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Lithium extraction from hard rock lithium ores (spodumene, lepidolite, zinnwaldite, petalite): Technology, resources, environment and cost

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ABSTRACT

Lithium production in China mainly depends on hard rock lithium ores, which has a defect in resources, environment, and economy compared with extracting lithium from brine. This paper focuses on the research progress of extracting lithium from spodumene, lepidolite, petalite, and zinnwaldite by acid, alkali, salt roasting, and chlorination methods, and analyzes the resource intensity, environmental impact, and production cost of industrial lithium extraction from spodumene and lepidolite. It is found that the sulfuric acid method has a high lithium recovery rate, but with a complicated process and high energy consumption; alkali and chlorination methods can directly react with lithium ores, reducing energy consumption, but need to optimize reaction conditions and safety of equipment and operation; the salt roasting method has large material flux and high energy consumption, so require adjustment of sulfate ratio to increase the lithium yield and reduce production cost. Compared with extracting lithium from brine, extracting lithium from ores, calcination, roasting, purity, and other processes consume more resources and energy; and its environmental impact mainly comes from the pollutants discharged by fossil energy, 9.3–60.4 times that of lithium extracted from brine. The processing cost of lithium extraction from lepidolite by sulfate roasting method is higher than that from spodumene by sulfuric acid due to the consumption of high-value sulfate. However, the production costs of both are mainly affected by the price of lithium ores, which is less competitive than that of extracting lithium from brine. Thus, the process of extracting lithium from ores should develop appropriate technology, shorten the process flow, save resources and energy, and increase the recovery rate of related elements to reduce environmental impact and improve the added value of by-products and the economy of the process.

1. Introduction

Due to its unique physical and chemical properties such as high specific heat, high conductivity, and strong chemical activity (Ebensperger A et al., 2005; Swain B, 2017; Zhang SJ et al., 2020), lithium has gradually expanded its application fields from traditional industries such as glass, ceramics, aluminum smelting and lubricants to new energy, new materials and other fields since the 21st century (Gu GZ and Gao TM, 2021). As an indispensable raw material for green technology (Alessia A et al., 2021), it has been listed as a critical mineral in many countries and has attracted more and more global attention. Scholars studied the supply and demand situation of global lithium resources in the future, and predicted that by 2050 and 2100, the demand for lithium carbonate will reach 1.69–2.12 Mt (Mohr SH et al., 2012) and 3.5–7.5 Mt (Ambrose H and Kendall A, 2019), and the supply will be 1.62–2.58 Mt (Mohr SH et al., 2012) and 4.4–7.5 Mt (Ambrose H and Kendall A, 2019), respectively. Although the supply of global lithium resources can meet its demand before 2100, low-grade lithium resources need to be developed after 2050 (Ambrose H and Kendall A, 2019). The existing lithium extraction process has been successfully applied to the development of high-grade lithium resources, but it is not suitable for the development of low-grade resources. With the increasing pressure of environmental protection, it is urgent to

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improve lithium extraction technology to realize the clean and comprehensive utilization of resources.

Lithium resources in nature are mainly stored in lithium deposits of brine, pegmatite, and sedimentary rocks (Talens PL et al., 2013; Liu LJ et al., 2017). Among them, brine mainly includes underground and salt lake brine, and pegmatite-type lithium ore is stored in spodumene, lepidolite, petalite, and zinnwaldite (Xi WW et al., 2022; Yu F et al., 2019), while sedimentary rock minerals include jadalite, lithium clay, etc (Zhu L et al., 2020). At present, lithium resource exploitation mainly depends on salt lake brine and hard rock lithium ore. Although lithium extraction from salt lake brine in China has shown a rapid growth trend in recent years, its lithium production is still dominated by ores (spodumene and lepidolite), accounting for 69.82% of China's lithium output (298.2 kt LCE) in 2021 (Fig. 1). In recent years, many scholars (Karrech A et al., 2020; Li H et al., 2019; Yelatontsev D and Mukhachev A, 2021; Liu YL et al., 2013; Su H et al., 2019; Zhang JF, 2020; Zhang XF et al., 2020) have reviewed the technologies for extracting lithium from ores, focusing on the improvement and mechanism of these processes, but paying less attention to their high energy consumption, large environmental impact, and weak competitiveness. This paper hopes to summarize the existing technologies for extracting lithium from ores, discuss their development status and existing problems, compare the resources, environment, and cost of industrial production, and explore the improvement direction of concise, efficient, clean, and comprehensive utilization of technologies for extracting lithium from ores.

2. Overview of lithium resources and lithium extraction process

The global lithium resource reserves are 22 Mt (metal) (USGS, 2022), of which 34% are from hard rock lithium mines (Li LJ et al., 2018), mainly including Australia Greenbushes, Canada Quebec, China Jiajika, Zimbabwe Bikita and other pegmatite lithium deposits (Zhang SJ et al., 2020; Yang HP, et al. 2019). There are more than 150 kinds of lithium minerals (Pan T et al., 2022), but only a few of them have commercial value (Chen Y et al., 2011a; Yelatontsev D and Mukhachev A, 2021), such as spodumene, lepidolite, petalite and zinnwaldite (Table 1). Spodumene is the main lithium-bearing mineral in the world, and its theoretical Li_2O content can reach 8.03% (Zhang XF et al., 2020), which is the main source of lithium extraction from ores (Liu H and Azimi G, 2021). Lepidolite with theoretical Li_2O content up to 7.7% is usually associated with potassium, rubidium, and cesium (Li H et al., 2019), which is a potential resource for lithium production. The famous Yichun lepidolite deposit in Jiangxi Province, China has a lithium reserve of 325 kt, but the lithium oxide content is only 0.88% (Su H et al., 2019). With the price of lithium carbonate rising in recent years, lepidolite has become an important resource for industrial lithium extraction in China. Petalite and zinnwaldite are also important lithium-bearing minerals, but their theoretical Li_2O content is significantly lower than that of spodumene and lepidolite, which are 3.42% and 4.50%, respectively (Li H et al., 2019). Scholars (Martin G et al., 2017a; Setoudeh N et al., 2020; Sitando O and Crouse PL, 2012; Tian J et al., 2020) have also carried out the extraction of lithium from these two minerals. The above four minerals are considered the main raw materials for lithium production from ores.

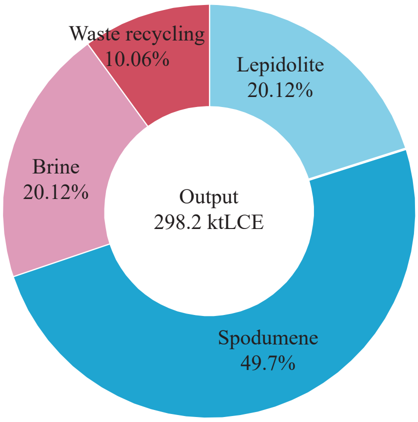
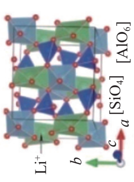
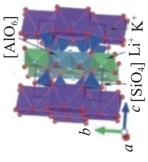
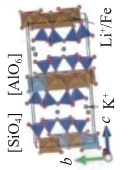
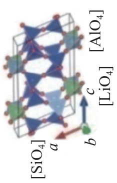


Fig. 1. Lithium production structure in China (2021).

Lithium minerals are usually associated with gangue minerals, such as quartz and feldspar, so the content of lithium oxide in the ore is low. These useful components are enriched through beneficiation to obtain lithium concentrate, which usually includes gravity separation, magnetic separation, foam flotation, and other processes (Tadesse B et al., 2019). Spodumene occurs in the form of α-phase in nature and resists reaction with various acids except for hydrofluoric acid (Hu Z, 2019; Su H et al., 2019; Li H et al., 2019). The common method is to calcine spodumene to convert it into β-phase, and then react with acid or alkali to form soluble lithium sulfate or hydroxide. To reduce the energy consumption of phase transfer, scholars also studied lithium leaching after the direct reaction of hydrofluoric acid and sodium hydroxide with α-spodumene. Lepidolite, rich in K, F, Rb, Cs, and Al_2O_3 (Table 1), is a monoclinic system, which is composed of two tetrahedral $[SiO_4]$ sheets with sandwiched octahedral $[AlO_6]$ sheets (Su H et al., 2019; Shang X et al., 2020). Monovalent cations such as Li^+, Rb^+, or Cs^+ often enter the interlayers to replace the Al in $[AlO_6]$ (Guo H et al., 2019). The lepidolite concentrate is generally roasted at a high temperature with certain additives to activate octahedral $[AlO_6]$ and liberate Li^+ from the encapsulated structure (Guo H et al., 2019). The work on lithium extraction from zinnwaldite and petalite is less than that from spodumene and lepidolite (Martin G et al., 2017b), but their route of lithium extraction is highly similar. Then, impurities such as calcium, magnesium, and iron are removed from the crude leaching solution leached from these minerals to obtain a lithium purification solution for the precipitation of lithium carbonate. According to the different media used for calcination and leaching, the existing processes for extracting lithium from

Table 1. Crystal structure and major components of typical lithium minerals.

