

Extraction of lithium from naturally occurring Li-bearing minerals

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Abstract

Lithium (Li) production in most of advanced countries depends on primary and secondary resources. Primary resources are Li-bearing minerals and brine, while secondary resources are mainly exhausted lithium-ion batteries (LIBs). This article focuses on reviewing the research and processes related to Li extraction from different Li-bearing minerals such as spodumene, lepidolite, zinnwaldite, and petalite by different techniques. These techniques include Li extraction by acid process (sulfuric acid, hydrofluoric acid, hydrochloric acid, and nitric acid), Li extraction by alkali process (sodium hydroxide, calcium hydroxide, and sodium carbonate), Li extraction by salt roasting process (carbonate roasting and sulfate roasting) and Li extraction by chlorination process using chloride salts or chlorine gas. The flow sheets of Li extraction processes from Li-minerals are reported. These flow sheets include but are not limited to pre-treatment of the Li minerals, chemical processing, leaching (mostly in water), and separation of Li pregnant solution from insoluble residues followed by purification and Li precipitation using sodium carbonate.

Keywords: Lithium primary ores, Acids lithium extraction processes, Alkali lithium extraction processes, Sulfating processes, Chlorination processes.

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1. Introduction

Owing to the unique lithium (Li) chemical and physical properties such as high conductivity and specific heat as well as very strong chemical activity, its applications are highly increased for advanced technologies [1-3]. Li is applied for conventional old industries such as glass, ceramic, lubricants, and aluminum smelting and has recently moved to new applications such as but not limited to green energy and advanced materials [4]. In general Li minerals are indispensable raw materials for green technology, so it has been listed as critical minerals in some countries in the world. [5]. Li resources are brine Li deposits as well as pegmatite, and sedimentary rocks [6, 7]. Pegmatite Li type rocks include spodumene, lepidolite, petalite and zinnwaldite [8, 9]. Moreover, sedimentary rock minerals include jadalite, lithium clay, etc. [10]. This review article summarizes and discusses the existing technologies for Li extracting from ores.

2. Lithium resources

Lithium resources can be classified into two main resources namely primary and secondary as shown in Fig. 1. This review article focuses on primary hard rock minerals from both resources and Li extraction processes points of view. The estimated global lithium resource reserves are 22 million tons (Mt) of Li metal [11], of which hard rock Li mines represent 34% [12].

Currently, there are about 150 kinds of Li minerals [13], however, a limited number of these minerals have commercial value [14, 15]. Table 1 shows some of the main commercial Li minerals found in pegmatite in addition to the chemical formula and theoretical and practical Li% [15]. Currently, the first four minerals in Table 1 are considered the more economical raw materials for Li production. Li rocks are commonly associated with gangue minerals, namely quartz, feldspar, etc., so the content of Li is lower than the theoretical one.

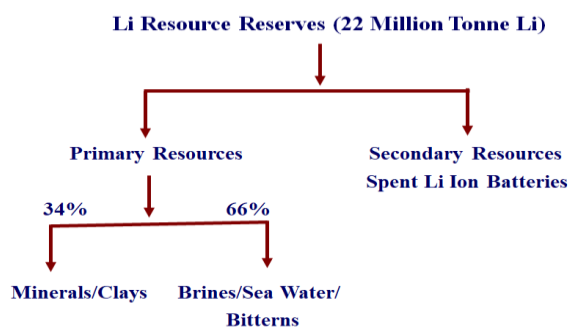


Fig. 1. Illustration of Li resources classification.

Generally, the above-mentioned minerals can be upgraded via beneficiation to obtain Li concentrate, which includes but is not limited to both gravity and magnetic separations, and froth flotation [18].

Table 1. Main commercial lithium minerals with chemical formulas and theoretical & practical Li content [16, 17].

