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REVIEW PAPER

Review of technology for lithium production from mineral raw materials

*Feruza Berdikulova [1], Akmaral Serikbayeva[2], Sholpan Akilbekova[1], Nazira Seidakhmetova[1, *]*

[1] *RSE National Center on Complex Processing of Mineral Raw Materials of the Republic of Kazakhstan, Almaty, Almaty Province, Kazakhstan*

[2] *Caspian State University of Technology and Engineering named after Sh. Yessenov, Yessenov University, Aktau, Mangystau, Kazakhstan*

**Corresponding author: erkej@mail.ru, tel.: +7 778 203 4223, 050036, Almaty, Kazakhstan*

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ABSTRACT

Rapid global electrification, nuclear power expansion, and nuclear energy will undoubtedly increase the demand for lithium. This article provides a detailed analysis of existing technologies for extracting lithium from various natural resources: spodumene, lepidolite, and sea salt, among other minerals. The technologies are summarised by the feedstock processing method. The article evaluates the various methods' economic feasibility, complexity, and technological viability. It also discusses promising methods for extracting lithium from low-grade resources that may transition from off-balance to on-balance categories. This article also presents a "future outlook", highlighting research gaps, possible technological improvements, and sustainability considerations.

Keywords: lithium, spodumene, lepidolite, joint processing, brine.

1. INTRODUCTION

Lithium has emerged as a crucial element in the past decade due to its role in technological advancements, particularly in electric vehicles and high-capacity batteries. Lithium is also important for mankind's gadgets and is used in small batteries in laptops and mobile phones. Experts predict lithium demand to triple by 2025, ensuring its continued status as a valuable resource [1,2].
According to the International Energy Agency (IEA) [3], Demand forecasts cover both clean energy and other uses, focusing on three IEA Scenarios: the Stated Policies Scenario (STEPS), the Announced Pledges Scenario (APS), and the Net Zero Emissions by 2050 (NZE) Scenario. Supply forecasts are based on a detailed analysis of all projects announced (**Fig. 1**). They show how the current geographic concentration of mining and refining activities changes over time and how expected supplies compare to primary supply needs in climate-sensitive scenarios.

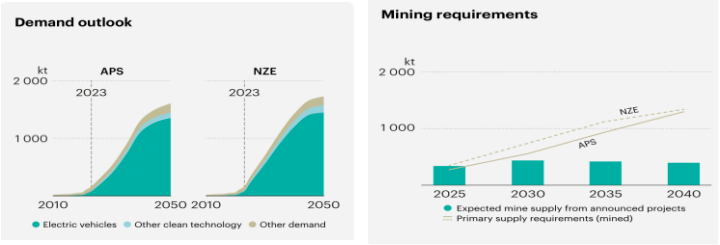

Fig. 1 The Announced Pledges Scenario (APS) and the Net Zero Emissions by 2050 (NZE) Scenario

As seen in the figures, batteries are still the leader in consumption. Lithium has technological applications and is used for other needs (lubricants, air purification, medicine, etc.).
According to the US Geological Survey's (USGS) published annual report, "Mineral Commodity Summaries, January 2025" [4], world lithium reserves have increased due to additional exploration and recalculation and now amount to 115 million tons (**Table 1**).
Due to low lithium prices, many lithium projects were delayed or cancelled in 2024, but production capacity has been expanded in Argentina, Chile, China, and Zimbabwe.

Table 1 The world reserves of lithium

Resources	Million tons	Resources	million tons	Resources	million tons	Resources	million tons
United States	19	Canada	5,7	Mali	1,2	Portugal	0,27
Argentina	23	Germany	4	Serbia	1,2	Namibia	0,23
Bolivia	23	Congo (Kinshasa)	3	Peru	1	Ghana	0,2
Chile	11	Mexico	1,7	Russia	1	Austria	0,06
Australia	8,9	Brazil	1,3	Zimbabwe	0,86	Finland	0,05
China	6,8	Czechia	1,3	Spain	0,32	Kazakhstan	0,045

By nature, lithium is the lightest chemically active natural metallic element. It is silvery white and very soft. Its density is only 0.534 g/cm^3, even lighter than water [5]. Lithium is usually present in the earth's crust as a compound with a content of approximately 0.0065 wt.%. Mankind had known of its existence since 1817, when the Swedish mineralogist Johan August Arfvedson discovered the substance. Metallic Li was first mined in 1818 by the British chemist Sir Humphrey Davy [6,7].
The main sources for the industrial realization of lithium are salt (chloride-sulfate, carbonate, chloride-nitrate) resources, pegmatite (spodumene, lepidolite, cinnwaldite, etc.) ores and sedimentary (bauxite, coal, kaolin, etc.) mineral resources [8]. Clay-type resources and natural brines are also of industrial interest [9]. Lithium is ideal for making high charge density batteries because it has all elements' highest standard positive oxidation potential, with a voltage of 3.05 V at 25 °C and an electrochemical equivalent of 13.9 kcal/g [10,11]. Lithium consumption in batteries is increasing by 15-20 % per year, already exceeding 60% of the total global lithium consumption in 2023. Other important applications of this metal are carbonate, hydroxide, chloride and other organic and inorganic compounds, representing 25 per cent of global consumption [12,13].
The demand for lithium will increase shortly due to the rapid development of global electrification and controlled nuclear fusion. Therefore, lithium from all possible lithium resources is being actively researched, and the main focus is on secondary lithium resources, namely, the development of ways to recycle spent lithium batteries [14-16]. However, the organisation of lithium production from waste batteries cannot yet compare with the scale of lithium production from natural resources. Lithium extraction technology from natural resources must be

improved to improve the overall efficiency of the processing stages and the lithium recovery rate. This article provides an overview of lithium recovery from natural resources.

2. RECOVERY OF LITHIUM FROM MINERALS

Natural lithium minerals mainly exist as aluminosilicate pegmatites, formed due to slow and complete crystallisation differentiation of highly volatile magma under certain conditions. Strong metasomatism is observed during the formation of the pegmatites. The metasomatism belt contains minerals such as quartz, albite, spodumene, mica, beryl, niobium-tantalite, caesium garnet, apatite and uranium minerals. The most typical lithium minerals of industrial importance among the above minerals are spodumene and lepidolite [17-19].

2.1 Preparation of lithium compounds from spodumene

One of the main sources of lithium is lithium pyroxenes, such as double lithium-aluminium pyroxenes 'spodumene' with the chemical formula $LiAl(SiO_3)_2$ or Li_2O-Al_2O_3-$4SiO_2$. Spodumene is a greyish-white mineral; depending on the content of impurities, the shade varies from yellowish to greenish [20]. Spodumene's chemical composition (mass fraction) is 3.0-7.6 % Li_2O, 25-30 % Al_2O_3 64.0-70 % SiO_2 [21-23]. Spodumene is a monoclinic crystal, often columnar, granular or lamellar, with a hardness of 6.5-7.0 and a 3.03-3.33 g/cm3 density. Nearly all lithium extraction technologies for spodumene involve spodumene enrichment, thermal activation, conversion of lithium to a water-soluble form, aqueous leaching of lithium and lithium product recovery.
Several methods are used to extract lithium from spodumene. The most common ones are:
Several methods are used to extract lithium from spodumene. The most common ones are:
1. The phase change and acid leaching method involve roasting, dissolving the resulting material, precipitation and purification. Spodumene is roasted at temperatures around 1000–1100°C, which converts it into a soluble compound. After roasting, the material is treated with sulfuric or hydrochloric acid. This results in the formation of a soluble lithium salt compound. The lithium is then precipitated and purified using various methods such as solvent extraction or ion exchange;
2. The high-temperature pyrometallurgical method involves roasting by adding fluxes (such as lime) to convert the mineral into a soluble compound. Reducing agents such as carbon are added during roasting to produce metallic lithium or its compounds;
3. The direct leaching method involves leaching spodumene with strong acids or pressure leaching. Then lithium is precipitated and purified using various techniques such as solvent extraction or ion exchange;
4. Flux roasting method also involves temperature. Still, the emphasis is on chemical reactions with fluxes (NaOH, KOH, Na_2CO_3, NaCl, Na_2SO_4, etc.), which reduce the melting point of spodumene and speed up its processing.
5. The microwave roasting method is a newer and more promising method that uses microwave ovens to roast spodumene. Microwave radiation can speed up the lithium extraction process and improve its recovery compared to traditional methods, as it allows for temperature control and reduced energy consumption. This method is still under active research, but it promises to be more efficient and environmentally friendly than traditional methods, as it reduces energy costs and processing time.
Each method has advantages and disadvantages, depending on the technologies used, cost, availability of raw materials, and environmental standards.

2.1.1 Spodumene ore enrichment

Before thermal treatment, the spodumene mineral undergoes a beneficiation stage. This process uses classical beneficiation methods, which combine jaw crushers, cone crushers, and high-pressure roller mills.
Using a local closed circuit crushing process with a linear vibrating screen to implement particle size control in the selection of coarse minerals, and then after the material is crushed in high-pressure rollers into pulp, it is sorted on a linear vibrating screen - mineral processing in heavy media- magnetic separation, and then the ore is crushed and sorted, and a spiral chute and shaker and a cylindrical magnetic separator are used for re-screening and sorting. [24-26].