Minerals	Crystal structure (Su H et al., 2019)	Chemical composition /% Li_2O	K_2O	CaO	SiO_2	Al_2O_3	Na_2O	MgO	Fe_2O_3	TiO_2	MnO	Rb_2O	Cs_2O	F	Sources
Spodumene		7.20	0.03	0.28	66.20	22.30	0.40	0.25	0.95	0.06	–	–	–	–	Barbosa LI et al., 2014
		7.03	0.14	0.52	68.30	18.60	0.80	0.30	3.20	0.11	–	–	–	–	Rosales GD et al., 2014
		6.80	0.75	–	60.30	22.70	1.13	0.65	1.26	–	0.28	–	–	–	Morozova LN, 2018
Lepidolite		3.27	5.91	0.2	60.88	24.96	2.28	–	0.14	–	–	1.02	0.08	2.24	Guo H et al., 2019
		3.94	7.57	0.42	55.75	22.54	1.63	0.40	0.20	–	–	1.52	0.23	5.80	Cheng Y et al., 2012
		3.85	9.15	1.91	57.7	22.9	0.8	0.47	0.17	–	0.13	0.81	0.25	3.08	Luong VT et al., 2014
		3.3	7.58	0.22	53.81	25.50	1.76	0.02	0.77	0.04	0.55	–	–	5.34	Kuai YQ et al., 2021
Zinnwaldite		3.00	8.40	–	50.60	17.30	–	–	11.50	–	1.10	0.60	–	4.10	Martin G et al., 2017a
		3.38	9.11	0.15	50.45	20.28	0.12	0.02	10.04	0.21	1.46	0.33	–	7.58	Schneider A et al., 2017
		2–5	10.10	–	42.80	21.70	0.19	–	11.00	–	–	0.45	–	6.1	Su H et al., 2019
Petalite		4.37	0.97	0.03	77.04	16.49	0.48	0.09	0.01	0.01	0.01	–	–	–	Setoudeh N et al., 2020
		4.10	0.45	0.11	76.11	17.76	0.54	–	0.05	–	0.02	0.09	0.03	0.01	Sitando O and Crouse PL, 2012
		4.93	0.01	–	78.05	16.74	0.03	0.02	–	–	0.02	–	–	–	Rajesh HM et al., 2020

ores are mainly divided into an acid method, alkali method, salt roasting method, and chlorination method (Karrech A et al., 2020; Li H et al., 2019; Su H et al., 2019; Zhang L et al., 2020). The method of lithium precipitation is relatively uniform. Generally, lithium carbonate is precipitated by reacting lithium purification solution with sodium carbonate, or further carbonized to prepare battery-grade lithium carbonate, and anhydrous sodium sulfate is produced as a byproduct.

3. Acid method

The acid process can be further divided into sulfuric acid (Bishimbayeva G et al., 2018; Ellestad RB and Milne LK, 1950), hydrofluoric acid (Rosales GD et al., 2016, 2014), hydrochloric acid (Margarido F et al., 2014), nitric acid (Hunwick R, 2017), etc. Among them, the mature sulfuric acid process has dominated industrial lithium extraction from spodumene ores, while hydrofluoric acid, hydrochloric acid, and other acid methods are mostly in the research stage due to equipment, cost, and other reasons.

3.1. Sulfuric acid method

After more than 50 years of development, the sulfuric acid process is the most widely used process for extracting lithium from ores (Zhao CL et al., 2018) with a mature process, easy to control and consistent quality (Hu Z, 2019; Meng GS, 2008). The technological process includes calcination, acid roasting, leaching, purification, evaporation, lithium precipitation, and anhydrous sodium sulfate concentration and crystallization. The crushed α-spodumene concentrate is calcined at 950–1100°C and converted into β-spodumene, and then acidified with excessively concentrated sulfuric acid (1.4 times) (Meshram P et al., 2014) in a rotary kiln at 250–300°C to form water-soluble sulfate (Equation 1). After water leaching at 90°C, neutralize the excess sulfuric acid with lime (Gmar S and Chagnes A, 2019), adjust pH to 7–10 to remove most impurities such as iron and aluminum (GB/T51382, 2019), and obtain crude lithium sulfate solution with lithium oxide content of about 10% (Kuang G et al., 2018; Ran JW et al., 2016; Tan B et al., 2021). Then add lime milk to the crude lithium solution to remove most of the magnesium, and adjust the solution to an alkaline environment (pH=11 –12) (GB/T51382, 2019; Ran JW et al., 2016; Zhu ZH et al., 2008), remove the remaining calcium, magnesium, etc. deeply by introducing sodium carbonate (Su H et al., 2019), evaporate and concentrate the filtered solution to obtain a purified lithium sulfate solution with a lithium content of more than 20%. Finally, lithium carbonate is precipitated by adding sodium carbonate (Equation 2), and centrifuging, dehydration, and drying to obtain lithium carbonate products. The separated mother liquor is concentrated and crystallized to produce anhydrous sodium sulfate, and the surplus water returns to the leaching process (Fig. 2). In early research, the calcination temperature and acid consumption of the sulfuric acid method were covering a wide range. For example, in the patent of Ellestad RB and Milne LK (1950), the calcination temperature, acid dosage, and acid roasting temperature range were 1000–1350°C, 1.3–2.4 times, and 250–300°C, respectively. But, Tian QQ et al. (2011) obtained *β*-spodumene transformation was completely calcined at 1050°C for 30 minutes, and the appropriate acidizing conditions were: The amount of sulfuric acid was 140% of the theoretical value, and the roasting temperature was 250°C, lasting for 30 minutes. Under the optimum water leaching conditions (solid to liquid (S/L) ratio 1∶1.85, reaction at room temperature for 15 minutes), the lithium leaching rate was 96.93% (Table 2; Tian QQ et al., 2011). To solve the problem that SO_4^{2-} in lithium carbonate produced by the sulfuric acid process is easy to exceed the standard, Qin YN (2004) used dilute sulfuric acid leaching, sodium oxalate to remove calcium, sodium hydroxide to remove magnesium, reducing sulfate, heavy metals, and other impurities, and improving the quality of lithium carbonate. And Liu H and Azimi G (2021) studied the influence of operating parameters on the efficiency and purity of lithium precipitation. Under the conditions that the concentration of both (lithium sulfate and sodium carbonate) was 2 mol/L, reacted at temperature 45°C and stirring speed 300 rmp, the lithium carbonate recovery rate and purity were 90.0% and 99.0%, respectively (Liu H and Azimi G, 2021).

$$Li_2O \cdot Al_2O_3 \cdot 4SiO_2 + H_2SO_4 \rightarrow Li_2SO_4 + Al_2O_3 \cdot 4SiO_2 + H_2O \tag{1}$$

$$Li_2SO_4 + Na_2CO_3 \rightarrow Li_2CO_3 + Na_2SO_4 \tag{2}$$

Scholars also studied lithium extraction from lepidolite by the sulfuric acid method (Table 2). Cheng Y et al. (2012) analyzed the influence of calcination temperature, sulfuric acid concentration, mass ratio, and reaction time on lithium recovery rate. Under the conditions: Lepidolite calcined at 900°C reacted with 70% sulfuric acid in a mass ratio of 1∶1 in an incubator at 130°C for 15 minutes, the lithium leaching rate was only 75%. Then Feng WP et al. (2016) studied the direct reaction of lepidolite with a certain concentration of sulfuric acid. When 55% sulfuric acid reacted with lepidolite (around 150 mesh) at a mass ratio of 2∶1 at 135°C for 9 h, the leaching rate of lithium can reach 96.72% (Table 2). However, this method has problems such as large residual acid and long reaction time (Li G et al., 2017). Vieceli N et al. (2017) also experimented with extracting lithium directly from lepidolite by sulfuric acid method and found that the conversion rate of lithium exceeded 70% at low temperatures (100°C). Then, their further research found that compared with the factors such as S/L ratio and leaching time, leaching temperature had a significant impact on lithium extraction. When the optimum leaching temperature is 50°C, the leaching rate of lithium can reach more than 90%, and rubidium, aluminum, and other elements in lepidolite can also be recovered (Vieceli N et al., 2018). The sulfuric acid process has a wide adaptability to raw material, also including zinnwaldite, petalite, and ores with only 1.0%–1.5% lithium oxide (Martin G et al., 2017a; Sitando O and Crouse PL, 2012), but its disadvantage is that the consumption of sulfuric acid is large, and sodium carbonate becomes low-value sodium sulfate (Peng AP and Song QR, 2016).

Energy consumption intensity and waste residue discharge of lithium extraction by the sulfuric acid method are large. At present, the sulfuric acid, comprehensive energy, and water resources intensities of this process in China are 2.29 t/t, 2.87 tce/t, and 20.93 t/t, respectively, producing a large amount of waste gas, wastewater such as COD (0.35 kg/t), SO_2 (11.39 kg/t) and sulfuric acid mist (0.83 kg/t) and leached residue (10.45 t/t) (Gu GZ and Gao TM, 2021). Therefore, scholars are exploring reducing the sulfuric acid concentration to reduce damage to equipment, optimize acidification conditions to improve lithium leaching efficiency and reduce the consumption of chemical raw materials. In addition, how to efficiently utilize silicon and aluminum in lithium ores to reduce resource consumption and waste residue discharge will become an important improvement content for lithium extraction by the sulfuric acid method.