Mineral	Chemical formula	% Lithium content	
		Theoretical	Range in commercial minerals
Spodumene	$\text{LiAlSi}_2\text{O}_6$ or $\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2$	3.73	1.9–3.3
Lepidolite	$\text{LiKAl}_2\text{F}_2\text{Si}_3\text{O}_9$ or $\text{LiF} \cdot \text{KF} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2$	3.56	1.4–1.9
Amblygonite	LiAlFPO_4 or $2\text{LiF} \cdot \text{Al}_2\text{O}_3 \cdot \text{P}_2\text{O}_5$	4.74	3.5–4.2
Triphylite	LiFePO_4 or $\text{Li}_2\text{O} \cdot 2\text{FeO} \cdot \text{P}_2\text{O}_5$	4.40	2.5–3.8
Petalite	$\text{LiAlSi}_4\text{O}_{10}$ or $\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 8\text{SiO}_2$	2.27	1.6–2.2
Zinnwaldite	$\text{LiKFeAl}_2\text{F}_2\text{Si}_3\text{O}_{10}$ or $\text{LiF} \cdot \text{KF} \cdot \text{FeO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2$	1.7	1.2–1.3
Eucryptite	LiAlSiO_4 or $\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$	5.5	2.3–3.3

α -phase spodumene occurs in nature and resists reaction with strong mineral acids except for hydrofluoric (HF) [19–20]. To activate α -spodumene to be highly reactive with acids, calcination can be applied which converts it to β -phase spodumene (high reactive). In the world, the applied research on Li extraction from petalite and zinnwaldite is less than that from lepidolite and spodumene [21].

3. Lithium (Li) extraction processes

Lithium (Li) extraction processes from hard rocks are summarized and given in Fig. 2.

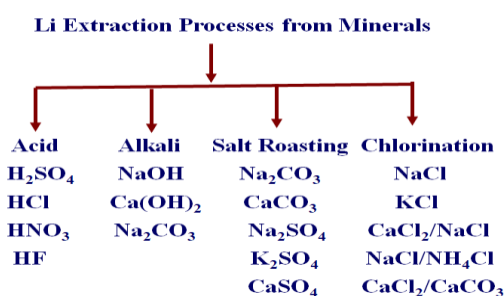


Fig. 2. The Flow-Sheet of Li Extraction Processes from Li Bearing Minerals.

Depending on the medium applied for Li leaching, roasting, and calcination, the existing processes are the acid process, alkali process, salt roasting process, and

chlorination process [20–24]. Commonly, Li_2CO_3 is precipitated by a substitution reaction with Na_2CO_3 , or Li-pregnant liquor is carbonized with CO_2 to prepare lithium carbonate, and anhydrous Na_2SO_4 is co-produced as a byproduct.

3.1. Li extraction by acid process

Li extraction by acid process can be classified according to the type of the applied acid such as:

- (1) Li extraction by sulfuric acid [25, 26],
- (2) Li extraction by hydrochloric acid [27],
- (3) Li extraction by nitric acid [28],
- (4) Li extraction by hydrofluoric acid [29, 30].

In addition, other acids are studied. For industry, the sulfuric acid process is already applied to extract Li from spodumene ores and is considered the main dominant process. HCl, HF, and other acids are less abundant processes, and some under the research stage.

3.1.1. Li extraction by sulfuric acid

A. Li Extraction from spodumene mineral

After more than 50 years of development, the Li extraction by sulfuric acid process after R&D for more than fifty years is considered the most widely applied process and has many advantages such as proven process, ease of operation and control, consistent quality, ...etc. [19, 31, 32]. The process includes calcination to convert low active α -spodumene to β -

spodumene (high active), roasting with acid, leaching with water, purification from impurities, evaporation to increase Li content, Li precipitation as carbonate, and anhydrous sodium sulfate concentration to increase supersaturation followed by crystallization.

The α -spodumene concentrate is crushed and calcined at 950–1100°C for conversion to β -spodumene. After that, an excess amount of concentrated sulfuric acid is added (1.4 times) [33] in a rotary kiln at temperatures from 250°C to 300°C to form water-soluble lithium sulfate. Then the roasted Li-bearing mineral is leached with water at 90°C, neutralize the excess sulfuric acid with ground limestone (calcium carbonate) [34], then adjust the pH to be in the range of 7–10 for iron and aluminum impurities removal [35]. The obtained crude lithium sulfate solution has about 10% Li₂O content [36–38]. After that, lime milk should be added to the crude Li solution to remove most of the magnesium ions, and the pH of the solution is adjusted to an alkaline medium in the range of pH 11–12 [35, 37, 38].

Moreover, during the final stage of purification, the remaining impurities of calcium, magnesium, and others are removed by adding sodium carbonate [20]. Then, the crude Li pregnant liquor is evaporated for concentration followed by filtration to obtain a purified Li₂SO₄ solution of more than 20 % Li₂O content [39]. In the final stage, Li₂CO₃ is precipitated by substitution reaction during the addition of a stoichiometric amount of Na₂CO₃ to Li₂SO₄ solution followed by centrifugation to separate wet Li₂CO₃ followed by drying to obtain lithium carbonate product.