Flotation of spodumene ore with lithium oxide content of 0.5-1.5% yields spodumene concentrate with lithium oxide content of 3.0-4.5%, with lithium oxide recovery of 60-70%. In mining, several tens of millions of tons of ore with lithium oxide content of about 0.25-0.30% accumulate in off-balance ore dumps, which can be used in processing [27]. However, direct flotation of off-balance sheet ores according to the known technology does not give the required indicators regarding the quality of the obtained concentrates and Li_2O extraction from them. Lithium oxide content in the concentrate does not exceed 2.0-2.5%, and the recovery is only about 30%.
The solution of the set task is achieved by the fact that before flotation enrichment is carried out, preliminary enrichment by methods of lump radiometric separation, due to *radiometric separation methods* (RMS), the content of Li_2O in the commercial product entering the flotation is increased to 0.55-0.60%. For the flotation of mica and other contaminating mineral impurities from spodumene concentrate without reducing the indicators, a cationic collector Sonkor was used [28]. Technical efficiency of the proposed method of lithium extraction consists in the transfer of off-balance dump ores into the category of balance ores, reduction of costs for crushing and grinding of ore due to the withdrawal of about 70% of separation tailings from the process of processing of dump ores.
The ore with a high alkaline impurity, such as calcium and magnesium, is pre-treated to create a high-quality spodumene concentrate. Spodumene ores with a high calcium and magnesium content are alternately subjected to photoelectric desalination from calcium and magnesium and flotation desalination, obtaining decalcified magnesium flotation essence [29].

2.1.2 The high-temperature pyrometallurgical method

The earliest method for lithium hydroxide extraction involved roasting spodumene concentrate with a large amount of lime at a temperature above 1100 °C because the mineral structure of spodumene is destroyed at high temperatures [30,31]. Reaction (1) presents the mechanism of spodumene degradation to form water-soluble Li_2O-Al_2O_3. After roasting, water-soluble Li_2O-Al_2O_3 is obtained, which, when reacting with water and lime during leaching, lithium hydroxide remains in solution, and aluminium binds into insoluble residue $3CaO$-Al_2O_3-$6H_2O$. In this way, lithium is separated from aluminium. $LiOH$-H_2O is obtained by evaporating, concentrating and crystallising the lithium in solution. Lithium extraction from the sinter into solution is more than 70 wt.%. Due to the excess of limestone in the process of subsequent leaching of sinter with water, the reaction (2) of caustification of the obtained lithium aluminate takes place:

$$Li_2O \cdot Al_2O_3 \cdot 4SiO_2 + 8CaCO_3 = Li_2O \cdot Al_2O_3 + 4(2CaO \cdot SiO_2) + 8CO_2 \quad (1)$$

$$Li_2O \cdot Al_2O_3 + Ca(OH)_2 = 2LiOH + CaO \cdot Al_2O_3 \quad (2)$$

The lime roasting method has wide applicability and low lithium content requirements for spodumene, lime, or limestone. It is inexpensive and easy to obtain. However, excess CaO ends up in the solid waste from leaching. Also, the main disadvantage of the technology is the low recovery percentage compared to newer technologies.
Extracting lithium using calcium carbonate has an environmental impact during the mining and processing stages.
The authors of [32] propose a method for directly obtaining metallic lithium. Spodumene, clay and brown coal are melted at a temperature of ~1450°C by the molar ratio of 6 to 7:1 (the amount of clay added is 8% of the total mass of spodumene and brown coal 1~12%). The duration of melting is 30~60 minutes. Increasing the melting temperature to 1550°C causes spodumene to react with brown coal under the action of the heat of carbon. The calcined volatile substances are condensed to obtain metallic lithium; the reduced product is condensed to obtain an aluminium-silicon alloy.
To obtain CaO from $CaCO_3$, high temperatures (1100-1300°C) must be reached. This requires significant energy input, especially if carbon-based energy sources such as coal are used, which increases the carbon footprint. One of the main factors affecting the environmental friendliness of the process is the release of carbon dioxide (CO_2) during the decomposition of $CaCO_3$. Although carbon dioxide can also be captured and used for other purposes, this still causes problems with global warming.

2.1.3 The phase change and acid leaching method

Thermal treatment is converting from α-spodumene to reactive β-spodumene [33, 34]. The most common natural form of spodumene is α-spodumene (monoclinic structure with a density of 3.184 g/cm^3), which can be converted to β-spodumene (tetragonal structure with a density of 2.374 g/cm^3) when heated above 900℃. A third polymorph of spodumene, γ-spodumene (hexagonal structure with a density of 2.399 g/cm^3), is believed [30,31] to form at a lower temperature (700-800℃) and then convert to β-spodumene at higher temperatures. The γ-spodumene phase is metastable concerning β-spodumene and is difficult to distinguish from β-spodumene because of the similarity of X-ray diffraction patterns. The conversion of monoclinic α -spodumene to tetragonal β-spodumene requires thermal treatment (1050-1100 ℃) to provide a Li release pathway with volume expansion due to a drop in specific gravity (from 3.2 to 2.4 g/cm^3), making it more accessible for reagent leaching.
The classic scheme for processing spodumene concentrate includes thermal treatment in a rotary kiln at a temperature of 1150-1250 ℃ for 3 hours [35]; sulfatizing roasting at a temperature of 250 ℃ with a sulfuric acid consumption of 140 wt.% of the theoretically required amount for 1 hour [36]; after that, the melt is leached with water and filtered; the filtered lithium sulfate solution, containing up to 40 g/l sulfuric acid and lithium sulfate up to ~15 g/l Li, is neutralized with limestone to a pH of 6.0 ÷ 6.5 to obtain lithium compounds; before precipitation, the sulfate solution is evaporated at least 2 times to increase the Li content in it to 20 ~ 30 g/l [37].
The total degree of lithium extraction in all the above technologies is 95%. The chemical reaction of thermal treatment and sulphatising firing are presented in Reactions (3) and (4):

$$\alpha\text{-spodumene } LiAl[Si_2O_6] \rightarrow \beta\text{-spodumene } LiAl[Si_2O_6] \quad (3)$$

$$\beta\text{-}Li_2O{\bullet}Al_2O_3{\bullet}4SiO_2 + H_2SO_4 \rightarrow Li_2SO_4 + H_2O{\bullet}Al_2O_3{\bullet}4SiO_2 \quad (4)$$

Fig. 2 shows the classic process flow diagram. The final result of processing is lithium hydroxide or lithium carbonate. Works [38-41] investigate the chemistry of the formation of these compounds and present technologies for obtaining lithium hydroxide or lithium carbide.

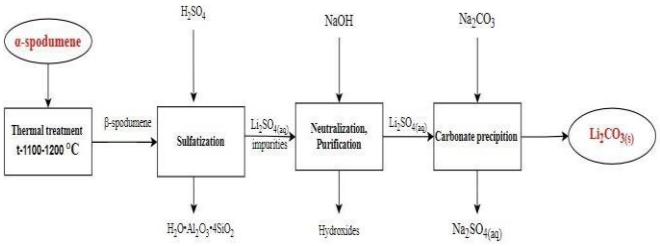

Fig. 2 Basic flow diagram of the method of thermal decrepitation of spodumene and sulfurization roasting