3.2. Hydrofluoric acid method

Based on the characteristic that fluorine can destroy

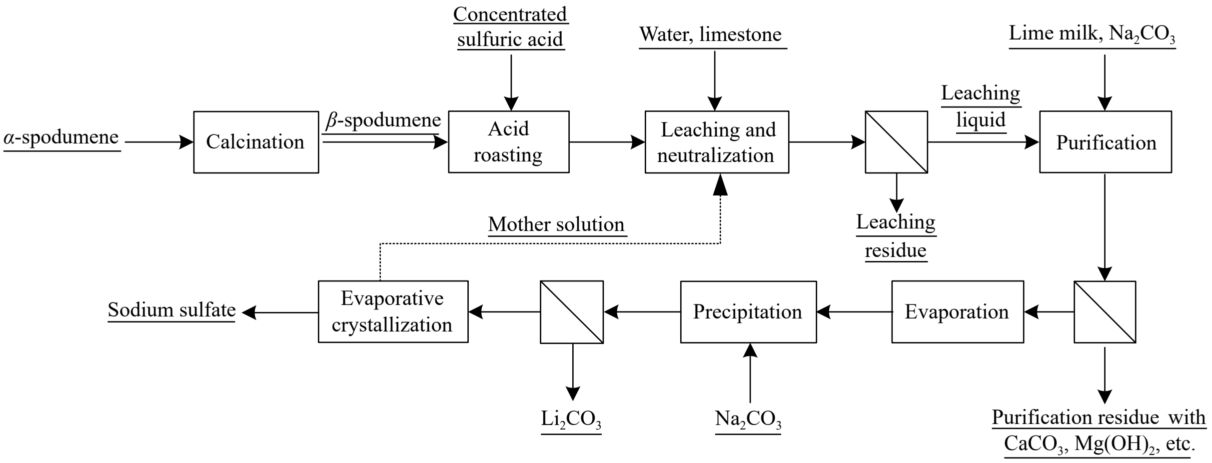


Fig. 2. Process flow sheet for extracting lithium from spodumene by the sulfuric acid method.

compact Si-O bonds at low temperatures, Rosales CD et al. (2014) experimented with leaching lithium from β-spodumene with hydrofluoric acid (Equation 3) and studied the effects of S/L ratio, temperature, hydrofluoric acid concentration and reaction time on the leaching rate. Under the optimized conditions, the leaching rate of lithium exceeded 90% (Table 3). Then their further analysis showed that temperature and reaction time are the main factors affecting the dissolution of lithium minerals (Rosales CD et al., 2016). To reduce the energy consumption and cost of spodumene calcination and conversion, Kuang G et al. (2012) proposed the lithium extraction process of α-spodumene corroded by hydrofluoric acid at low temperature, and the generated Li_3AlF_6 and AlF_3 were dissolved in sulfuric acid, which provided theoretical guidance for direct lithium extraction from α-spodumene. Kuang G et al. (2010) proposed the process route of extracting lithium from lepidolite by fluorine chemical method, which has the advantages of low energy and material consumption, comprehensive utilization of multiple resources, and significant economic benefits (Liu XK et al., 2014). Later, Guo H et al. (2017) applied this method to extracting lithium from α-spodumene and analyzed the effects of mass ratio (spodumene/hydrofluoric acid/sulfuric acid =1∶3∶2), reaction temperature (100°C) and time (3 h) on the lithium leaching rate (96%). The behavior revealed that the α-spodumene and albite are dissolved before quartz, and insoluble residues, fluoroaluminates, fluorosilicates, etc. are also generated. Fluosilicic acid can provide the hydrofluoric acid required for the reaction. Guo H et al. (2021) employed mixed acid of sulfuric and fluosilicic acid to leach lithium from lepidolite and investigated the influence of different factors on leaching efficiency. Under the optimized conditions, effective leaching of lithium (97.9%), potassium (96.4%), rubidium (97.6%), and cesium (96.7%) can be obtained. These studies revealed an effective method of extracting lithium directly from lithium minerals (Guo H et al., 2017). This process does not need calcination at high temperatures, which avoids a large amount of energy consumption and pollutant emissions. However, the process has high requirements for equipment and has not yet been industrialized.

$$LiAlSi_2O_6 + 19HF \rightarrow LiF + H_3AlF_6 + 2H_2SiF_6 + 6H_2O \tag{3}$$

3.3. Hydrochloric acid and nitric acid method

Scholars used hydrochloric acid instead of sulfuric acid to leach lithium from β-spodumene, and their results showed that the higher the concentration, the better the lithium leaching efficiency (Margarido F et al., 2014). Some scholars (Hunwick R, 2017) also used nitric acid as a substitute and analyzed that the recovery rate of lithium nitrate can reach 95% at 170°C and 2 MPa. Martin G et al. (2017a) proposed to use of hydrochloric acid instead of sulfuric acid to acidize zinnwaldite to avoid the generation of toxic hydrogen fluoride. After 6 h of acid leaching with 29% hydrochloric acid, the leaching rate of lithium reached 94%. Then further concentration and removal of impurities, precipitate industrial-grade lithium carbonate, and the total lithium yield was about 70%. At present, the extraction of lithium by hydrochloric acid or nitric acid is mostly in the research stage.

4. Alkali method

To reduce the energy consumption and lithium extraction cost of the sulfuric acid process, scholars try to use alkaline substances to extract lithium. Alkaline substances, mainly sodium hydroxide, calcium hydroxide, and sodium carbonate, can directly react with lithium minerals or calcined lithium minerals (Table 4).

4.1. Sodium hydroxide method

Through hydrothermal alkali treatment, α-spodumene is converted into hydroxy sodalite, and lithium in the ore is released into solution, and then precipitated for recovery (Fig. 3). Anovitz LM et al. (2006) found that the reaction rate of α-spodumene with sodium hydroxide solution at 500°C was very slow, and after three days, only a part of α-spodumene was decomposed into sodalite and lithium solution. Then Albertani BM (2018) further analyzed the influence of the S/L ratio, reaction temperature, time, and particle size on the leaching rate of this method. Under the optimized conditions, the leaching rate was only 40% (Table 4). This low leaching rate is due to the low concentration of sodium hydroxide (Li H et al., 2019). Raised the concentration to 600 g/L, and reacted for 2 h under the conditions: S/L ratio of 1∶5, the temperature of 250°C and stirring speed of 500 rmp, the leaching rate of lithium from spodumene can reach 95.8% (Xing P et al., 2019). The reaction is shown in Equation 4. Some scholars (Chubb PA, 1963) also tried to leach lithium from β-spodumene with sodium hydroxide and other substances and studied the feasibility under temperature (100 –200°C) and pressure (0.1–1.7 MPa).

For lepidolite, Wang D et al. (2014) proposed a new process for extracting lithium by sodium hydroxide method and studied the effects of alkali concentration, S/L ratio, reaction temperature, and time on lithium conversion rate. Under the optimum conditions, the conversion rate was 98.2% (Table 4). Increasing the pressure can shorten the reaction time, reduce the amount of alkali, and cut the cost of post-treatment. Under the optimized conditions: Steam pressure of 9 MPa, the mass ratio of lepidolite to alkali of 1∶1.2, the reaction time of 2 h, and particle size of lepidolite of 150 μm, the conversion rate of lithium from lepidolite was 96.9% (Wang D and Chen S, 2020; Table 4). In addition, the fluorine in lepidolite will not generate highly corrosive hydrofluoric acid in an alkaline environment, thus avoiding the corrosion of equipment.

$$\begin{gathered} 6\alpha - LiAlSi_2O_6 + 14NaOH \rightarrow 2Na_4Al_3Si_3O_{12}(OH) + \\ 3Li_2SiO_3 + 3Na_2SiO_3 + 6H_2O \end{gathered} \tag{4}$$

Table 2. Various reports on the best conditions and results of extracting lithium from lithium ores by the sulfuric acid method.

Minerals	Li_2O content /%	Calcination		Acid roasting			Leaching						References
		Temperature /°C	Time/ min	H_2SO_4 dosage	Temperature/ °C	Time/ min	Leaching medium	S/L ratio	Temperature /°C	Time /min	Stirring speed /rmp	Leaching rate/%	
Spodumene	6.05	1050	30	β-spodumene∶H_2SO_4= 1∶1.4 times theoretical quantity	250	30	H_2O	1∶1.85	Room	15	–	96.93	Tian QQ et al., 2011
Lepidolite	3.94	900	–	Calcined lepidolite∶ 70%H_2SO_4=1∶1	130	15	–	–	–	–	–	75	Cheng Y et al., 2012
Lepidolite	4.52	–	–	Lepidolite∶ 55% H_2SO_4=1∶2	135	540	H_2O	1∶2	60	360	–	96.72	Feng WP et al., 2016
Lepidolite	4.20	–	–	Lepidolite∶ H_2SO_4=0.65∶1	165	240	H_2O	1∶10	80	15	–	87	Vieceli N et al., 2017
Lepidolite	4.20	–	–	Lepidolite∶ H_2SO_4=0.98∶1	130	15	H_2O	1∶2	50	–	–	90	Vieceli N et al., 2018
Petalite	4.10	1100	120	Calcined petalite∶ H_2SO_4=1∶1.15 times theoretical quantity	300	60	H_2O	1∶7.5	50	60	320	97.3	Sitando O and Crouse PL, 2012

Table 3. Extraction of lithium from spodumene and lepidolite by the hydrofluoric acid method.