The separated mother liquor -containing sodium sulfate- is concentrated by evaporation under vacuum and crystallized to produce anhydrous sodium sulfate. The condensed water vapors are returned to the leaching process.

In previous research, the calcination temperature and sulfuric acid consumption were reported but covered a wide range. For example, in an old patent [26] it was reported that the calcination temperature, sulfuric acid dosage, and acid roasting temperature ranges were 1000–1350°C, 1.3–2.4 times the theoretical value, and 250–300°C, respectively, while in a recent paper [40], the results of the previous parameters were 1050°C for 30 minutes, 1.4 times the theoretical value, and 250°C lasting for 30 minutes, respectively.

The optimum conditions of water leaching are:

Solid to liquid (S/L) ratio 1:1.85,

Reaction temperature ambient (room temperature)

Reaction time lasting for 15 minutes,

The Li reaction efficiency was 96.93% [40].

The problem of excess sulfuric acid consumption was solved [41] by leaching with dilute sulfuric acid, precipitating calcium ions by adding sodium oxalate, precipitating magnesium hydroxide by reacting with sodium hydroxide, reducing the contents of sulfates, heavy metals, and other impurities, as well as improving the quality of Li₂CO₃.

Recently, the effect of operating conditions on the Li₂CO₃ precipitation efficiency and purity was studied [42]. The applied optimum operating conditions are the concentration of both reactants (Li₂SO₄ and Na₂CO₃) was 2 mol/L, reacted at a temperature of 45 °C, and stirred under 300 ppm stirring speed. Li₂CO₃ precipitation recovery and purity were 90.0% and 99.0%, respectively [42]. Fig. 3 shows the flow-sheet of lithium extraction from spodumene minerals using the sulfuric acid process.

The main physical and chemical reactions during the sulfuric acid process are:

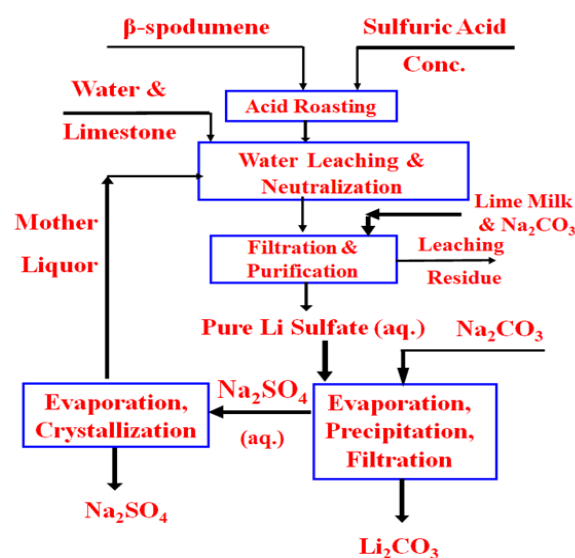
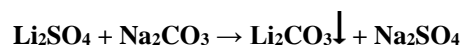
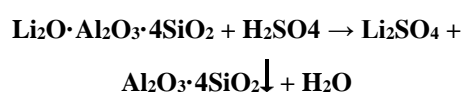
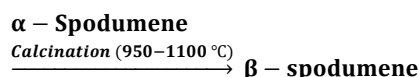


Fig. 3. The Flow-Sheet of Li Extraction from Spodumene Mineral Applying Sulfuric Acid Process.

B. Li Extraction from lepidolite mineral

Li extraction from lepidolite by the sulfuric acid method was studied [43]. The main results reveal that the optimum extraction conditions are:

Calcination temperature: 900 °C

Sulfuric acid concentration: 70 %

Mass ratio: 1:1

Reaction time: 15 min.

Reaction temperature: 130 °C

These conditions gave Li leaching efficiency of only 75%

Four years after the previous research, a direct reaction of lepidolite with sulfuric acid was studied [44]. The main applied conditions and the results are:

Lepidolite mineral; particle size: 100% less than 150 mesh (0.10 mm)

Sulfuric acid concentration: 55 %

Mass ratio: 2:1

Reaction time: 9 hours.

