ [104–108] and $\text{LiMn}_2\text{O}_4/\lambda\text{-MnO}_2$ [98,109–112]. Zhao *et al.* [104] showed that Li^+ was easily embedded into the FePO_4 lattice and had excellent reversible properties. However, only a small amount of Mg^{2+} embeds at a higher voltage. Therefore, the selective extraction of lithium in brines can be achieved by controlling the operation voltage of the system. A chemical precipitation method was proposed by Liu *et al.* [105] to convert the Li^+ in a lithium-containing anolyte into the precipitation of lithium phosphate. A high-concentration Fe^{3+} solution was used to convert lithium phosphate, resulting in a high-concentration Li^+ solution and iron phosphate precipitation. The product of Li_2CO_3 was eventually obtained by carbonization precipitation. Xiong *et al.* [106] proposed an efficient and controllable method for the preparation of olivine– FePO_4 cathodes. The prepared cathodes were

used to treat the brine in West Taijinar, successfully reducing the Mg/Li mass ratio from 54.27 to 1.65. Xu *et al.* [109] demonstrated the possibility of separating magnesium and lithium with $\text{LiMn}_2\text{O}_4/\lambda\text{-MnO}_2$ electrodes. The Mg/Li mass ratio could be reduced from 147.8 to 0.37 when processing low-lithium brines and from 58.8 to 1.7 when high-lithium brines were processed. The separation effect was similar to that of the $\text{LiFePO}_4/\text{FePO}_4$ electrodes. Liu *et al.* [110] performed a kinetic analysis on the intercalation process of lithium, indicating that the control step was the surface reactions. To accelerate the process, the West Taijana brines were treated with porous LiMn_2O_4 electrodes, and the concentration of lithium was reduced from 1.91 to 0.60 g/L in 21 h. Mu *et al.* [98] reported a mesoporous LiMn_2O_4 with a specific surface area of 183 m^2/g . At the same time, the three-dimensional graphite felt conductor was used as the support of LiMn_2O_4 to enhance the diffusion and migration effects. The time required for the system to achieve the separation equilibrium of magnesium and lithium was only one quarter of that of ordinary electrodes.

3.2. Adsorption method

The adsorption method uses a highly selective adsorbent to adsorb Li^+ in brines. Manganese-based adsorbents such as LiMn_2O_4 [113], Li_2MnO_3 [114], and $\text{Li}_4\text{Mn}_5\text{O}_{12}$ [115] were first used. However, the loss of manganese was inevitable during the pickling process. Titanium-based adsorbents have gradually attracted the attention of researchers because of their stronger chemical stability. Both Li_3TiO_3 [116–117] and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ [118–119] have excellent selective adsorption properties for lithium. The easy agglomeration of titanium-based adsorbents led to a decrease in adsorption capacity; as a result, the selection of binder and porogen was crucial. Ryu *et al.* [120] combined the advantages of manganese-based and titanium-based adsorbents to prepare $\text{Li}_{1.33}(\text{Ti}_{0.1}\text{Mn}_{0.9})_{1.67}\text{O}_4$ composite adsorbents. The structure was more stable than that of a single manganese-based adsorbent, which effectively reduced the loss of manganese. Recently, lithium–aluminum layered double hydroxide (LDH) adsorbents have been discovered. Although their adsorption capacity is less than that of traditional adsorbents, they are still getting attention because of their facile elution properties. Paranthaman *et al.* [121] synthesized LDH with different Li/Al molar ratios. Preliminary experiments verified that the adsorbent synthesized with a Li/Al molar ratio of 1:1.25 had the highest selectivity for lithium, and the extraction yield of lithium reached approximately 91%. Yu *et al.* [122] and Chen *et al.* [101] proposed magnetic double-layer hydroxide adsorbents (MLDH) combined with Fe_3O_4 to solve the difficult separation of LDH. The increase of Fe_3O_4 content (from 13.11wt% to 30.58wt%) resulted in a decrease in Li adsorption capability from 5.83 to 3.46 mg/g; however, the enhancement of saturation magnetization facilitated its separation and recovery. At the same time, the Mg/Li mass ratio in the desorption solution decreased from 6.37 to 2.10, indicating that the addition of Fe_3O_4 improved the selectivity of the

adsorbent for lithium.