Minerals	Li_2O content/%	Reagent and dosage	Temperature	Reaction time	Stirring speed /rmp	Lithium recovery/%	References
Spodumene	7.03	β-spodumene: 7%HF=1.82% w/v	75°C	10 min	330	>90	Rosales GD et al., 2014
Spodumene	7.03	β-spodumene: 4%HF=0.95% w/v	308 K	30 min	330	88	Rosales GD et al., 2016
Spodumene	4.31	α-spodumene∶Fluorite ∶98% H_2SO_4= 2 g∶3 g∶7 mL	Heating: 400 K/ constant: 525 K	Heating: 1 h/ constant: 2 h	-	95.7	Kuang G et al., 2012
Lepidolite	≥3.0	Lepidolite∶Reagent（F>10%）∶H_2SO_4 (>50%)=1∶0.1–2∶0.5–5	Preheat: 50–150°C/ reaction: 150–350°C	Preheat: 0.1–2.0 h/ reaction: 0.5–4.0 h	-	-	Kuang G et al., 2010
Spodumene	5.48	α-spodumene∶HF∶H_2SO_4=1 g∶3 mL∶ 2 mL	100°C	3 h	-	96	Guo H et al., 2017

4.2. Calcium hydroxide method

Scholars also studied the extraction of lithium from calcined lithium ores by calcium hydroxide. Yan QX et al. (2012a) calcined lepidolite at a high temperature (860°C) for 30 minutes for defluorination and then leached it with lime milk. The influence of factors such as defluorination rate, S/L ratio, leaching temperature, time, and lime-to-defluorinated lepidolite ratio in the leaching process was optimized. The lithium extraction efficiency reached 98.9% under the optimum conditions (Table 4). The process has a small material flow and slag produced, but the defluorination gas is difficult to treat (Su H et al., 2019). Kuang G et al. (2014) applied for a patent for extracting lithium by mixing calcined β-spodumene, lime, sodium hydroxide, and water. Under the conditions including spodumene/lime/sodium hydroxide/water of 1∶0.05–0.35∶0–0.03∶1.5–6, the pipe flow speed of 0.8–8 m/s, reaction temperature of 90–250°C, and time of

Table 4. Optimum operating conditions and recovery efficiency of lithium extraction by alkali method.

Minerals	Li$_2$O content /%	Reagent and dosage	Temperature	Time	Stirring speed/rmp	Others	Lithium recovery /%	References
Spodumene	–	α-spodumene∶50% NaOH=1∶38.34 (w/w)	200°C	3 d	–	–	–	Anovitz LM et al., 2006
Spodumene	7.6	α-spodumene∶NaOH= 1∶14 (w/v)	573.15 K	6 h	–	Granularity: 325 μm>80%	>40	Albertani BM, 2018
Spodumene	8.03	α-spodumene∶NaOH= 1∶1.5	600°C	1 h	–	–	63.8	Lee S, 2018
Spodumene	5.51	α-spodumene∶(600 g/L) NaOH=1∶5 (w/v)	250°C	2 h	500	–	98.5	Xing P et al., 2019
Spodumene	2–6	β-spodumene∶NaOH∶Ca(OH)$_2$/CaO	212–400 K	–	–	Pressure: 1.72 MPa	–	Chubb PA, 1963
Lepidolite	4.47	Lepidolite∶50% NaOH= 1∶3.5 (w/w)	190°C	4 h	–	–	98.2	Wang D et al., 2014
Lepidolite	4.47	Lepidolite∶NaOH=1∶1.2	–	2 h	–	Pressure: 9 MPa, granularity: 150 μm	96.9	Wang D and Chen S, 2020
Lepidolite	3	Partially defluorinated lepidolite∶Ca(OH)$_2$=1∶1; S/L ratio=1∶4	150°C	1 h	400	–	98.9	Yan QX et al., 2012a
Lepidolite	3	Lepidolite∶Ca (OH)$_2$=1∶1; S/L ratio=1∶4	150°C	1 h	400	–	7.9	Yan QX et al., 2012a
Spodumene	4.5–6.5	β-spodumene∶CaO∶NaOH ∶H_2O =1∶0.05–0.35∶0–0.03∶1.5–6	90–250°C	0.5–5 h	–	Pressure: 0.1–1.5 MPa	>91	Kuang G et al., 2014
Petalite	3.7–3.9	400–500 g/L NaO$_2$, Ph=14–16, CaO∶SiO$_2$=1∶1	280°C	0.5–1 h	32	–	89–92	Yelatontsev D and Mukhachev A, 2021
Spodumene	6.05	β-spodumene∶(105g/L) Na$_2$CO$_3$=1∶4	225°C	1 h	300	–	>96	Chen Y et al., 2011b
Spodumene	6.05	Na (NaCO$_3$ solution) ∶Li (β–spodumene)=1.25; S/L ratio=1∶4	225°C	1 h	300	–	>94	Chen Y et al., 2011a

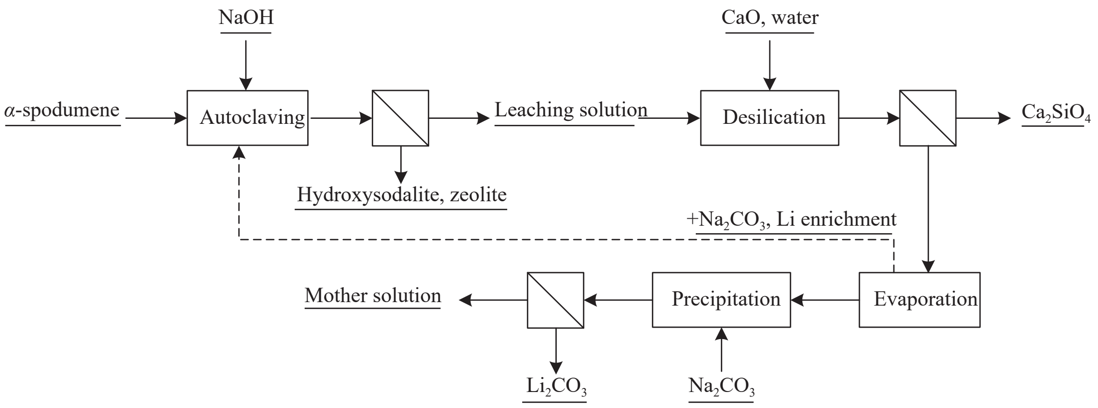


Fig. 3. Process of lithium extraction from spodumene by sodium hydroxide method (after Li H et al., 2019).

0.5–5 h, the dissolution rate of lithium reached more than 91% (Table 4). This method has a simple process, reduced acidification and sodium sulfate crystallization stage of the sulfuric acid method, and low material and energy consumption. Yelatontsev D and Mukhachev A (2021) studied the effects of sodium hydroxide concentration, reaction time, etc. on the extraction of aluminum and lithium from petalite, and found that the initial alkali concentration had nothing to do with the extraction of aluminum and lithium, but calcium oxide added in the solution played a decisive role (Equation 5). Under the optimal conditions (initial alkaline solution =400–500 g/L Na_2O, pH=14–16, $CaO:SiO_2$=1∶1, time=0.5–1 h) the extraction rate of lithium reached 89%–92% (Yelatontsev D and Mukhachev A, 2021).

$$\begin{gathered}\mathrm{Li(AlSi_4O_{10}) + 5NaOH + 4Ca(OH)_2 \rightarrow LiOH +} \\ \mathrm{2NaAl(OH)_4 + NaCa(HSiO_4) + 2H_2O}\end{gathered} \tag{5}$$

4.3. Sodium carbonate autoclaving method

Chen Y et al. (2011a, 2011b) used the sodium carbonate method to extract lithium from β-spodumene, in which lithium-ion in spodumene was replaced by sodium ion in solution (Equation 6). The autoclave process is to add 3.5–7 times of sodium carbonate according to the proportion of lithium oxide, leach at 200°C and pressure >2.0 MPa, inject CO_2 to generate soluble lithium bicarbonate solution, and precipitate lithium carbonate after heating (Fig. 4; Zhu ZH et al., 2008). Chen Y et al. (2011a) investigated the effects of S/L ratio, sodium lithium ratio, stirring speed, reaction time, and temperature on lithium conversion efficiencies. Their result showed that the conversion efficiencies were≥94% under optimal conditions. Another similar study (Chen Y et al. 2011b) also obtained a high lithium recovery (>96%) (Table 4). The sodium carbonate autoclave method has obvious advantages for defluorinated lepidolite: Simple process, high lithium leaching rate, and high overall process efficiency. However, the following problems need to be solved in industrial production: High requirements for equipment, large investment in high-pressure reactions, and environmental pollution caused by defluorination roasting.

$$\begin{gathered}\beta-\mathrm{Li_2O\cdot Al_2O_3\cdot 4SiO_2 + Na_2CO_3} + n\mathrm{H_2O \rightarrow Li_2CO_3 +} \\ \mathrm{Na_2O\cdot Al_2O_3\cdot SiO_2}\cdot n\mathrm{H_2O}\end{gathered} \tag{6}$$

Alkaline method simplifies the lithium leaching and impurity removal process, reduces chemical raw materials and energy consumption, and decreases emissions of sulfur, chlorine, etc. Meanwhile, the purified solution is convenient for the evaporation and crystallization of lithium hydroxide and the precipitation of lithium carbonate. At present, only China ENFI Engineering Co., Ltd has conducted a pilot test of the sodium carbonate autoclave method, and the result showed that the technology is feasible, has broad market prospects, and has the conditions to carry out expanded tests and semi-industrial tests (CMCA, 2020).