Reaction temperature: 135 °C

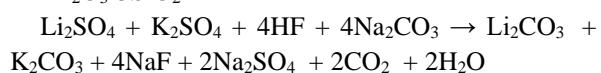
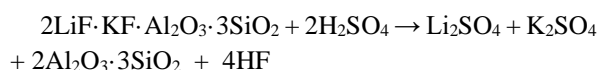
These conditions gave a very high Li leaching efficiency of about 96.7%

The problems that arise from this method are large residual sulfuric acid and long retention time of reaction that needs voluminous reactors and large surface area of filters (high costs).

The sulfuric acid process can adapt to other raw materials of Li minerals such as zinnwaldite, petalite, and ores with Li₂O content down from 1.0 to 1.5% only [45,46]. The disadvantages of this process are the high consumption of sulfuric acid and the co-production of low-value sodium sulfate via the consumption of high-value sodium carbonate [47]. In addition, the costs of energy consumption and waste residue discharge are relatively high.

In China, at 2021 the consumption and production pattern for this process was calculated [4]. It was found that sulfuric acid consumption, energy consumption, and water consumption are 2.29 t/t, 2.87 tce/t, and 20.93 t/t, respectively. However, the disposal of huge amounts of waste gas and wastewater of relatively high contents of pollutants such as 0.35 kg/t COD, 11.39 kg/t SO₂, and 0.83 kg/t sulfuric acid mist as well as 10.45 t/t leached residue [4].

The chemical reaction equations for extraction of Li from lepidolite (LiKAl₂F₂Si₃O₉ or LiF·KF·Al₂O₃·3SiO₂) are given below:



3.1.2. Li extraction by hydrofluoric acid

Li was extracted from α -spodumene after a reaction with HF acid at a relatively low temperature. In parallel, the intermediate products (Li₃AlF₆ and AlF₃ can dissolve in sulfuric acid [48]. Li recovery from this process was 95.7% [48]. Guo H et al. (2017) applied this method to extract the lithium from α -spodumene. The applied operation conditions are [49]:

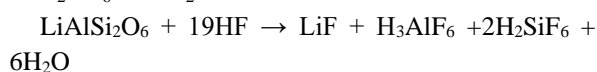
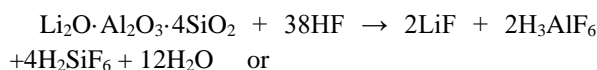
Mass ratio of spodumene: HF acid: H₂SO₄ acid = 1:3:2

Reaction temperature: 100°C

Reaction time: 3 h

The obtained Li recovery was 96%.

Fluosilicic acid can be dissociated to provide the HF acid required for the reaction [50]. Also, a mixture of Fluosilicic acid and Sulfuric acid can be used for Li leaching]. from lepidolite [49, 50]. The results revealed that applying the optimum conditions gave Li recovery of 97.9% [49, 50]. Extracting of Li from lepidolite mineral using HF acid was tested [51]. The advantages are low energy consumption and low material consumption as well as utilization of by-products [52].



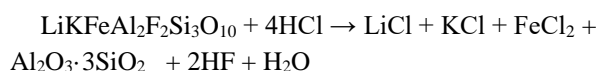
3.1.3. Li extraction by hydrochloric acid

On laboratory scale tests, Li extraction from β -spodumene was studied using hydrochloric acid [27]. The achieved results showed that with increasing HCl concentration, a high increase in the Li leaching (reaction) efficiency [27]. The chemical reaction equation is suggested as mentioned below:



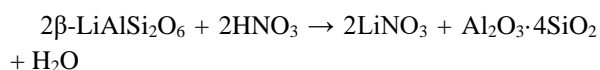
Also, in another lab study, HCl was used to leach Li from zinnwaldite Li-bearing mineral [45]. Li leaching efficiency was 94% after 6 hours of reaction time using 29% HCl concentration which is above azeotropic concentration of HCl (about 20%). So, HCl gas can easily be released while heating. After that, the obtained solution was concentrated for purification (removal of impurities). Then, sodium carbonate was added to the purified solution for Li₂CO₃ precipitation. The achieved total Li yield (Li recovery) was about 70% [45].

The suggested chemical reaction equation is mentioned below. In addition, the F in lepidolite mineral will evolve as HF acid highly corrosive to the equipment.



3.1.4. Li extraction by nitric acid

In a laboratory scale study, Li was extracted using nitric acid similar to HCl acid from β -spodumene [26]. The obtained LiNO_3 recovery was about 95% at 170 °C in an autoclave reactor under pressure of 2 MPa [26]. The chemical reaction equation is suggested as mentioned below:



3.2. Li extraction by alkali process

For the reduction of energy consumption and Li extraction cost of the sulfuric acid process, different alkaline and relatively cheap materials are tested. The alkaline chemicals are mainly NaOH, $\text{Ca}(\text{OH})_2$ and Na_2CO_3 . These alkaline materials can react with Li minerals or calcined Li minerals.