To reduce the energy consumption of the thermal treatment of spodumene, the researchers in [42] proposed replacing the rotary kiln with a fluidized bed reactor. Concentrate or ore with a size of 20-1000 μm is processed in a reactor at a temperature of 800-1000 °C, and the roasting time is 15-60 minutes. The fluidized bed is a bubble layer. Oxygen-saturated air is supplied to the reactor to create a fluidized bed. The essence of the technology is as follows: heat transfer to the particle nuclei occurs faster in fine-grained material than in coarse-grained material, i.e. the heating time is shorter in fine-grained material. The fluidizing gas is supplied to the reactor in a free state at a speed of 0.3-1 m/s. The oxygen content in the supplied gas is 10%, corresponding to the oxygen required to oxidize the fuel used to heat the reactor.
The technology's advantage is the low heat treatment temperature; however, it becomes more complicated with complex technical parameters and the need to ensure very fine grinding of the material.
In work [43], the technology is practically identical to the classical scheme; the difference is that the leaching of the cinder after sulfurization is carried out in a counter-current mode with closed circuits. The first and second washing solutions are sent for leaching to obtain a productive solution with a lithium sulfate concentration of 25÷26 g/l. Previously, an expensive evaporation process obtained a concentration of 25 g/l. The additional concentration of the solution does not occur since the solution is oversaturated with lithium sulfates, impurities, and sulfuric acid at the specified lithium content.
When processing spodumene, attention is paid to obtaining other products and lithium.
In works [44, 45], spodumene concentrate is processed using a classical scheme; the difference between the works is obtaining additional material, calcium aluminate. A solution of sodium aluminate is added to the productive solution of lithium sulfate at ambient temperature at a mass ratio of Al:Li = 11.5÷12.5, then lithium hydroxydialuminate is causticized at a CaO consumption of 4.0: 4.5 g per 1 g of lithium in its hydroxydialuminate, followed by separation of the lithium hydroxide solution from the waste calcium aluminate.
The paper [46] presents a method of spodumene processing, where activation and subsequent sulfurization and leaching are carried out according to the classical scheme. However, the concentrate's sulfurization is carried out at a temperature of 170÷200 ℃. Before separating the pulp into a lithium sulfate solution and an insoluble cake, it is neutralized with limestone to pH 6.0÷6.5. The final product is lithium stalls.
In [47], the initial stages of lithium conversion are similar to the classical scheme. However, after neutralizing the leaching slurry and separating the neutralized slurry into cake and sulphate solution, the leaching slurry is neutralized with chemically active β-spodumene concentrate to obtain a lithium-rich cake and used for the production of lithium ceramics and stalls.
The works [48,49] present studies where, after thermal treatment, the ore is leached with hydrochloric acid. Then, the solution is sent to multi-stage purification stages from cation impurities (iron, calcium and sodium are largely removed). The purified lithium chloride solution is passed through the electrolysis stage, which is the result of which a lithium hydroxide solution is obtained. HCl is extracted from the treated solution at the bubbling stage with hydrochloric acid and reused.
After purification, the productive solution is sent to electrolysis, which results in a lithium hydroxide solution. The solution is then evaporated to obtain lithium monohydrate crystals and carbonated with carbon dioxide to obtain lithium carbonate.
The works [50, 51] studied leaching β-spodumene with hydrofluoric acid and leaching proceeds according to reaction 5. At a solid-to-liquid ratio of 1.82% (by weight) and a hydrofluoric acid concentration of 7% (by volume), the degree of lithium extraction into solution exceeded 90%.

$$\beta\text{-}LiAlSi_2O_6 + 19HF \rightarrow LiF + H_3AlF_6 + 2H_2SiF_6 + 6H_2O \quad (5)$$

The technology of lithium sulfate solution purification from sodium and potassium includes electrodialysis of 50~60 V. The lithium, sodium and potassium molar ratio in the solution is 200:4~10:0.5~5. Bipolar membrane electrolysis of lithium sulfate solution is carried out to obtain a solution of lithium hydroxide and dilute sulfuric acid. The lithium hydroxide solution is concentrated and crystallized to obtain lithium hydroxide products [52].
The work [53] presented a technology for extracting lithium from β-spodumene by sequential calcination and aqueous leaching of CaO. Four leaching stages based on particle size reduction to 75 μm, reaction temperature of 100 ℃, mass ratio of CaO and β-spodumene of 3:1 and total reaction time of 9 h allowed to obtain 97% yield of lithium from spodumene. The method allowed to reduce the total amount of chemicals used compared to the traditional spodumene processing process. In addition, considering that the final residue after leaching consists of $Ca(OH)_2$ and $CaCO_3$, it can be reused in the water leaching process after calcination at 900 °C, further improving the proposed process's environmental friendliness.
All technological schemes of thermal activation of α-spodumene to β-spodumene described above show good results in terms of leaching degree above 90%. However, due to high energy consumption, scientists are looking for alternative ways to activate spodumene and methods for extracting lithium.

2.1.4 Direct processing spodumene

Direct opening or direct leaching of α-spodumene involves eliminating the thermal activation stage and, accordingly, reducing energy costs. Due to the stability of the mineral structures of α-spodumene, it is necessary to use highly reactive strong acids or a mixture of acids to destroy it.

In [53], the α-spodumene structure was destroyed with a mixture of hydrofluoric and sulfuric acids HF and H_2SO_4. The process diagram is shown in **Fig. 3**. The acid ratio was HF: H_2SO_4 = 1 g: 3 ml:2 ml, i.e. more than 500 wt.%. After leaching at 100 ℃ and for 3 hours, the degree of lithium extraction into the solution was 96%. Kinetic studies of the process of acid opening of α-spodumene showed that lithium extraction corresponds to the model of a contracting core and is controlled by both a chemical reaction and diffusion of the product in the layer. The apparent activation energy Ea was 32.68 kJ/mol. Cryolite contained in the mineral and the formed aluminium fluoride form a layer on the surface of the mineral particles and close the access of the acid mixture to the spodumene grains, thus limiting the kinetics of the leaching process. The proposed method of direct acid leaching allows the processing of α-spodumene, significantly reducing energy consumption. However, this development has the following disadvantages: selective extraction of lithium into the solution is not ensured; since this acid mixture dissolves other elements in addition to lithium, expensive equipment is required to avoid rapid corrosion of the reactors.

$$2\alpha\text{-}LiAlSi_2O_6+4H_2SO_4+24HF\rightarrow Li_2SO_4+Al_2(SO_4)_3+4H_2SiF_6+12H_2O \quad (6)$$

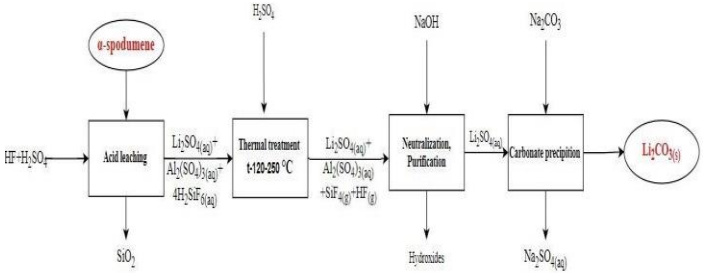

Fig. 3 Technological scheme of direct acid leaching

A two-stage heat treatment method of the solution after leaching was proposed in [54] to improve the direct processing process. After each heat treatment of the solution at 120 and 250 ℃ for 3 hours, the residual content of fluoride ion was 2.03 wt.%. The scheme of heat treatment is presented in reaction 5. In this case, silicon evaporation in the form of SiF_4 is observed. Nevertheless, the consumption of hydrofluoric and sulfuric acids has not been reduced more effectively.

Autoclave leaching experiments were conducted to process spodumene directly (**Fig. 4**). Various solvents, such as alkaline ones, were used as reagents.

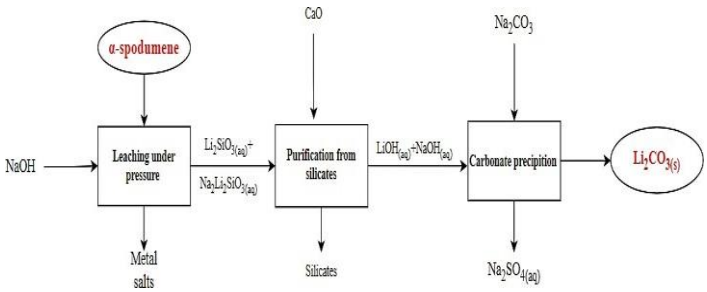

Fig. 4 Technological scheme of leaching under high pressure

The work [55] presents a technology for leaching lithium-phosphorus-aluminum-containing material with a sodium hydroxide or potassium hydroxide solution. Spodumene ore containing 0.3~3% Li is added to the reactor, the particle size is less than 100 mesh, the temperature is 260~350℃, and the pressure is 10 atm. Then, the pulp is diluted with water and filtered. After filtration, a lithium-containing solution and zeolite or potassium-nepheline products are obtained. The lithium-containing solution is added to sodium carbonate or sodium phosphate to precipitate lithium carbonate or phosphate.

Studies have been conducted on leaching spodumene with CaO or $Ca(OH)_2$ [56]. Spodumene is crushed to a size of 90≤180 μm. The content of Li_2O in spodumene is 0.5~6.5%. The mass ratio of spodumene, additives, and water is 1(0.5~5):(0.1~5):(1~10). The leaching temperature is 180~260℃, the pressure in the autoclave is 5~6 MPa, and the duration is 0.5~8 hours. After that, the pulp is cooled to 40~50 ℃ and filtered. The degree of lithium extraction by the technology is 95%.

A study on the leaching of spodumene with sodium hydroxide and sodium carbonate has been conducted [57]. Low-grade α-spodumene is ground to a powder state with a particle size of ≤150 μm, then the resulting powder is mixed with sodium hydroxide, sodium carbonate and water. The mass ratio of the used powder material to sodium hydroxide, sodium carbonate and water is 1: (0.2 ~ 4): (0.1 ~ 0.5): (3 ~ 10). When spodumene interacts with sodium hydroxide, lithium silicate is formed. The process is described in reaction 7, and reaction 8 presents the general mechanism of the technology. Then, hydrothermal treatment is carried out at 240 ℃ for 0.5 ~ 12 hours with the addition of CO_2 to the reactor. After that, the filtrate is heated, concentrated and subjected to thermal decomposition to obtain a lithium carbonate suspension.

$$6\alpha\text{-}LiAlSi_2O_6+14NaOH\rightarrow 3Li_2SiO_3+2Na_4Al_3Si_3O_{12}(OH)+3Na_2SiO_3+6H_2O \quad (7)$$

$$\alpha\text{-}LiAlSi_2O_6+3NaOH+2CaO+2H_2O \rightarrow LiOH+2NaCaHSiO_4+NaAl(OH)_4 \quad (8)$$

Alkaline compounds were used as a solvent in the above methods. In work [58], a method of leaching under pressure with the addition of nitric acid is described. Conditions: temperature - 170°C and/or pressure 15 bar. At the end of the experiment, the lithium nitrate solution is heated to evaporate water from it and further heated to a temperature exceeding the melting point of lithium nitrate to cause the lithium nitrate to melt and turn into a mobile liquid, exceeding 600°C to decompose liquid lithium nitrate.