5. Salt roasting method

The salt roasting method has low cost, less corrosion to equipment, and fewer impurities in the leaching solution compared with the acid process, which is easy to purify. Salt reagents used by scholars mainly include carbonate, such as calcium carbonate and sodium carbonate, and sulfates, such as potassium sulfate, sodium sulfate, and calcium sulfate.

5.1. Carbonate method

The limestone roasting method was proposed by Lileev I et al. (1968) and was first successfully applied to the industrialized lithium extraction process. Its reaction is shown in Equation 7. The process flow is as follows: Spodumene and limestone are made into slurry in a certain proportion for roasting, water leaching, removal of calcium, aluminum, and other impurities, and finally lithium carbonate precipitation (Zhang JF, 2020). Scholars further studied the relationship between limestone demand and lithium recovery. The lower the spodumene grade, the greater the limestone consumption; when $CaO:SiO_2$ is 2.4–2.6, the lithium recovery rate is the highest; if the optimum ratio is exceeded, the lithium recovery rate will be decreased (Yelatontsev D and Mukhachev A, 2021), but it is beneficial to reducing the roasting temperature (White GD and McVay TN, 1958). Tu T et al. (2020) investigated the effect of sintering conditions on the leaching

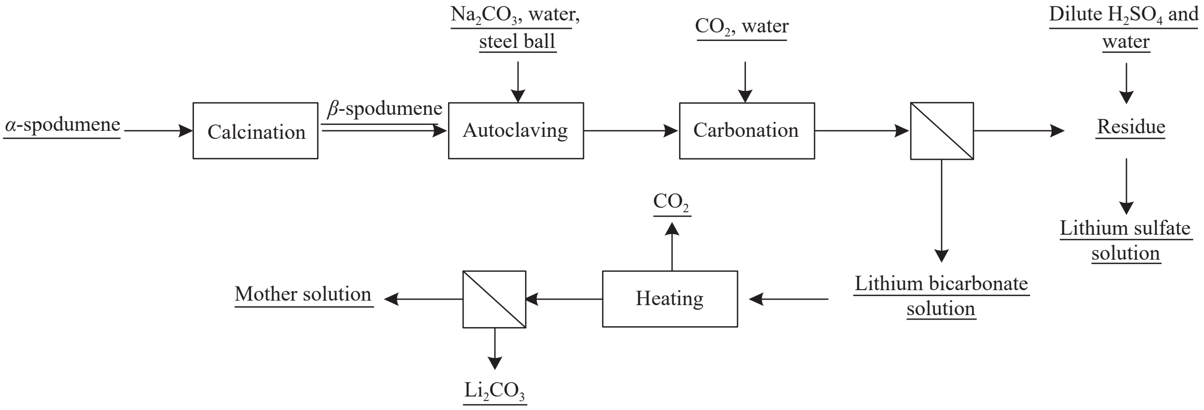


Fig. 4. Lithium recovery process of β-spodumene by sodium carbonate autoclave method (modified from Chen Y et al., 2011a, 2011b).

rate of lithium, and their results indicated that the leaching rate can reach 92.14% under the optimal conditions (spodumene/CaO ratio of 1∶1.25, sintering temperature of 1150°C, and sintering time of 60 minutes). The limestone roasting method for extracting lithium from spodumene has many problems, such as low lithium concentration (3–4 g/L), high energy consumption, large slag production, and low economy (Su H et al.,2019), which has been replaced by the sulfuric acid method.

The limestone roasting method can also be used to extract lithium from lepidolite (White GD and McVay TN, 1958; Shi Y, 1982). Sun YR (1984) studied the influences of different operating conditions, including mass ratio, roasting temperature and time, particle size, and other factors on the lithium leaching rate of lepidolite. Sun YR found that roasting temperature was the main factor, and the reaction temperature range was very narrow (830–850°C). Within the range of roasting temperature, the influences of particle size, mass ratio, and time on lithium recovery gradually decrease. Under optimal conditions, the lithium leaching rate is above 89.6% (Sun YR 1984; Table 5). The leaching rate of lithium and rubidium was more than 90% after roasting of zinnwaldite concentrate and limestone and then water leaching (Jandová J et al., 2010). However, similar studies (Siame E and Pascoe RD, 2011) failed to obtain the above results, which is due to the formation of an amorphous glass phase when calcination temperature exceeds 835°C, limiting the leaching of lithium and rubidium (Vu HB et al., 2013). The optimum leaching conditions of lithium (84%) and rubidium (91%) are roasting at 825°C and leaching at 95°C (Vu HB et al., 2013).

$$\alpha - Li_2O \cdot Al_2O_3 \cdot 4SiO_2 + 8CaCO_3 \rightarrow \beta - Li_2O \cdot Al_2O_3 + 4Ca_2SiO_4 + 8CO_2 \uparrow \tag{7}$$

Samoilov VI et al. (2008) confirmed the feasibility of extracting lithium by roasting sodium carbonate and

Table 5. Extraction of lithium from lithium-bearing ores by the salt roasting method.

Minerals	Li_2O content /%	Roasting			Leaching				Recovery/%			References
		Reagent and dosage	Temperature /°C	Time /min	Reagent	S/L ratio	Temperature /°C	Time /min	Li	Rb	Cs	
Lepidolite	4.21	Li∶Ca=1∶3–3.5, granularity: 180–200 mesh	830–850	30	–	–	–	–	>89.6	–	–	Sun YR, 1984
Zinnwaldite	2.76	Zinnwaldite∶$CaCO_3$=1∶5	825	60	H_2O	1∶10	95	60	84	91	–	Vu H et al., 2013
Spodumene	8.03	α-spodumene∶Na_2CO_3=1∶1	850	60	1.5 M H_2SO_4	–	–	300	99.80	–	–	Lee S, 2018
Spodumene	5.73	α-spodumene∶CaO=1∶1.25	1150	60	H_2O	1∶5	90	180	92.14			Tu T et al., 2020
Lepidolite	3.91	Lepidolite∶Na_2SO_4∶CaO= 40∶15∶4	950	120	H_2O	1∶2	96	120	90	–	–	Feng YL et al., 2018
Lepidolite	4.30	Lepidolite∶Na_2SO_4∶K_2SO_4∶CaO= 1∶0.5∶0.1∶0.1	850	30	H_2O	1∶2.5	Room	30	91.61	74.73	84.66	Yan QX et al., 2012b
Lepidolite	4.30	Lepidolite∶Na_2SO_4∶$CaCl_2$= 1∶0.5∶0.3	880	30	H_2O	1∶2.5	Room	30	94.80	93.50	90.10	Yan QX et al., 2012c
Lepidolite	3.90	Lepidolite∶K_2SO_4∶$CaSO_4$= 1∶0.2∶0.25	900	60	0.1 M H_2SO_4	1∶3	Room	60	95	–	–	Guo CP et al., 2014
Lepidolite	3.84	n(SO_4∶Li)=3∶1, n(Ca∶F)=1∶1,	850	90	H_2O	1∶1	Room	60	93	33.20	21.60	Luong VT et al., 2014
Lepidolite	4.20	Lepidolite∶$CaSO_4$∶Na_2SO_4 =1∶0.45∶0.15	875	60	H_2O	1∶10	80	240	>90	75	–	Vieceli N et al., 2016
Zinnwaldite	2.07	Zinnwaldite∶$CaSO_4$=2∶1	1050	60	H_2O	1∶10	85	30	84	<14	–	Siame E and Pascoe RD, 2011
Zinnwaldite	2.07	Zinnwaldite∶Na_2SO_4=2∶1	850	60	H_2O	1∶10	85	30	97	10	–	Siame E and Pascoe RD, 2011
Zinnwaldite	2.99	Zinnwaldite∶$CaSO_4$∶$Ca(OH)_2$=6∶4.2∶2	950	60	H_2O	1∶10	90	30	96	–	–	Jandová J et al., 2009
Petalite	4.37	Petalite∶Na_2SO_4=1∶1	1000	60	H_2O	1∶25	80	60	>99	–	–	Setoudeh N et al., 2020

spodumene. Almost all of the lithium and silicon and 75% of aluminum were leached at a sodium carbonate/α-spodumene ratio of 1∶1, roasting at 850°C for 1 h, and then leaching in concentrated sulfuric acid for 5 h (Lee S, 2018; Table 5). Samoilov VI et al. (2018) also tested the sodium carbonate roasting method to extract lithium from lepidolite. When the molar ratio of $SiO_2/(Na_2O+K_2O+Li_2O)$ was 2.9–3.0, the conversion rate of lithium in sulfate leaching solution was (99.2 ± 0.2)%.