3.2.1. Li extraction by sodium hydroxide process

A. Li Extraction from spodumene mineral

Li mineral α -spodumene without calcination can be reacted with sodium hydroxide hydrothermally to convert into hydroxy sodalite $\{\text{Na}_4\text{Al}_3\text{Si}_3\text{O}_{12}(\text{OH})\}$. The Li metasilicate from the ore is released into the solution followed by precipitation for recovery [21, 22]. The optimum conditions of alkali hypothermal leaching are [53]:

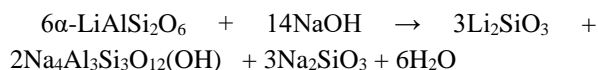
Sodium hydroxide concentration: 600 g/L

Reaction timer: 2 h

Reaction temperature: 250°C

S/L ratio, g/mL: 1:5

The achieved Li leaching reaction efficiency was 98.5% [53]. Fig. 4 shows the flow-sheet of lithium extraction from spodumene minerals using the sodium hydroxide process. The main chemical reaction equation is given below [53].



B. Li Extraction from lepidolite mineral

Li-bearing mineral (Lepidolite) can react with sodium hydroxide for extracting Li using an autoclave reactor (under pressure). By applying the following conditions; the achieved Li recovery was 98.2% [54]:

Lepidolite: 100% NaOH S/L Ratio, w/w: 1: 1.75

NaOH concentration, %: 50

Reaction time, hr: 4

Reaction temperature, °C: 190

After 6 years, both Wang D and Chen S [55] modified their previous operating conditions to be cost-effective. The applied Li extraction operation conditions are given below.

Lepidolite: 100% NaOH S/L Ratio, w/w: 1 : 1.2

Lepidolite particle size, % -150 μm : 100

NaOH concentration, %: 50

Reaction time, hr: 2

Autoclave pressure, MPa: 9

The achieved Li recovery was 96.9% [55]. Moreover, the F in lepidolite will not evolve the high corrosive HF acid while NaOH leaching thus avoiding the corrosion.

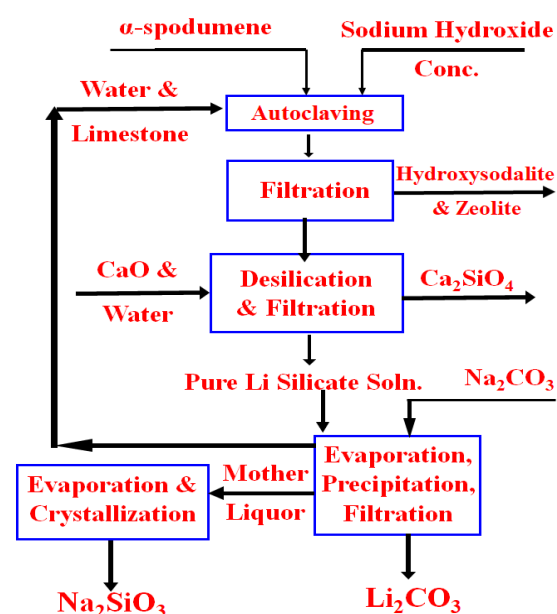


Fig. 4. The Flow-Sheet of Li Extraction from Spodumene Mineral Applying Sodium Hydroxide Process.

3.2.2. Li extraction by calcium hydroxide process

Li-bearing mineral (Lepidolite) can react with calcium hydroxide after calcination at 860 °C for half an hour. Then defluorination of lepidolite is performed followed by leaching with lime milk using an autoclave reactor. The applied Li extraction operation conditions are given below.

Calcination temperature of lepidolite, °C: 860

Calcination time, min.: 30

Partially defluorinated lepidolite: $\text{Ca}(\text{OH})_2$: 1 : 1

S/L Ratio, g/mL: 1 : 4

Reaction time, hr: 2

Reaction temperature, °C: 150

The achieved Li recovery was 98.9% [56].

Li bearing mineral (Petalite $\text{LiAlSi}_4\text{O}_{10}$) can react with calcium hydroxide and sodium hydroxide using autoclave reactor [15]. The applied Li extraction operation conditions are given below.