The technology of direct leaching of spodumene with various reagents is quite an environmentally friendly recycling process. However, solutions are formed in large quantities that must be disposed of.

2.1.5 Flux roasting method

The method of roasting with fluxes also aims to reduce the temperature of the structural change of spodumene using fluxes.

In [59] the roasting of spodumene concentrate and soda is presented. The mass ratio of silicon and the sum of sodium and lithium (in terms of oxides) $SiO_2/(Na_2O+Li_2O)$ should be within 1.91÷2.61. Melting is carried out in a shaft furnace at a temperature of ~1350ºC in graphite crucibles. To cool the melt, it is poured into cold water; then the resulting granules are crushed. The crushed melt is pulped in water at a ratio of S:L=1:0.8. 93% sulfuric acid is added to the resulting pulp at 0.7 ml per 1 g of melt. The resulting sulfates are leached with water at S:L =1:3 (based on the original melt), a temperature of 95oC for 40 minutes. The resulting sulfuric pulp is filtered, and the filtered cake is subjected to a 2-fold filter-reputation wash with water acidified with sulfuric acid to a concentration of 10 g/l H_2SO_4, at S:L= 1:6 (by the original melt) and a temperature of 90ºC for 15 minutes. The completeness of lithium and aluminum extraction is determined by the residual content of lithium and aluminum in the cake. According to this technology, lithium extraction is 99.3% and aluminum 98.8%. The advantage of the technology is the extraction of aluminum together with lithium. The disadvantage of the technology is the high consumption of soda, and this technology is economically impractical if the Li_2O content in the ore is below 3%.

Studies have been conducted on roasting spodumene with fluorinated compounds [60, 61]. According to the studies, fluorinated compounds are added to 50-200 mesh ore in a molar ratio of 1:1 or 1:3, mixed and uniformly ground to 100-200 mesh and roasted at 200 to 600 ℃. After roasting, 1-6 mol/l of sulfuric acid is added to the cinder in a liquid-solid ratio of 1:1 or 1:5 and leached for 2-3 hours and filtered. Then, the lithium sulfate solution is evaporated and concentrated, and soluble carbonates are precipitated in the mother liquor. The technology allows lithium carbonate extraction with a purity of more than 96.4%.

The basic flow chart of the methods for opening spodumene with salt compounds is shown in **Fig. 5**.

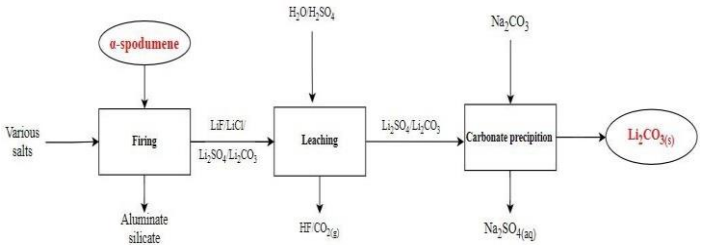

Fig. 5 The main technological scheme of processing with salt compounds

In addition to lithium, spodumene contains useful components, and the technology is designed to extract all useful components to the maximum. According to the method [62], the batch of beryllium-spodumene concentrate and sodium carbonate is roasted with a mass ratio of SiO_2/Na_2O+Li_2O) equal to 2.0÷ 2.3. In the smelting and aqueous granulation of the melt, beryllium-lithium-containing granulate phases are obtained that are easily opened with sulfuric acid. Lithium is extracted simultaneously with beryllium. This makes it possible to reduce the cost of extracting lithium from mineral raw materials due to the complex use of this raw material.

In work [63], sodium sulfate and/or sulfuric acid are added to the spodumene concentrate in 2.5% of the concentrate mass, 1~10.0% caustic soda and/or soda ash. The granulated material is fired at a phase transition temperature lower than α-spodumene. Sulfuric acid during sulfating firing is 20 to 30% of the quality of spodumene concentrate, the firing temperature is 200~250℃, and the time is 60~120 minutes.

The paper presents a method for processing spodumene with sodium and calcium salts [64]. The lithium precipitation is carried out after mixing, firing, leaching, cleaning, and removing impurities. According to this technology, the yield of the target product is 88-92%.

2.1.6 Microwave roasting method

Electrochemical technologies offer unique opportunities for ore processing, providing controllable methods that can be integrated with renewable energy sources and existing process technologies [65]. The microwave roasting method is a newer and more promising method that uses microwave furnaces to roast spodumene. Microwaves accelerate the lithium extraction process and improve recovery compared to traditional methods since they allow temperature control and reduce energy consumption.

To exploit the advantages of microwave calcination over conventional heating, this work [66] studied the effect of microwave power on the phase transformation and leaching of spodumene. The effect of microwave power on spodumene's phase transformation and leaching is significant. The optimum lithium recovery through the microwave calcination-acid roasting-leaching process reached 97% at a microwave power of 2.0 kW, comparable to conventional heating. In addition to the faster, less energy-consuming and greenhouse gas-free calcination, microwave heating also resulted in lower Fe, Na and Ca recovery values in the leaching process, which provided an advantage in the downstream treatment processes. Microwave temperature profiles of spodumene and characterisation results confirmed that α-spodumene started to convert to γ- and β-spodumene at about 900 °C.

The use of microwave ovens in the acid roasting of spodumene in the lithium extraction process was investigated and compared with conventional furnace heating [67]. The effects of various key process factors were evaluated. Conventional acid roasting of 5 g β-spodumene at 250 °C for 60 min was highly efficient in recovering lithium with 80% excess concentrated sulfuric acid. The microwave process achieved nearly complete lithium recovery with 20 s of irradiation. The possibility of reducing the amount of excess acid required to grind the sample to achieve a small particle size reduction was explored, and nearly complete recovery was observed with only 15% excess acid. Microwave irradiation of the sample for longer than 20 s resulted in decreased lithium recovery, with the lowest value being 42% after 240 s of microwave irradiation. The heating mechanism and the back reaction of Li^+ and H^+ were explored as possible explanations for this effect. The energy consumption of this study's conventional muffle heating method was calculated to be 10.4 MJ, significantly higher than the microwave energy of 15.4 kJ required to achieve the same percentage of Li extraction from β-spodumene.

This method is still under active research, but it promises to be more efficient and environmentally friendly than traditional methods, as it reduces energy costs and processing time.

Several disadvantages of the method are that microwave radiation causes differential heating of minerals, which can be both an advantage and a disadvantage; microwave roasting can reduce the energy costs of processing compared to traditional methods; the initial capital costs of installing microwave furnaces can be quite high.

Microwave processing of spodumene has significant potential to improve the efficiency of the lithium extraction process, but it is accompanied by several disadvantages that must be considered. For the method to become widely applicable, problems with heating uniformity, scalability, and process control accuracy must be solved, and capital costs for equipment must be reduced.

Each method has advantages and disadvantages, depending on the technology used, cost, availability of raw materials, and environmental standards.

Table 2 summarizes the different processes for Li extraction from spodumene published in patents and studies.

Table 2 A summary of the various processes for extracting Li from spodumene that have been published in patents and studies

Process	Experimental Conditions	End Product/Recovery %	Ref
Lime firing	Roasting: ore/ $CaCO_3$ above 1100 ℃ 3 hours; leaching at 70 ℃	Li extraction - 70%	[30,31]
Thermal activation of spodumene	Thermal decomposition of ore at 1150-1250 ℃ for 3 hours; roasting: ore/H_2SO_4 140mas.% at 250 °C for 1 hour; leaching at 50 °C	Li extraction - 95%	[30-36]
	Fluidized bed+O_2 at 800-1000 ℃ for 15-60 minutes; roasting: ore/H_2SO_4 140mas.% at 250 °C for 1 hour; leaching at 50 ℃	Li extraction - 95%	[41]
	Thermal decomposition of ore at 1100 °C; roasting: ore/H_2SO_4 140mas.% at 170-200 °C 1 hour; leaching at 50 °C	Li extraction - 95%	[46]
Direct processing of the spodumene	Ore/Na_2CO_3/$CaCO_3$ at 1100 °C; H_2SO_4 leaching; purification from impurities	Li extraction - 98%; Be-98%	[48]
	Ore/$CaCO_3$ at 1000 °C; HCl leaching; purification from impurities; electrolysis	Li extraction - 99,5%	[49-50]
	Leaching: ore/HF/H_2SO_4=1:3:2 at 100°C for 3 hours	Li extraction - 96%	[53]
	Firing 1:ore/HF/H_2SO_4 at 120 °C; Firing 2:ore/HF/H_2SO_4 at 250 °C;	Li extraction - 95%	[54]
	Leaching: ore/CaO at 100 °C, CaO/β-spodumene 3:1 reaction time 9 h	Li extraction - 97%	[57]
	Roasting: Ore/NaOH at 280 ℃ 3 h; H_2O leaching; electrolysis	Li extraction - 95%	[59]
	Pressure leaching: Ore/NaOH at 260~350℃, pressure 10 MPa	Li extraction - 95%	[60]
	Pressure leaching: Ore/Na_2SO_4/CaO/$Ca(OH)_2$ at 180~260 ℃, pressure 5~6 Mpa, 0.5~8 h.	Li extraction - 97%	[61]
	Pressure leaching: Ore/ HNO_3 at 170°C, pressure 15 Mpa, 3 hours; melting 600 °C	Li extraction - 93%	[63,64]