The main advantage of the carbonate roasting method is that it has strong universality, does not need scarce reagents, and uses typical equipment. However, this method has high energy consumption (Kuang G et al., 2018; Margarido F et al., 2014), low lithium recovery rate, and serious resource waste (Zhang JF, 2020; Yelatontsev D and Mukhachev A, 2021). In addition, when it is used to extract lithium from lepidolite, there are some problems, such as a narrow range of suitable reaction temperatures and difficult control of operating conditions.

5.2. Sulfate method

To reduce the environmental pollution and alkali consumption of sulfuric acid method, scholars studied the extraction of lithium by the sulfate roasting method (Table 5). The process flow is to convert lithium in ore into lithium sulfate by mixing roasting lithium mineral and excessive potassium sulfate (or calcium sulfate or a mixture of both), leach with dilute sulfuric acid, and obtain lithium carbonate after purification and precipitation of lithium solution (Zhu JQ et al., 2018). Zelikman AN et al. (1966) studied the calcination of potassium sulfate and α-spodumene to extract lithium. However, this method has the disadvantage of the high cost of potassium sulfate and lithium products polluted by potassium (Zhu ZH et al., 2008). Replacing part of potassium sulfate with sodium sulfate can reduce the cost of this method. Kuang G et al. (2018) then proposed a closed-loop process of extracting lithium from β-spodumene by leaching it with sodium sulfate, which reduced the dissolution of aluminum and iron and simplified the subsequent purification process (Li H et al., 2019).

The sulfate method is mainly used to extract lithium from lepidolite. The metal ions in the sulfate occupy the structural position of lithium ions in ore, separating lithium ions from insoluble aluminosilicate to form soluble sulfate. The reaction can be expressed by Equation 8. Yan QX et al. (2012b) calcined lepidolite with potassium sulfate, sodium sulfate, and calcium oxide (1∶0.5∶0.1∶0.1) at 850°C for 0.5 h, and the lithium recovery rate reached 91.61%. Salt roasting with sodium sulfate and calcium chloride followed by water leaching was used to extract alkali metals from lepidolite. The extraction efficiency of lithium, rubidium, and cesium were all above 90% with a mass ratio of lepidolite/sodium sulfate/calcium chloride of 1∶0.5∶0.3, and roasting at 880°C for 0.5 h (Yan QX et al., 2012c; Fig. 5). Guo CP et al. (2014) studied the relationship between lithium recovery rate and the amount of potassium sulfate: The extraction rate is positively related to the amount of potassium sulfate, but its growth rate will slow down when the amount exceeds a certain proportion. The leaching rate of lithium reached 95% after calcining lepidolite, potassium sulfate, and calcium sulfate (1∶0.20∶0.25) at 900°C for 1 h (Guo CP et al., 2014). Substituting cheap sodium sulfate for potassium sulfate, and calcining with calcium sulfate and lepidolite (0.15∶0.45∶1) at 900°C, the lithium recovery rate can also reach more than 90% (Vieceli N et al., 2016), but the leaching rate of lepidolite was 84% when calcining only with calcium sulfate at 1050°C (Siame E and Pascoe RD, 2011). Scholars also tried to use other sulfates to extract lithium from lepidolite, such as iron sulfate (Luong VT et al., 2014).

$$Li_2O \cdot Al_2O_3 \cdot 3SiO_2 + K_2SO_4 \rightarrow K_2O \cdot Al_2O_3 \cdot 3SiO_2 + Li_2SO_4 \tag{8}$$

The sulfate method can also be used to extract lithium from zinnwaldite and petalite. Calcination of zinnwaldite and calcium sulfate at 975°C and then leaching with water, Kondás J and Jandová J (2006) obtained a lithium leaching rate of 93%. Subsequently, this group increased the lithium leaching rate to 96% with a mass ratio of zinnwaldite/calcium sulfate/sodium hydroxide of 6∶4.2∶2, roasting at 950°C for 1 h, and leached at an S/L ratio of 1∶10 and 90°C for 30 minutes (Jandová J et al., 2009; Table 5). Scholars also studied the effects of different sulfate and operating

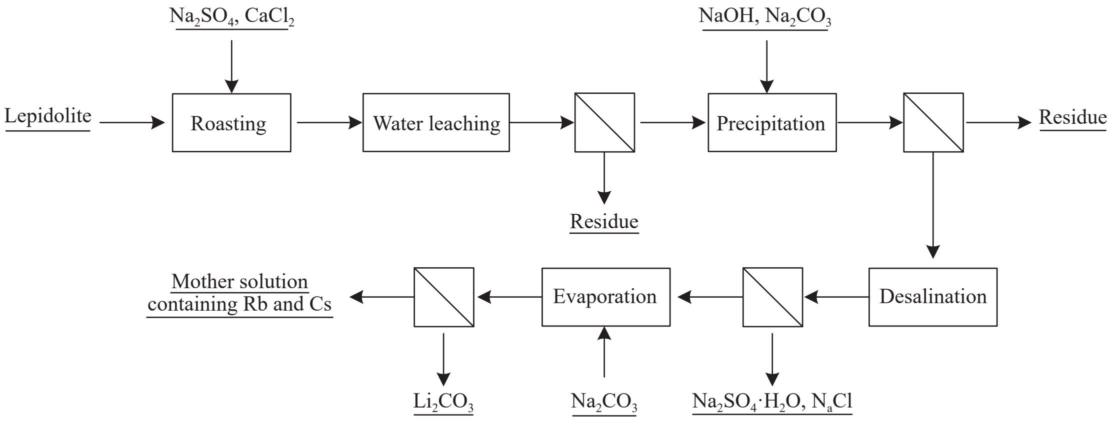


Fig. 5. Process for lithium recovery from lepidolite by sodium sulfate roasting method (modified from Li H et al., 2019; Yan QX et al., 2012c).

conditions on the lithium leaching rate of minerals. Siame E and Pascoe RD (2011) calcined zinnwaldite with sodium sulfate and calcium sulfate at 800°C and 1050°C, respectively, and the lithium leaching rate were 97% and 84%, while the rubidium leaching rate was only 14%–23% (Table 5). Setoudeh N et al. (2020) obtained that increasing reaction temperature and the proportion of sodium sulfate in the mixtures can improve the leaching of lithium from petalite. When the mass ratio of petalite to sodium sulfate was 1∶1 and calcined at 1000°C for 1 h, the leaching rate of lithium can reached 99% (Table 5).

This method uses sulfate instead of sulfuric acid, which has less corrosion to equipment but requires more energy than the sulfuric acid method due to large material flow and high reaction temperature. In addition, the process is also studying to replace potassium sulfate with cheap sulfate, but it is necessary to find a balance in adjusting the proportion of various sulfate to increase lithium recovery and reduce operating costs.

6. Chlorination method

This method uses a chlorination agent to convert lithium and other valuable metals in ore into chloride for extraction (Zhu ZH et al., 2008). The chlorinating agent used is mainly chloride and chlorine (Table 6).

6.1. Chloride method

Peterson JA and Gloss GH (1959) research showed that potassium chloride and sodium chloride can convert lithium in *α*-spodumene into soluble lithium chloride at high temperatures (>1000°C). When ammonium chloride and sodium chloride are calcined together with spodumene at 750°C, a higher conversion rate (98%) can also be obtained (Zelikman AN et al., 1966). Scholars also studied the feasibility of replacing part of chlorates with other salts, such as carbonate. Zhu ZH et al. (2008) calcined spodumene, calcium chloride, and limestone at a mass ratio of 1∶1∶3 and a temperature of 1000°C to volatilize lithium chloride and separate it from impurities, and then collected and washed lithium chloride solution to precipitate lithium carbonate (Fig. 6). The reaction of extracting lithium from sodium chloride and *β*-spodumene by chlorination roasting is shown in Equation 9. Using sodium chloride as the only chlorinating agent for extracting lithium from *β*-spodumene, Gabra GG et al. (1975) found that increasing the reaction temperature or reducing particle size could improve the lithium conversion, and the maximum lithium leaching rate was 98%. Then Barbosa LI et al. (2015) analyzed the influences of chlorination roasting temperature and time on lithium extraction rate. Under the condition of chlorination roasting of *β*-spodumene and calcium chloride at 900°C for 2 h, they attained an optimal conversion degree of 90.2%.

$$\beta-\mathrm{Li_2O\cdot Al_2O_3\cdot 4SiO_2+2NaCl+2H_2O}\rightarrow \mathrm{2LiCl+Na_2O\cdot Al_2O_3\cdot 4SiO_2\cdot 2H_2O} \tag{9}$$

Calcination of calcium chloride, calcium carbonate, and lepidolite at high temperatures (950°C) can achieve a lithium conversion rate of 80% (Vyas MH et al., 1975). Then, Xu SM and Wang XX (1993) investigated the effects of roasting temperature, time, S/L ratio, mass ratio, and other factors on the lithium extraction of lepidolite roasted with ammonium chloride, and obtained a leaching rate of 91% under the optimal conditions. Due to the low melting point of lithium, it is better to extract lithium with a mixture of calcium chloride and sodium chloride (Meshram P et al., 2014). The extraction rates of lithium, rubidium, and cesium were 92.86%, 93.60%, and 93.01%, respectively when sodium chloride, calcium chloride, and lepidolite (0.6∶0.4∶1) were calcined at 880°C for 30 minutes (Yan QX et al., 2012d). Only using calcium chloride, the leaching rate of lithium can reach 95.36% under optimized roasting (calcium chloride to lepidolite=3∶4, roasting temperature 900°C) and leaching conditions (S/L ratio=1∶3, room temperature, leaching time 40 minutes) (Liu L et al., 2021; Table 6).