Stoichiometric $\text{CaO} : \text{SiO}_2$ ratio: 1 : 1

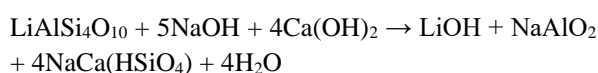
NaOH concentration, Na_2O g/L: 400-500

Reaction pH: 14

Reaction temperature, $^{\circ}\text{C}$: 280

Reaction time, min.: 30-60

The achieved Li recoveries ranged from 89-91%. Moreover, the chemical reaction equation is given below [15]:



3.2.3. Li extraction by sodium carbonate process

Li-bearing mineral (β -spodumene) can react with calcium carbonate using an autoclave reactor. The applied Li extraction operation conditions are given below.

Stoichiometric $\text{Na} : \text{Li}$ ratio equivalent to: 1.25

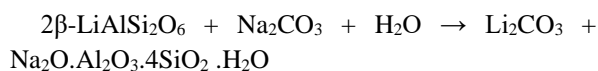
Na_2CO_3 concentration, g/L: 105

Solid/Liquid ratio: 1 : 4

Reaction temperature, $^{\circ}\text{C}$: 225

Reaction time, hr.: 1

The achieved Li recovery was > 94%. Moreover, the chemical reaction equation is given below [14, 57, 58]:



In 2020 Chinese Company (ENFI Engineering, Ltd) carried out pilot tests of the sodium carbonate process using an autoclave reactor. They proved that; this process is technologically feasible and the applied conditions can be scaled up and tested for semi-industrial level [59]. Fig. 5 shows the flow-sheet of lithium extraction from calcined spodumene minerals using the sodium carbonate process.

3.3. Li extraction by the salt roasting process

Li extraction by the salt roasting process has the following advantages:

- * Low corrosion rate of equipment
- * Low levels of impurities leached to the solution
- * Easy to purify Li-bearing solution
- * Relatively cost-effective process

Different salts can be used for roasting. These salts include sulfates such as sodium sulfate, potassium sulfate, and calcium sulfate as well as carbonates such as sodium carbonate and calcium carbonate.

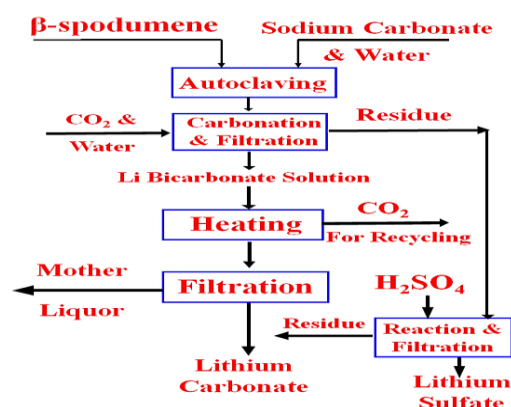


Fig. 5. The Flow-Sheet of Li Extraction from Spodumene Mineral Applying Sodium Carbonate Process.

3.3.1. Li extraction by carbonate roasting process

Li-bearing mineral (α -spodumene) is roasted with calcium carbonate followed by leaching with water. The optimum applied Li roasting and leaching operation conditions are given below.

α -spodumene : CaO ratio: 1 : 1.25

Roasting temperature, $^{\circ}\text{C}$: 1150

Roasting time, hr.: 1

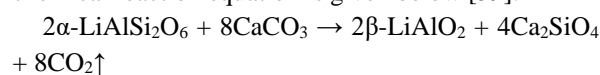
Leaching reagent: water

Solid/Liquid ratio: 1 : 5

Leaching temperature, $^{\circ}\text{C}$: 90

Leaching time, hr: 3

The achieved Li recovery was 92.1%. Moreover, the chemical reaction equation is given below [59]:



Also, α -spodumene mineral can be roasted with sodium carbonate followed by leaching with dilute sulfuric acid. In the following, the optimum applied roasting and leaching conditions are given.

α -spodumene : sodium carbonate ratio: 1 : 1

Roasting temperature, $^{\circ}\text{C}$: 850

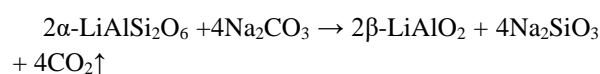
Roasting time, hr.: 1

Leaching reagent: sulfuric acid

H_2SO_4 concentration, M: 1.5

Leaching time, hr: 5

The achieved Li recovery was 99.8%. Moreover, the chemical reaction equation is given below [60]:



Recently, a review on Li extraction efficiency from spodumene-bearing pegmatites was reported [61]. This

review includes data about geological reserves as well as the beneficiation of spodumene minerals.