2.2 Extraction of lithium from lepidolite

Lepidolite $K(Li,Al)_3(Si,Al)_4O_{10}(OH,F)_2$ as well as spodumene is an important industriallysignificant mineral [68]. The chemical composition of lepidolite is highly variable due to different degrees of crystallisation differentiation. The content of components varies in the following ranges Li_2O is 1.2– 5.9 wt.%, K_2O-4.8- 13.8 wt.%, Al_2O_3-11.3-28.8 wt.% and SiO_2- 46.9-60 wt.%. Iron, calcium, magnesium, rubidium and caesium are also present in the composition of lepidolite [69]. Due to its complex chemical and mineralogical composition and lower lithium content than spodumene, lepidolite is involved in processing in a small volume and was previously considered an off-balance ore [70,71]. However, the increasing demand for lithium has moved lepidolite to the category of balance ores. The main processing methods include sulphate roasting, chlorination, sulphuric acid leaching, weak acid leaching and high-pressure alkaline leaching.
The crystal structure of lepidolite is layered prismatic crystals with convex pinacoidal discontinuities. It forms pseudo-hexagonal "books." It is also found in mica or granular masses. The influence of the crystal structure of lepidolite on lithium extraction methods can be manifested in the technological process of its processing. It includes four stages: crushing, separation, and dehydration [72].

2.2.1. Thermal direct processing

The sulfate method [73] is based on sintering lepidolite to form water-soluble lithium sulfate and water-insoluble aluminosilicate cake. The completeness of the aqueous leaching of lithium from the sinter is achieved due to the sintering temperature of 720-920 °C, with a mass ratio of lepidolite and K_2SO_4 equal to 7:(3-7).
Reference [74] presents a firing method with potassium sulfate (t-1000 °C, τ-30 min). Lithium transforms into a water-soluble form, $LiKSO_4$ and $Li_2NaK(SO_4)_2$.
In [75], a technology was proposed that includes the preparation of a charge from concentrate and alkaline flux, its melting with alkaline flux, aqueous granulation of the melt to produce granules, their grinding and sulfuric acid leaching, sodium carbonate is used as an alkaline flux to obtain the required ratio of silicon contained in the charge and the amount of sodium, potassium and lithium in Terms of oxides, equal to 2.89-3.45. It reduces the consumption of alkaline flux, sulfuric acid for sulfurization of melt and energy consumption.
The authors of [76] conducted studies where lepidolite is mixed with various salt additives (phosphates, amino carboxylic acids and their metal salts, organic phosphoric acids and their metal salts or hydroxycarboxylic acids). The mass ratio of lithium-containing ore to the additive varied 1: (0.1-5). The mixture is ground in a ball mill for mechanic-chemical activation of lepidolite. After that, the mixture is leached with sulfuric, hydrochloric and nitric acid. The extraction of lithium into the solution is 95%. After cleaning, the required purity of 99.9% lithium carbonate is achieved.
The authors of [77] mechanically activated lepidolite by grinding in a planetary ball mill for 5 hours using zirconium dioxide and Na_2SO_4. The temperature required for sulfate firing was significantly reduced due to mechanical activation. A brief description of the process is presented in the reaction (9):

$$K(Li,Al)3(Si,Al)_4O_{10}(OH,F)_2+Na_2SO_4\rightarrow Li_2SO_4+K_2SO_4+NaAlSi_3O_8+HF+H_2O \quad (9)$$

There were also studies [78] where a mixture of CaSO4 sulphate with Na_2SO_4, Na_2SO_4, with K_2SO_4 and K_2SO_4 with CaO at different ratios was used for firing, and the process is shown in reaction 10. The firing time was from 30 minutes to 1 hour, and the temperature was 850-900 °C. When CaO was added, fluorine remained in the residue as CaF_2 and $Ca_4Si_2O_7F_2$ according to reaction 11. The recovery under these conditions was over 90% of lithium:

$$K(Li,Al)_3(Si,Al)_4O_{10}(OH,F)_2+Na_2SO_4+CaSO_4\rightarrow Li_2SO_4+K_2SO_4+NaAlSi_3O_8+CaAl_2Si_2O_8+CaF_2+H_2O \quad (10)$$

$$K(Li,Al)_3(Si,Al)_4O_{10}(OH,F)_2+Na_2SO_4+K_2SO_4+CaO\rightarrow Li_2SO_4+NaAlSi_3O_8+KAlSi_2O_6+CaF_2+Ca_4Si_2O_7F_2+H_2O \quad (11)$$

Also, $FeSO_4$ is used as a flux for firing, which produces SO_3 gas during heat treatment and reacts with lepidolite according to reactions (12)-(14) [79,80], at 200 wt.% $FeSO_4$ consumption and 675 °C, heat treatment time of 1.5 hours, the lithium recovery rate is 92.7%. SO_3 obtained from $FeSO_4$ decomposition first reacts with the outer layer of lepidolite and albite to form Na_2SO_4 and K_2SO_4 by reactions (15)-(16). The sulphates then react with SO_3 to form the corresponding pyrosulphates by responses (17)-(18). Pyrosulphates further break down the lepidolite structure according to reactions (19)-(20), which leads to an accelerated firing process. Compared to Na_2SO_4 and K_2SO_4, SO_3 gas, formed during the decomposition of $FeSO_4$, plays an important role in the firing process. Thus, this process is more similar to the acidic method, although it is also called sulfate firing.

$$FeSO_4\cdot 7H_2O \rightarrow FeSO_4+7H_2O \quad (12)$$

$$12FeSO_4 +3O_2 \rightarrow 4Fe_2(SO_4)_3 +2Fe_2O_3 \quad (13)$$

$$Fe_2(SO_4)_3 \rightarrow Fe_2O_3 +3SO_3 \quad (14)$$

$$K(Li,Al)_3(Si,Al)_4O_{10}(OH,F)_2+SO_3\rightarrow Li_2SO_4+K_2SO_4+Al_2(SO_4)_3+AlF_3+SiO_2+H_2O \quad (15)$$

$$2NaAlSi_3O_8+4SO_3\rightarrow Na_2SO_4+Al_2(SO_4)_3+6SiO_2 \quad (16)$$

$$K_2SO_4+SO_3\rightarrow K_2S_2O_7 \quad (17)$$

$$Na_2SO_4+SO_3\rightarrow Na_2S_2O_7 \quad (18)$$

$$K(Li,Al)_3(Si,Al)_4O_{10}(OH,F)_2+K_2S_2O_7\rightarrow Li_2SO_4+K_2SO_4+Al_2(SO_4)_3+AlF_3+SiO_2+H_2O \quad (19)$$

$$K(Li,Al)_3(Si,Al)_4O_{10}(OH,F)_2+Na_2S_2O_7\rightarrow Li_2SO_4+K_2SO_4+Na_2SO_4+Al_2(SO_4)_3+AlF_3+SiO_2+H_2O \quad (20)$$

Thus, the researchers studied the lepidolite treatment process by sulfate firing, and the lithium extraction yield generally exceeded 90%. However, the disadvantage of the sulfate technology is the high consumption of expensive fluxes at the sintering stage.

2.2.2. Chlorination

In addition to salt roasting, there are chlorination technologies for lithium-containing minerals. The chlorination temperature is above 1100 ℃ in an argon atmosphere. After chlorination roasting, the recovery rate of Li is 50 to 90%, and lithium is extracted as LiCl. The recovery rate of Li depends on the content of LiO, the type of Li-containing phase, and the impurities in each Li-containing material. In addition, the distribution of major impurity elements such as K, Na, Mn, and Fe occurs between the evaporated chloride gas and the solid residue after chlorination roasting. The purity of LiCl is 89%, 93%, 77%, and 22% for the chlorination products isolated from lithium-ion battery (LIB) recycling slag samples, kunzite, hidenite, and lepidolite, respectively. Experimental results show [81,82] that lithium-ion battery (LIB) recycling slag, in particular, has great potential as an alternative (secondary) lithium-containing source for the production of high-purity, “technical grade” LiCl (~90%) recycled by the chlorination process. Even if the chlorination process produces pure LiCl, a further refining process is required to bring the “technical grade” LiCl (90% purity) to battery-grade quality (>99.5% purity).
Studies have been conducted on chlorination of lepidolite in the presence of Na_2SO_4 [83]. The ore/sodium sulfate/calcium chloride ratio is 1:0.5:0.3. When roasting at temperatures above 800 °C, lithium extraction is above 90%. After leaching the cinder, a solution is cooled to -5 °C to crystallize 92.1% of sulfates. Then, the solution is heated to evaporate Li_2CO_3 with a purity of >99.5%. Lithium extraction is 93.8%. The mechanism of the proposed technology is presented in reaction 21.

$$K(Li,Al)_3(Si,Al)_4O_{10}(OH,F)_2+NaCl+CaCl_2\rightarrow LiCl+KCl+NaAlSi_3O_8+CaAl_2Si_2O_8+CaSiO_3+CaF_2+H_2O \quad (21)$$

When lepidolite is chlorinated with the chlorinating agents CaCl2 and NaCl together with lithium, valuable components such as rubidium and caesium are chlorinated. The authors of [84] achieved a high degree of extraction of these elements except lithium from lepidolite by firing a lepidolite/CaCl2/NaCl mixture; it is equal to 1/0.3/0.2 at 750 ℃ and has a duration of 45 minutes. The mechanism of the proposed technology is presented in reaction (22).