3.3. Electrodialysis and membrane methods

Electrodialysis and membrane methods are two new environmental separation technologies that have been rapidly developed and used for lithium extraction from brines [123–125]. Zhao *et al.* [99] and Liu *et al.* [126] proposed an improved solution: a sandwiched liquid membrane electro-dialysis system comprising two cation exchange membranes and one Li-loaded organic liquid membrane. This system achieved identification and fast electromigration of Li^+ assisted by an electric field, indicating the Mg/Li mass ratio in brines could be reduced from 100 to below 2 under optimal conditions. The system had strong adaptability, separating K, Mg, Ca, and other impurities from lithium, and the specific energy consumption was significantly less than the traditional electro-dialysis method, only 0.13 kWh per mol Li. However, because of the competition between high concentrations of Na^+ and Li^+ during electromigration, this process is more suitable for treating low-sodium brines. Shi *et al.* [127] assembled a cation exchange membrane in the membrane capacitive deionization system to achieve the separation of lithium and magnesium. The selectivity coefficient of lithium reached 2.95 under the conditions of a flow rate of $30 \text{ mL}\cdot\text{min}^{-1}$, 1.0 V, and 10 min. The specific energy consumption was only 0.0018 kWh per mol Li, which was much less than that of traditional electro-dialysis. Hou *et al.* [128] summarized the current separation techniques of Li^+ using a metal-organic framework (MOF)-based membranes. Membranes with high selectivity already achieve efficient separation of magnesium and lithium at the laboratory scale [16,129], providing a new possibility for lithium extraction from brines by the membrane method.

3.4. Solvent extraction method

The solvent extraction method has been widely used in metallurgical and chemical industries, and research on this method to extract lithium from brines has also developed rapidly. The most commonly used system is tributyl phosphate (TBP) combined with FeCl_3 [130–131]. TBP has high selectivity to Li^+ under the synergistic effect of Fe^{3+} . The greatest issue with this process is that a high concentration of 6–9 $\text{mol}\cdot\text{L}^{-1}$ hydrochloric acid is usually required for stripping. Researchers have conducted studies on this issue recently. Yu *et al.* [132] proposed a new technique of multi-stage centrifugal extraction with the isomer tri-isobutyl phosphate. The extraction yield of lithium reached 90.1% after a five-stage centrifugal extraction, and only 1 $\text{mol}\cdot\text{L}^{-1}$ hydrochloric acid achieved nearly 100% lithium stripping. A novel solvent extraction system, trialkylmethylammonium di(2-ethylhexyl)orthophosphinate ($[\text{N}_{1888}] [\text{P}_{507}]$) + TBP + FeCl_3 , was developed by Bai *et al.* [15]. The extraction yield of lithium was slightly reduced to 70%, and the concentration of hydrochloric acid required for stripping was also reduced to 1–1.5 $\text{mol}\cdot\text{L}^{-1}$. Cai *et al.* [133] prepared a functional extractant that was named 3-methyl-1-octylimidazolium

thenoyltrifluoroacetone [Omim][TTA]. The extractant was aimed at high-concentration sodium brines, and the separation coefficient between lithium and sodium reached 227, which was the maximum that could be achieved in a single extractant.

3.5. Precipitation method

The precipitation method is the first and simplest method to extract lithium from brines. However, it can only be applied to the brines with a low Mg/Li mass ratio. The process uses natural solar energy to evaporate and concentrate brines. As a result, sodium and potassium salts are crystallized. After removing impurities, such as boron and calcium, sodium carbonate is added to precipitate lithium carbonate. The process is mature, and the industrial production of low-magnesium brines in Chile and the United States has been realized. Recently, new precipitants have been invented. Liu *et al.* [134] prepared Al/ Na_2SO_4 composites for sulfate-type brines that could precipitate the lithium in the form of $\text{Li}_2\text{Al}_4(\text{OH})_{12}\text{SO}_4\cdot x\text{H}_2\text{O}$. However, the presence of magnesium was not conducive to the precipitation of lithium. When the Mg/Li mass ratio in brines reached 20, the precipitation rate of lithium decreased from 89.2% to 54.7%. Liu *et al.* [135] proposed a method for activated Li_3PO_4 -induced precipitation for carbonate brines. Active Li_3PO_4 with exposed high surface energy (110) facets was successfully prepared. The experimental results proved that the precipitant greatly reduced the temperature required (from 90 to 30°C), thereby reducing the process energy consumption.

4. Conclusion and outlooks

Lithium is an important national strategic reserve metal and a key raw material for many strategic emerging industries. The demand for lithium will continue to rise for a long time, along with the popularity of global electrification and the development of controllable nuclear fusion. The main conclusion and outlooks are as follows.

The phase transition and sulfuric acid digestion method for spodumene is currently the most important process for lithium extraction. However, it consumes a large amount of energy and sulfuric acid. A few companies use lepidolite as the raw material for industrial production of lithium extraction without considering high-value rubidium and cesium. The existing problems mentioned above need to be solved. At the same time, emerging technologies are expected to be applied to the extraction of lithium from minerals. The improvement of traditional technologies and the development of new technologies should go hand in hand. Various methods were proposed for brines with a high Mg/Li mass ratio. The research and development of each process are conducted based on the characteristics of the brines targeted because of the significant differences in composition in different origins. The establishment of a lithium extraction process library from brine is expected to be realized. The system automatically matches the appropriate process according to the charac-

teristics of the brine.

This paper provides an overview of the recent technological developments in the extraction of lithium from natural resources and provides a reference for the research, development, optimization, and industrial application of future processes.

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Conflict of Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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