3.3.2. Li extraction by sulfate roasting process

Li-bearing mineral is roasted with calcium sulfate, potassium sulfate, or sodium sulfate, or a mixture of two of these salts followed by leaching with water or dilute sulfuric acid. Li is leached as lithium sulfate solution followed by purification and precipitation of lithium carbonate.

Li in lepidolite mineral can be roasted with sodium sulfate, potassium sulfate, and calcium oxide at 850 °C. Then, solid liquid separation is performed followed by purification of Li pregnant liquor for precipitation of Li as carbonate. The applied Li extraction operation conditions are given below.

Roasting temperature, °C: 850

Lepidolite: sodium sulfate: potassium sulfate: CaO Ratio: 1: 0.5: 0.1: 0.1

Roasting time, min.: 30

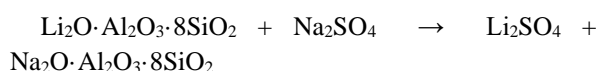
Leaching reagent: Water

S/L Ratio, g/mL: 1 : 2.5

Reaction temperature, °C: Ambient

Reaction time, min.: 30

The achieved Li recovery was 91.6% [62]. The chemical reaction between Li mineral (Petalite) and sodium sulfate is given below [63]:



The extraction operation conditions of the previous reaction are given below.

Roasting temperature, °C: 1000

Petalite : sodium sulfate ratio: 1 : 1

Roasting time, min.: 60

Leaching reagent: Water

S/L Ratio, g/mL: 1 : 25

Reaction temperature, °C: 80

Reaction time, min.: 60

The achieved Li recovery was >99% [63].

Fig. 6 shows the flow-sheet of lithium extraction from roasted lepidolite mineral with sodium sulfate carbonate process.

3.4. Li extraction by the chlorination process

Li-bearing minerals can be chlorinated to convert Li into lithium chloride for extraction [38]. Chlorination can be achieved by sodium chloride, calcium chloride, or a mixture of them, the mixture from sodium chloride and ammonium chloride, the mixture from calcium chloride and calcium carbonate, or chlorine gas [35].

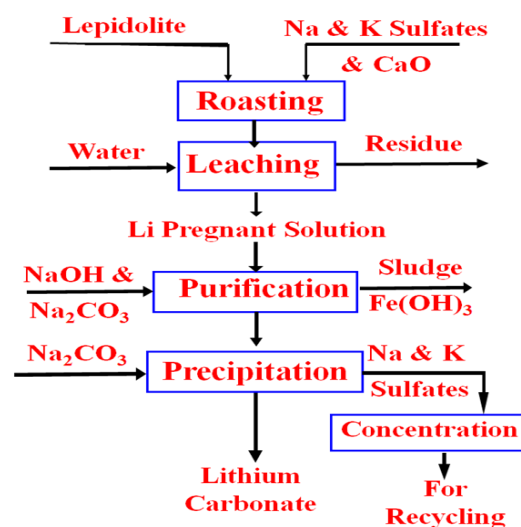


Fig. 6. Flow-Sheet of Li Extraction from Lepidolite Mineral using Sulfate Roasting Process.

3.4.1. Li extraction by chloride salt process

Lithium in α -spodumene can be reacted with a mixture of sodium chloride and ammonium chloride to form soluble lithium chloride at 750 °C. The achieved Li recovery was 98% [64]. In addition, Li in β -spodumene can be chlorinated with calcium chloride under the following operation conditions.

β -spodumene : CaCl_2 ratio: 1 : 2

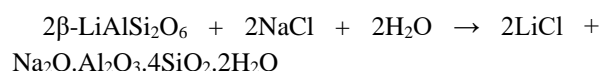
Chlorination reaction temperature, °C: 900

Chlorination reaction time, hr.: 2

Leaching reagent: water

The achieved Li recovery was 90.2% [65].

The chemical reaction equation of chlorination of Li in β -spodumene with sodium chloride is represented below [66].



Using sodium chloride and calcium chloride for chlorinating of lepidolite mineral to extract Li was performed under the following conditions.

Lepidolite : NaCl : CaCl_2 ratio: 1 : 0.6 : 0.4

Chlorination temperature, °C: 880

Chlorination time, hr: 0.5

Under these conditions of chlorination, the achieved Li recovery was about 92.9% [67]. In addition, Li in lepidolite can be chlorinated with calcium chloride under the following operation conditions.