$K(Li,Al)_3(Si,Al)_4O_{10}(OH,F)_2+Na_2SO_4+CaCl_2 \rightarrow Li_2SO_4+K_2SO_4+LiCl+KCl+NaAlSi_3O_8+CaAl_2Si_2O_8+CaF_2+H_2O$ (22)

The stub was leached with water at room temperature 25 ℃, S:L ratio=1:3. 92.49% Li, 98.04% Rb, 98.33% Cs and 92.90% K were extracted into the solution. The lithium content of the leach solution was 5.15 g/l. The bulk of the insoluble residue was $CaAl_2Si_2O_8$, CaF_2 and $NaAlSi_3O_8$.

2.2.3. Acid direct processing

The authors [85] experimented in which lepidolite was leached at t-138 ℃, t -10 h, and atmospheric pressure in a three-necked flask with a dense tube. Under these conditions, lithium, rubidium, and caesium recovered 94.2%, 91.8%, and 89.2%, respectively. Leachings were carried out with hydrochloric acid at a 6.21 mol/L concentration. An 8-hour leaching at 108 ℃ recovered 95.7% of lithium. The leaching mechanism is shown in reaction 23.

$K(Li,Al)_3(Si,Al)_4O_{10}(OH,F)_2+HCl \rightarrow LiCl+KCl+AlCl_3+SiO_2+AlF_3+H_2O$ (23)

The leaching of lepidolite with hydrofluoric acid HF (concentration of 7 vol. %) at 123 ℃ was investigated, and the lithium recovery was 90% [86]. Lithium, aluminium and silicon were subsequently isolated as LiF, Na_3AlF_6 and K_2SiF_6 by precipitation and evaporation, and all processes are shown in Reactions (24)-(26). Also, leaching was carried out in [87-89] with a mixture of HF and H_2SO_4 acids, as described in the reaction (27). H_2SO_4 affected the recovery of up to 98 % lithium and 90 % rubidium and caesium. The kinetic data were consistent with the shrinking nucleus model. Initially, the process was controlled by chemical reactions at the interface and internal diffusion. As the reaction proceeded, internal diffusion gradually became the dominant limiting factor. A step heating method was proposed to treat the leach liquor to remove fluoride. After heat treatment at 120 ℃ for 3 h and 200 ℃ for 6 h, only 0.68 wt.% of fluorine remained in the solution. At this time, the lithium yield could still be maintained at 94.3%.

$K(Li,Al)_3(Si,Al)_4O_{10}(OH,F)_2+HF \rightarrow LiF+KF+H_3AlF_6+H_2SiF_6+H_2O$ (24)

$3NaOH+H_3AlF_6 \rightarrow Na_3AlF_6+3H_2O$ (25)

$2KOH+H_2SiF_6 \rightarrow K_2SiF_6+2H_2O$ (26)

$K(Li,Al)_3(Si,Al)_4O_{10}(OH,F)_2+HF+H_2SO_4 \rightarrow Li_2SO_4+K_2SO_4+Al_2(SO_4)_3+H_2SiF_6+H_2O$ (27)

Lithium extraction from lepidolite was performed similarly to the method of β – spodumene processing. The concentrate was ground to a coarseness of -0.16mm, mixed with sulfuric acid at a ratio of 0.8mL:1g of concentrate, and sulfatised at 150℃ for five hours. The sulfated product was leached with water at a ratio of S:L=1:5 for 30 min. The lithium recovery rate is more than 94% [90].

Research work has been carried out on the production of syntals [91] from lithium concentrate. The method includes sulfatisation of the concentrate with sulfuric acid 95÷100℃ for 4-6 min, leaching the sulfatised concentrate, separating the leaching pulp into sulfate solution and insoluble cake. After washing the cake, the washed cake is dry. Then, prepare the charge from dry cake with lithium, potassium, sodium carbonates, oxides of magnesium, calcium, titanium, zinc, trivalent chromium and cryolite. At preparation of charge from dry cake with carbonates, oxides, and cryolite, consumption of lithium carbonate and potassium carbonate is 11,1÷11,3 wt.% and 4,2÷4,3 wt.% accordingly. Then, the charge is melted, and the obtained melt is poured into the casting mould, which is cooled. The mould is extracted, and heat treatment is done by forming a sitall. The technical result is the complete extraction of lithium and potassium into target products and the reduction of energy costs due to the decrease of decrepitation time and consumption of reagents.

In [92], mechanical activation converted lepidolite to an amorphous state with high reactivity. Sulfatisation was carried out at 165℃ for 4 h with a dosage of 65% by weight of concentrated sulfuric acid. Under these conditions, the lithium recovery is at 85%. Studies were carried out to optimize the process parameters: dosage of concentrated sulphuric acid 130% by weight, temperature 190℃ and duration 15 min [93].

When lepidolite is treated with sulfuric acid, the structure of minerals is destroyed. While further leaching, lithium passes into the solution as sulfate. The process is summarized in reaction (28).

$K(Li,Al)_3(Si,Al)_4O_{10}(OH,F)_2+H_2SO_4+H_2O \rightarrow Li_2SO_4+KAl(SO_4)_2+Al_2(SO_4)_3+SiO_2+HF+SiF_4$ (28)

Further, leaching revealed the release of many impurities, which, in the case of spodumene, was avoided by adjusting the roasting technology. Also, [94] found that the lithium content in the solution decreases due to the formation of $LiAl_2(OH)_7$-H_2O lithiumalumohydroxides in the residue. By correcting the sulphatisation at 800℃ and a time of 2 hours, the formation of these compounds was avoided, and the yield of aluminium and iron could be reduced to 0.08% and 0.02%.

In [94], an improved sulphuric acid method with fluorine addition was proposed to enhance lithium recovery using an acid mixture of hydrofluoric acid and sulphuric acid (HF/H_2SO_4). A stepwise thermal treatment for fluoride removal was proposed based on the different boiling points of the HF-H2O and H2SO4-H2O subsystems of the acid-leaching solution. The effects of heating temperature (200-350℃), heating time (6 h, 12 h), initial ore/H_2SO_4 ratio (1:1.5-1:3.5 g/ml) and different heating methods (one-step or stepwise) on fluoride removal and lithium recovery were investigated. Based on elemental and compositional analyses of the liquid phase and the corresponding solid phase, the optimum conditions for fluoride removal were established: about 0.68% fluoride remained in the leach slurry after stepwise heat treatment at 120℃ for 3 h and 200℃ for 6 h with an initial ore/HF/H_2SO_4 ratio of 1:2:2:2 g/ml. The Li retention remained at a relatively high level of 94.26%.

2.2.4. Pressure leaching

During lepidolite processing, all stripping techniques similar to spodumene were carried out, and the high-pressure leaching method was no exception.

Studies have been conducted on leaching lepidolite under high pressure at 150 ℃ for 60 minutes using 100 wt.% CaO and lithium recovery reached 98.9% [96]. The process is shown in reaction (29). The concentration of NaOH had a significant effect; the leached residue was high-purity sodalite under optimal conditions. The combined method uses NaOH and $Ca(OH)_2$ (320 g/l NaOH, 30 g/l $Ca(OH)_2$, 250 °C and 2 hours). The chemistry of the process is presented in reaction (30). The lithium extraction yield is 94%. The advantage of the alkali process is that the residue can be processed into products with high value; however, high pressure and alkali concentration cannot be avoided during the operation.

$K(Li,Al)_3(Si,Al)_4O_{10}(OH,F)_2+CaO+H_2O \rightarrow LiOH+KOH+CaAl_2Si_2O_8+Ca_{2,9}Al_{1,97}Si_{0,64}O_{2,56}(OH)_{9,44}+CaF_2$ (29)

$K(Li,Al)_3(Si,Al)_4O_{10}(OH,F)_2+CaO+NaOH \rightarrow LiOH+KOH+Na_2SiO_3+Ca_3Al_2Si_3O_{12}+CaF_2+H_2O$ (30)

Table 3 summarises the various Li extraction processes from lepidolite published in patents and studies.