6.2. Chlorine method

Chlorine is also a chlorinating agent commonly used by

Table 6. Lithium extraction from lithium-bearing ores by chlorination process.

Minerals	Li_2O content /%	Chlorination			Recovery/%			References
		Reagent and dosage	Temperature /°C	Time/ min	Li	Rb	Cs	
Spodumene	–	*α*-spodumene, NH_4Cl, NaCl	750	–	98	–	–	Peterson JA and Gloss GH, 1959
Spodumene	–	*α*-spodumene∶$CaCl_2$∶$CaCO_3$=1∶1∶3	1000	–	–	–	–	Zhu ZH et al., 2008
Spodumene	–	*β*-spodumene∶NaCl=2∶1	200	180	–	–	–	Gabra GG et al., 1975
Spodumene	7.20	n(*β*-spodumene)∶n($CaCl_2$)=1∶2	900	120	90.2	–	–	Barbosa LI et al., 2015
Lepidolite	4.65	Calcined lepidolite∶NaCl∶NH_4Cl= 1∶1∶3.5	–	–	91	–	–	Xu SM and Wang XX, 1993
Lepidolite	4.30	Lepidolite∶NaCl∶$CaCl_2$=1∶0.6∶0.4	880	30	92.86	93.60	93.01	Yan QX et al., 2012d
Lepidolite	3.23	$CaCl_2$∶lepidolite concentrate=3∶4	900	40	95.36	–	–	Liu L et al., 2021
Lepidolite	3.65	Lepidolite, Cl_2	850	180	92.49	–	–	Wu XF et al., 2012
Lepidolite	3.65	Cl_2, CaO∶lepidolite=0.7	900	30	92.50	–	–	Wu XF et al., 2012
Spodumene	7.20	Cl_2 flow rate =100 mL/min, n(Cl_2)=1, *β*-spodumene=400 mg	1100	150	100	–	–	Barbosa LI et al., 2014

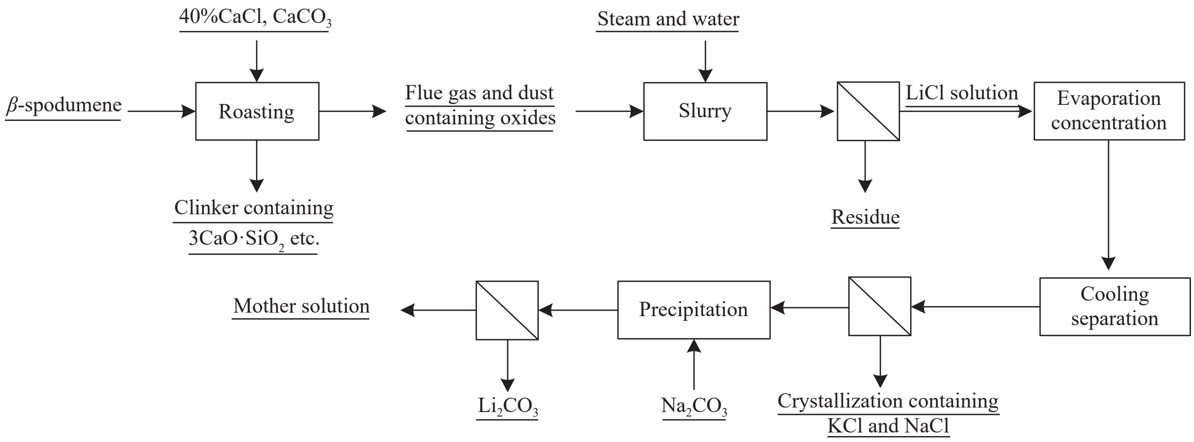


Fig. 6. Process flow chart of lithium carbonate production by chlorination roasting method (modified from Zhu ZH et al., 2008).

scholars for chlorination roasting. The extraction rate of lithium and potassium reached 92.49% and 71.06%, respectively after chloridizing roasting of lepidolite and chloride at 850°C for 3 h (Wu XF et al., 2012); Wu XF et al. (2012) also found that adding calcium oxide can improve the extraction rate of lithium and potassium and shorten the roasting time. Barbosa LI et al. (2013) investigated the effect of temperature, the mass of the sample, flow rate, and pressure on the reaction rate of the β-spodumene chlorination process. Their analysis revealed temperature and reaction time was the most important variable affecting the reaction rate, and the roasting of spodumene with pure chlorine at 1100°C for 150 minutes led to the complete extraction of lithium as lithium chloride (Barbosa LI et al., 2014).

Ganfeng Lithium once built a pilot production line for extracting lithium from lepidolite by sodium chloride chlorination roasting. The advantages of the chloride method are a short process, high lithium recovery rate, less residue, and comprehensive recovery of potassium, rubidium, and cesium. The disadvantages include severe corrosion of equipment (Peng AP and Song QR, 2016; Zhu JQ et al., 2018), high requirements for equipment, and difficulty utilization of leached residue and fluorine (Hu P et al., 2016). As a chlorinating agent, chlorine is easy to react with iron, calcium, etc., affecting the purity of the solution and product. In addition, the chorine process requires pure chlorine, and the reaction temperature is higher than that of the sulfuric acid process, which challenges its industrialization in terms of equipment, safety, energy consumption, etc.

7. Environmental impact and economy of lithium extraction from ores

7.1. Environmental impact

The sulfuric acid method is the most widely used industrial spodumene lithium extraction process, with the advantages of high yield (88%) (Kuang G et al., 2018; Rosales s GD et al., 2014), being suitable for low-grade ores (1%–1.5%), and high lithium content in the leaching solution (33–55 g/L) (Peng JZ, 2019). Raw materials required for this process include spodumene concentrate, sulfuric acid, sodium hydroxide, calcium hydroxide, sodium carbonate, water, etc. The consumption intensity of the above raw materials of a typical enterprise is 8.67 t/t, 3.02 t/t, 0.55 t/t, 0.65 t/t, 2.26 t/t, and 49.46 t/t, respectively (Jiang SY et al., 2020), which is close to the average level of China (Gu GZ and Gao TM, 2021). Energy consumption includes fossil energy in the transformation and acidification stages, and electricity and steam in the purification and evaporation stages. The comprehensive energy consumption of China ’s ore lithium extraction enterprises is 2.87 tce/t (Gu GZ and Gao TM, 2021). Pollutants mainly include NO_x, SO_2, and sulfuric acid mist generated during calcination and acidification, as well as waste residue generated in leaching and purification stages, with emission intensity of 6.67 kg/t, 7.52 kg/t, 0.90 kg/t, and 10.93 t/t, respectively (Gu GZ and Gao TM, 2021; Fig. 7). Due to the different types of fossil fuels used (coal/natural gas) and research boundaries, the emission intensity of these pollutants are somewhat different from the Jiang SY et al.(2020) ’s results. Meanwhile, the process can recover about 2.5 t/t of anhydrous sodium sulfate by-products (Gu GZ and Gao TM, 2021).

It is difficult to purify the leaching solution from lepidolite by the sulfuric acid method, the lithium yield is low, and the silicon aluminum slag generated is difficult to use, so there is no large-scale industrialization. Lithium extraction from lepidolite usually adopts the sulfate process in China. Lithium carbonate is obtained by calcining lepidolite (800–1000°C) in a certain proportion with potassium sulfate, calcium carbonate, and sodium sulfate, and then leaching, purifying, evaporating, and precipitating. According to survey data of a lepidolite enterprise in Jiangxi Province, China, the consumption intensity of lepidolite concentrate produced by lithium carbonate is 17.86 t/t, that of potassium sulfate, calcium carbonate, and sodium sulfateis 1.43 t/t, 3.03 t/t and 16.3 kg/t, and that of natural gas and electricity is 2952 m^3/t and 767 kWh/t, respectively. The lithium recovery rate (84.83%) and emission intensity of pollutants such as NO_x and SO_2 in this process are lower than those of the spodumene sulfuric acid method, but the production intensity of hydrofluoric acid and the waste residue is significantly higher