Lepidolite : CaCl_2 ratio: 1 : 0.75

Chlorination reaction temperature, °C: 900

Chlorination reaction time, min.: 40

Leaching reagent: water

The achieved Li recovery was about 95.4% [68].

The chemical reaction equation for extraction of Li from lepidolite ($\text{LiKAl}_2\text{F}_2\text{Si}_3\text{O}_9$ or $\text{LiF} \cdot \text{KF} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2$) using the calcium chloride chlorination process is given below:

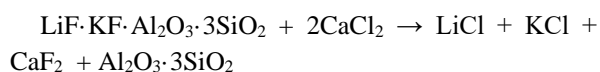


Figure 7 shows the flow sheet of Li extraction from lepidolite minerals using the calcium chloride chlorination process [68].

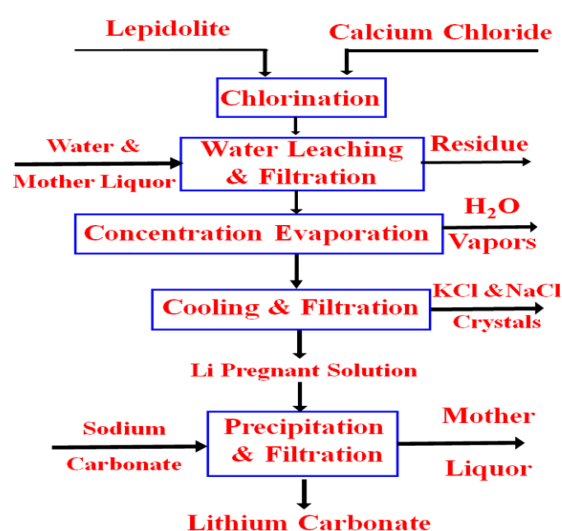


Fig. 7 Flow-Sheet of Li Extraction from Lepidolite Mineral using Calcium Chloride Chlorination Process

Recently, a green method for chlorination roasting of clay-bearing Li metal was performed [69]. The optimum process parameters were: 800 °C roasting temperature, 2 h roasting time, 1:0.5 mass ratio of the clay to CaCl_2 , 90 °C water leaching temperature, 3 h leaching time, and 1:15 solid-liquid ratio. The achieved recovery of Li was 92.35 %.

3.4.2. Li extraction by chlorine gas process

Lithium in lepidolite was chlorinated with chlorine gas in the presence of CaO under the following operation conditions.

Lepidolite : Cl_2 , CaO ratio: 1 : 0.7

Chlorination reaction temperature, °C: 900

Chlorination reaction time, min.: 30

The achieved Li recovery was 92.5% [70].

Furthermore, for basic studies Li in β -spodumene was chlorinated with chlorine gas under severe conditions of temperature (1100 °C) and a high chlorine gas flow rate of 100 mL/min for 150 minutes. The obtained Li recovery was 100% [71, 72].

4. Conclusions

Lithium is an important metal for altering to green economy in the near future. Consequently, Li demand will increase rapidly. Li extraction methods from different Li-bearing minerals are reviewed. Most Li extraction techniques are on the laboratory scale. However, some data about Li extraction on semi-industrial and industrial scales are briefly described and reported. The 202ed processes are Li extraction by acid process (sulfuric acid, hydrofluoric acid, hydrochloric acid, and nitric acid), Li extraction by alkali process (sodium hydroxide, calcium hydroxide, and sodium carbonate), Li extraction by salt roasting process (carbonate roasting and sulfate roasting), Li extraction by chlorination process using chloride salts or chlorine gas. This review research focuses on extracting Li from lithium-bearing minerals such as lepidolite, spodumene, petalite, and zinnwaldite by the previously mentioned methods. The flow sheets of industrial Li extraction from lepidolite and spodumene are presented. The applied technology depends on the type, nature, and composition of the Li-bearing mineral. The results show that Li extraction using sulfuric acid is the main process for extracting from spodumene minerals.

The salt roasting process has been scaled up and applied on the industrial level for Li extraction from lepidolite. The process has relatively low energy consumption. In general, Li extraction costs from lepidolite minerals are relatively higher than that of spodumene minerals. In addition, the capital and operation costs as well as the environmental impact of Li extraction from minerals are significantly higher than that of Li extraction from brines.

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