Table 3 Summary of various Li extraction processes from lepidolite that have been published in patents and research

Process	Experimental Conditions	End Product/Recovery %	Ref
Thermal direct processing	Roasting: ore/K_2SO_4 t-1000 °C, τ-30 min; H_2SO_4 leaching; purification from impurities	Li extraction - 92%	[75-76]
	mechanical activation: ore/salt additives=1:(0.1-5) grinding; HCl leaching; purification from impurities	Li extraction - 95%	[78]
	mechanical activation: ore/Na_2SO_4/ZrO_2 5 h. grinding; roasting 1 hour at 850-900 °C; purification from impurities	Li extraction - 90%	[79]
	Roasting ore/$FeSO_4$ at 1100 °C; leaching of H_2SO_4; purification from impurities	Li extraction - 92,7%	[80,81]
Chlorination	Chlorination of ore at 1100 °C in an argon atmosphere	Li extraction - 90%	[82]
	Ore chlorination at 880 °C 30 min	Li extraction - 92,9% Rb-93,6%, Cs-93%	[83,84]
	Chlorination/roasting) ore/Na_2SO_4/$CaCl_2$ at 880 °C 30 min	Li extraction - 94,8% Rb-93,5%, Cs-90,1%	[86]
Acid direct processing	Leaching: ore/H_2SO_4 at t-138 °C, τ-10 h	Li extraction - 94,2% Rb-91,8%, Cs-89,2%	[87]
	Thermal activation of ore at 1345 °C; Leaching: ore/H_2SO_4 at t- 100 °C, τ-3 h	Li extraction - 95%	[89]
	Leaching: ore/HF at 123°C, τ-3 h	Li extraction - 90%	[90]
	Leaching: ore/HF/H_2SO_4 at 125 °C, τ-3 h	Li extraction - 98%, Rb-90%, Cs-90%	[92,94]
	Sulfurization of H_2SO_4 at 150 °C for 5 h, Leaching of H_2O τ-30 min	Li extraction - 90%	[95]
Pressure leaching	Pressure leaching: Ore/CaO, at 150 °C, pressure 10 MPa, 1 hour; melting 600 °C	Li extraction - 98,9%	[96]
	Pressure leaching: Ore/Na_2SO_4/CaO, at 100°C, pressure 10 MPa, 1 h.	Li extraction - 96%	[97]

2.3. Joint processing of lepidolite and spodumene concentrates

Many known methods can extract lithium from its minerals: sulfuric acid, sulfate, and lime [98]. However, most of these methods are designed to process only individual lithium minerals, significantly narrowing the raw material base of lithium industries. The number of known techniques for co-processing lithium concentrates is currently limited.

The kinetics of co-firing were investigated in [99]. According to the study's results, lepidolite reduces the temperature of the transition of spodumene from the α-phase to the β-phase by 150 °C. Fluorine exits the lepidolite lattice during synergetic firing and attacks the bonds in the α-spodumene lattice. Further, 97.60% of Li was extracted using classical technology.

The paper [100] presents a method for processing lepidolite and spodumene concentrates. The method includes preparing a charge from a mixture of concentrates and flux, activating the preparation of the charge, and aqueous leaching of the activated charge. The charge is prepared from a mix of concentrates calculated to obtain a $SiO_2/(Na_2O+K_2O+Li_2O)$ mass ratio in the mixture equal to 4.5, and soda ash calculated to obtain a $SiO_2/(Na_2O+K_2O+Li_2O)$ mass ratio in the charge equal to 2.5, activating preparation of the charge is carried out by melting it at a temperature of 1350 °C for 30 minutes. The melt is poured into cold water (water temperature 15 °C), the resulting granules are crushed. The crushed pellet is pulped in water at a ratio of S:L=1:0.8. 93% sulfuric acid is added to the resulting pulp at 0.7 mL per 1 g of melt. The resulting sulfates are leached with water at S:L=1:3 (according to the initial granulate), at a temperature of 95 °C for 40 minutes. The resulting sulfuric acid pulp is filtered, the filtered cake is subjected to 2-fold filter-repulpation washing with water acidified with sulfuric acid to an acid concentration in water of 10 g/l, at S:L=1:6 (according to the initial granulate) and a temperature of 90 ° C for 15 minutes. The residual lithium content in the cake determines the completeness of lithium extraction from the concentrate into the solution. The total recovery of lithium by this technology is over 90%.

The work [101] presents a technology almost similar to the above, and the difference is the use of different amounts of lithium carbonate.

As a result of grinding a mixture of lepidolite and spodumene concentrates, crystal lattices are destroyed and the specific surface area of lepidolite and spodumene increases, i.e., mechanical activation of these minerals, which increases their chemical activity and provides, during sulfuric acid leaching of a mechano-activated mixture of concentrates, the possibility of deep opening of lithium minerals activated in this way with sulfuric acid to form water-soluble lithium sulfate and insoluble silica. In [102], a method for extracting lithium from a mixture of lithium concentrates includes the preparation of a charge from lepidolite and spodumene concentrates, calculation of the resulting mass ratio of lepidolite and spodumene concentrates in their mixture equal to 2.5÷99.0. For the experiment, a mixture of lepidolite and spodumene concentrates with a lithium content of 2.29 and 3.28% by weight, respectively. The prepared mixtures are ground in a planetary mill to obtain an X-ray amorphous product with a grain size of 45 microns. The mechanically activated mixtures are pulped in water at a ratio of S:L = 1:0.8. 93% sulfuric acid is added to the pulp at 0.6-0.8 mL per 1 g of the mechanically activated mixture. The resulting sulfates are leached with water at S:L = 1:5 (according to the mechanically activated mixture), at 95 °C for 2 ± 1 h. The resulting sulfuric acid pulp is filtered, and the filtered cake is subjected to 2-fold filter repulpation washing with water acidified with sulfuric acid to pH 3.0-3.5, at S:L = 1:(5-6) (according to the mechanically activated mixture) and a temperature of 70 °C for 15 minutes. The technical result of the invention is a high recovery of lithium into solution without the use of fluxes.

Reference [103] presents a technology where thermal activation with alkaline leaching is carried out for the synergistic extraction of Li and Rb from a mixture of spodumene and lepidolite. The authors found that this method reduces alkali consumption during leaching compared with the selective processing of each mineral. The technology achieved the following extraction results: 93.0% Li, 88.1% Rb, 41.3% Si, and 2.8% Al.

Table 4 summarizes the various Li extraction processes from spodumene and lepidolite published in patents and research.

Table 4 Summary of the various Li extraction processes from spodumene and lepidolite that have been published in patents and research

Process	Experimental Conditions	End Product/Recovery %	Ref
Thermal direct processing	Thermal activation of ore at a temperature of 1000 °C Firing: a mixture of ores/F; leaching; purification from impurities	Li extraction - 97.6%	[99]
	Melting: ore/$CaCO_3$ mixture at 1350 °C 30 min; H_2SO_4 leaching at t-95 °C, 40 min; purification from impurities	Li extraction - 90%	[100]
	Thermal activation of ore at a temperature of 1000 °C leaching of NaOH; purification from impurities	Li extraction - 93% Rb-88,1%,	[101]
Acid direct processing	mechanical activation: ore mixtures 5 h; leaching of H_2SO_4 at t- 95°C, 40 min;	Li extraction - 90%	[102]

2.4. Extraction of lithium from other minerals

Due to the growing demand for lithium, researchers are looking for various ways to involve other lithium-containing minerals, such as monttebrazite, amblygonite, petalite, lithium porcelain stone, and others, in processing. The general problem with their involvement in production is low lithium concentrations and high concentrations of host rocks. Below are works on the extraction of lithium from these minerals.

Montebrasite ($LiAl(PO_4)(F,OH)$) is a pegmatite mineral that is combined with spodumene and lepidolite. It is the richest mineral in lithium content, with a theoretical Li2O content of approximately 10% by weight. However, the mineral does not lend itself to traditional enrichment methods.

The team of authors [104] presented a technology where dilute sulfuric acid was mixed with montebrasite and fired; the chemistry of the technology is shown in the reaction (31). At 800 °C, a lithium recovery yield exceeding 95% was achieved within 15 minutes. In addition to the target product, the extraction of associated valuable components is also considered in these minerals. Aluminum phosphate was obtained as a by-product, which increased the cost-effectiveness of the process.

$$2LiAl(PO_4)(F_{0,5},OH_{0,5})+4H_2SO_4 \rightarrow Li_2SO_4+Al_2(SO_4)_3+P_2O_5+HF+4H_2O \quad (31)$$

In [105], lithium extraction from minerals rich in lithium and amblygonite phosphates was investigated. The first process is obtaining amblygonite concentrate by grinding it. Leaching of amblygonite in a sufficient sulfuric acid solution under atmospheric conditions to convert lithium, sodium and aluminum into soluble sulfates, as well as to extract all fluorides and phosphates present. Impurities present in the lithium-containing filtrate, such as sodium, aluminium, phosphate, and fluoride, are removed by precipitation using a suitable substrate such as limestone, lime, or monovalent carbonate or hydroxide salts, but preferably limestone. Adding a base increases the solution's pH, ensuring the neutralization and precipitation of impurities. Separation of impurity metals and sulfates from lye by filtration or decantation, in which the resulting filtrate contains most of the lithium in the initial amblygonite ore or concentrate. The solid particles are washed with water to extract the residual lithium. Precipitation of calcium ions by adding a monovalent carbonate salt such as Li_2CO_3 or Na_2CO_3.