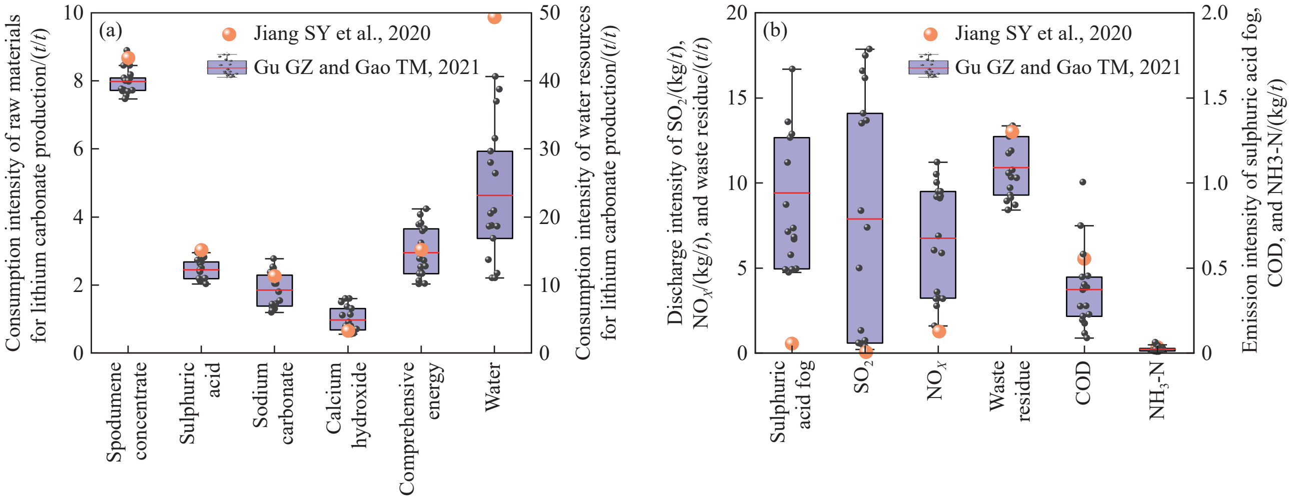


Fig. 7. Resource consumption (a) and pollutant emission (b) of lithium extraction from spodumene by the sulfuric acid method.

than that of the latter, with an intensity of 12.70 kg/t and 23.22 t/t, respectively.

In general, extracting lithium from ores requires a large amount of energy and resources, resulting in a large emission of pollutants. The impact of these pollutants on the environment is 9.3–60.4 times that of extracting lithium from brine (Jiang SY et al., 2020). Taking global warming potential as an example, the intensity of lithium extraction from ore is 15.69 tCO_{2eq}/t, 47.7 times that from brine (0.33 tCO_{2eq}/t) (Jiang SY et al., 2020).

7.2. Cost and composition

According to the raw materials consumption and enterprise operation data of extracting lithium from ores, Peng JZ (2019) estimated that the processing cost of spodumene sulfuric acid method is about 3030 $/t (20000 RMB/t), which is equivalent to the processing cost of projects in Europe and North America to extract lithium from ores, such as Cínovec (2914 $/t) in the Czech Republic and Whabouchi (2785 $/t) in Canada (Sterba J et al., 2020), but this is close to the production cost of major brine lithium extraction enterprises (ALB, SQM) (3030−3787 $/t). Due to the use of potassium sulfate, the processing cost of the lepidolite sulfate method is relatively higher, about 4545 $/t (30000 RMB/t) (Peng JZ, 2019). The composition of processing cost for extracting lithium from the above two ores is shown in Fig. 8, in which auxiliary materials such as fuel power and sulfate account for more than 75% of the processing cost. However, their production cost is highly related to the price of lithium concentrate. When the price of spodumene concentrate is 1000 $/t, the production cost of lithium carbonate is about 12.12 –13.64 k$/t (Hu Z, 2019). According to the price of spodumene concentrate in the first auction of Pilbara in 2022 (5650 $/t), it is estimated the production cost of lithium carbonate has exceeded 53030 $/t. When the price of lepidolite concentrate is 227–303 $/t, the production cost of lithium carbonate is about 10.61 k$/t (Hu Z, 2019). The above research shows that the production cost of extracting lithium from ores is closely related to the price of lithium concentrate, which is much higher than that of extracting lithium from brine.

The processing cost of lepidolite is higher than that of spodumene, but it has the advantage of comprehensive development. The comprehensive utilization of rubidium, cesium, potassium, and other metals can greatly increase the comprehensive income of lepidolite, thereby reducing the production cost of lithium carbonate. Compared with the single extraction of lithium from lepidolite and the overall extraction of multiple elements, the value of each ton of lepidolite after the overall extraction can be increased from 454 $/t to 1060−2197 $/t (Yi M et al., 2014), which means that the comprehensive development of lepidolite will significantly improve its lithium extraction competitiveness.

8. Conclusions

Lithium is the key metal for the future green economy transformation, and its demand will grow rapidly. Limited by resources and technology, China's lithium salt production is still dominated by extracting lithium from ores. To ensure the demand for lithium resources and clean and comprehensive utilization, it is urgent to develop efficient and sustainable lithium extraction processes. The research progress of extracting lithium from lithium-bearing minerals such as spodumene, lepidolite, petalite, and zinnwaldite by acid, alkali, salt roasting, and chlorination methods, and the resource consumption, environmental impact and economy of industrial extraction of lithium from spodumene and lepidolite are reviewed in this paper. The main conclusions are as follows:

(i) Sulfuric acid process is the mainstream process for extracting lithium from spodumene, with a complex process, high energy consumption, and large discharge of waste residue, waste gas, and wastewater. Therefore, it is necessary to simplify the process and reduce environmental impact. Both alkali and chlorination methods can directly react with lithium ores, reducing energy consumption and having a high lithium recovery rate. However, it is necessary to investigate the optimal reaction conditions, equipment, and safe operation to accelerate its industrialization. The salt roasting method has

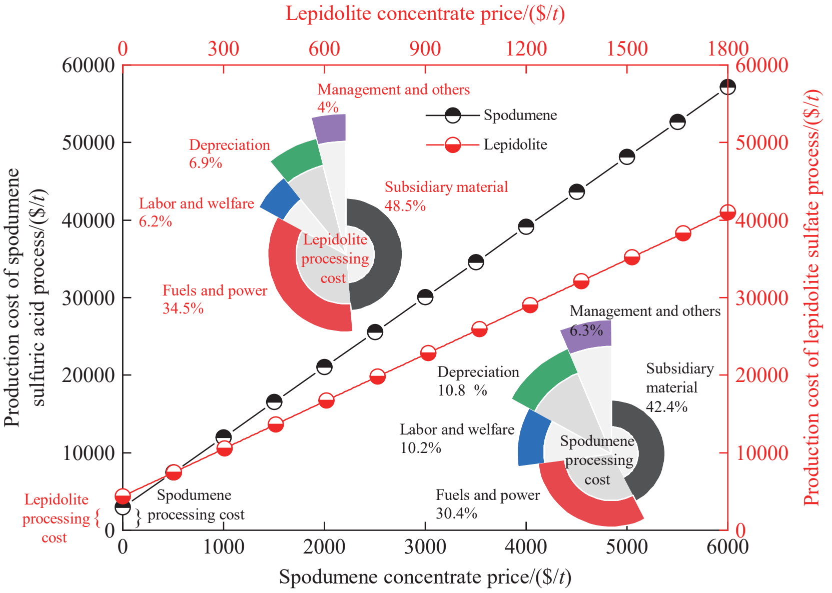


Fig. 8. Comparison of production cost between spodumene sulfuric acid and lepidolite sulfate method.

been applied to the industrial lithium extraction from lepidolite, which has a large material flux and high energy consumption. It is necessary to optimize the proportion of sulfates to improve efficiency and reduce production cost while strengthening the comprehensive utilization of other elements.

(ii) The process of extracting lithium from ores, such as calcination, leaching, and purification, requires a large number of resources and fossil energy, such as sulfuric acid/sulfate, calcium oxide, sodium carbonate, and discharges a lot of pollutants mainly from energy consumption. Therefore, the resource consumption intensity and environmental impact of extracting lithium from ores are significantly higher than that of extracting lithium from brine.

(iii) The processing cost of lithium extraction from lepidolite is higher than that of spodumene, in which auxiliary materials and fuel power account for more than 75% of the processing cost of both. In addition, the production costs of both are obviously affected by the price of lithium ores, and their competitiveness is weaker than that of extracting lithium from brine. Therefore, the acquisition of lithium ore assets and the reduction of lithium ore prices have become the main path for lithium ore extraction enterprises to reduce production costs and improve competitiveness.

Various methods for extracting lithium from lithium ores have their advantages and room for improvement. Therefore, it is necessary to strengthen the research on the process of extracting lithium from ores to save energy and improve the selectivity of lithium, develop appropriate technologies to simplify the process steps, solve the limitations of extracting all valuable metals from lithium ores, and improve the recovery of valuable elements to achieve the comprehensive utilization of associated resources and the economy and competitiveness of extracting lithium from ores.

CRediT authorship contribution statement

Tian-ming Gao designed the conceptualization, presented the idea, and wrote the manuscript with input from all authors. Na Fan contributed to the investigation, data curation, and visualization. Wu Chen carried out the sample preparation and formal analysis. Tao Dai supervised the findings of this work. All authors discussed the results and contributed to the final manuscript.

Declaration of competing interest

The authors declare no conflicts of interest.

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