The next mineral is petalite from the silicate group, with the chemical formula ($LiAlSi_4O_{10}$). In general, petalite is already used in the production of high-quality ceramics and special glass. The theoretical Li_2O content is 4.88 wt.%. Petalite has a similar structure to spodumene. It undergoes thermodecription at 1100 °C with decomposition into β-spodumene and quartz. Therefore, this mineral can be processed according to the technological scheme of processing spodumene. Mixing petalite with Na_2SO_4 at a flow rate of 100 wt.%, followed by grinding the mixture in a planetary ball mill and heat treatment at 1000 °C for 1 hour, allowing 99% of lithium to be extracted into a soluble form by reaction (32) [106].

$$LiAlSi_4O_{10}+Na_2SO_4 \rightarrow LiNaSO_4+NaAlSi_3O_8+SiO_2 \quad (32)$$

The third mineral is lithium porcelain stone. The lithium content in lithium porcelain stone is relatively low (on average, Li_2O is only 1 wt.%). Due to its low price, this mineral was also used to produce ordinary ceramics and glass [107]. The processing technologies of this mineral are similar to those of spodumene and lepidolite. Roasting is carried out at 850 °C for 1 hour, while the lithium yield is 95% due to aqueous leaching [108].

Further, clay reserves of lithium minerals of the clay type account for about 7% of the total world reserves of lithium. However, due to their complex chemical and mineralogical composition, they have not yet been developed and are potential sources for lithium extraction. Below are some clay processing works.

The technology of lithium extraction from zinnvaldite is presented in [109]. The mechanism of the mineral's decomposition is as follows: the process begins at 300 °C, and the complete decomposition of zinnvaldite occurs at 900 °C. The release of SiF_4 accompanies it and leads to the formation of several solid decomposition products. As a result of the identification of structural changes after annealing at 700 °C, the final member of some solid solutions is transformed into a structure similar to polylithionite.

The paper [110] presents a technology for processing zinnvaldite using CaO and B_2O_3 as additives for thermal activation and H_2SO_4 as a leaching agent. The authors have shown that destroying Fe-O and Si-O-Si will increase extraction efficiency. In the end, 91.32% Li, 93.09% Rb.

In [111], a method for extracting lithium from lithium-bearing carbonaceous-clay carbonate rocks is presented, including roasting of initial rocks with calcium carbonate and catching dust from sublimations, characterized in that to increase the efficiency and reducing the cost of extracting lithium, rubidium and caesium, the roasting process with calcium carbonate is carried out at their weight ratio equal to 1:2 - 1:3, and a temperature of 1600 – 1700 ℃ under conditions of direct contact of the flame of the torch with the raw mixture.

The paper [112] presents a technology for extracting lithium from low-grade lithium- containing clay ore. The new process avoids the disadvantages of the traditional lithium extraction with complex technology and high production cost. This method was able to achieve 91% lithium recovery. Extracting lithium from clay ore includes grinding low-grade lithium-containing clay ore to 2 mm, adding fluxes (calcium sulfate, calcium fluoride and sodium sulfate) and firing. The mass ratio of lithium-containing clay ore: calcium sulfate: calcium fluoride: sodium sulfate = 1:0.7:0.2:0.5: The charge is immersed in a muffle furnace and fired at a temperature of 800 ° C, and the time is 2-3 hours. After firing, we leached with sulfuric acid in a 1:1 configuration to obtain a 50% sulfuric acid concentration. The solution obtained after filtration is sent for neutralization with lime to pH = 11, then sodium carbonate is added, and ions of impurities of calcium, magnesium, iron and aluminum are precipitated. After filtration, a pure lithium sulfate solution is obtained, and a concentration of 20% is carried out. Further, according to the classical scheme, sodium carbonate is added, and lithium carbonate is precipitated.

The paper [113] presents a method for extracting lithium from lithium-containing micas. The method includes the activation and sulfatizing firing of lithium mica with sulfuric acid to extract lithium hydroxide monohydrate and lithium carbonate. The process consists of mixing lithium mica concentrate with calcium sulfate, barite ore powder or barium sulfate return slag, carbon fuel and the addition of water. Firing is carried out in a vertical furnace.

3 LITHIUM EXTRACTION FROM BRINES

The brine contains a mixture of salts such as chlorides and sulfates of sodium, potassium, calcium, magnesium, boron and lithium, which are extracted by evaporation in ponds for 12-18 months using solar energy. More than 60% of the world's lithium reserves are stored in these bribes, and they are one of the most important sources for lithium extraction. There are 3 types of brine: geothermal brine, oil field brine and continental brine. More than 50% of lithium is found in continental brines. The specifics of brine processing at lithium plants differ dramatically due to their chemical composition and lithium content. The lithium content in rich brines is 600-1500 ppm, and in lean brines 200-700 ppm, and some brines contain 600-1500 ppm. [114].

Brines have a complex and unstable chemical and mineralogical composition and many impurity metals, including Mg, Na, K, Ca, and B. In particular, Mg impurity significantly affects lithium extraction [115]. Magnesium is removed by two-stage precipitation using sodium carbonate ($NaCO_3$) and lime (CaO). Brines are divided into three categories: geothermal, oilfield, and continental brines, with the latter being the largest global production source (59%).

Due to the differences in the chemical composition of various salt solutions worldwide, the specifics of the technological process may differ [116,117]. Lithium production technologies are new and specific; they can be grouped by electrochemical, adsorption, and precipitation methods.

The electrochemical method is considered innovative in producing lithium from brines [118,119]. A device consisting of 2 cells is used to extract lithium. Lithium-containing brine is supplied to the first cell, and hydrochloric acid solution is provided to the other. The battery charging process is simulated by controlling the system's potential. As a result, the lithium contained in the brines passes into the second cell in a hydrochloric acid solution. In this way, the selective extraction of lithium from a multicomponent brine is realised.

Lithium is adsorbed from brines in highly selective manganese-based sorbents: $LiMn_2O_4$, $Li_{1.6}Mn_{1.6}O_4$, and $Li_4Mn_5O_{12}$ [120-122]. However, manganese is lost during sorption, reducing the adsorbent's operational characteristics. Recently, titanium-based adsorbents have been characterized by higher chemical stability: Li_2TiO_3 and $Li_4Ti_5O_{12}$ [123, 124]. They have high selective adsorption properties.

The brines are dominated by magnesium content relative to lithium. Enrichment of the lithium solution due to a decrease in the magnesium content can be achieved by the membrane method of electrodialysis. A reduction in the mass

ratio of Mg/Li in brines to 0.5:1 (initial 20:1) with a multilayer liquid membrane consisting of two cation exchange membranes and one membrane with an organic liquid filled with lithium. Selective electromigration of Li^+ is carried out using an electric field [125].
Lithium can be extracted from saturated $MgCl_2$ solutions by extracting tributyl phosphate (TBP). When $FeCl_3$ is added as a co-extractant, 99.5% of lithium has passed into the organic phase in a complex with the Fe ion [126,127].
The precipitation method is the simplest method for extracting lithium from brines. No additional reagents are used in this process, and natural solar energy evaporates and concentrates on brines. As a result, sodium and potassium salts crystallize. After removing impurities such as boron and calcium, sodium carbonate is added to precipitate lithium carbonate. Recently, scientists have proposed to extract lithium from brines using sorption, extraction, and electrodialysis methods to eliminate the loss of water, a valuable resource for the population. Another disadvantage of natural evaporation is the production of magnesium salts (carnallite and bischofite) and lithium salts, which require further separation [128,129].

4. CONCLUSIONS

Demand for lithium is expected to stabilize and even increase, which in turn requires the development of an effective technology for processing lithium-containing mineral raw materials. Solid minerals such as spodumene, lepidolite ores, and natural brines serve as feedstock for lithium production. The production of spodumene concentrate processing with the activation of non-reactive α-spodumene into the β-form by thermal treatment with subsequent sulfation of the concentrate dominates. The process is considered resource-intensive; the phase transition reaction is carried out at high temperatures of 1100 -1250 ℃, but very efficient, and the degree of lithium extraction is 95%. Other reagent modes (hydroxides, carbonates, alkali metal chlorides, chlorination, fluorination) of spodumene opening are proposed, which are mainly tested in the laboratory mode and have not yet found wide application on an industrial scale due to the aggressiveness of the reagents requiring corrosion-resistant equipment, as well as special sanitary conditions for the chlorination and fluorination processes. The processes of lepidolite processing are similar to those of spodumene ore processing.
To improve the efficiency of lithium-containing concentrates processing, it is necessary to develop microwave decomposition processes at the stages of cinder sulfatization, since an increase in the degree of lithium extraction by 5-10% is observed compared to the traditional method. The proposed methods of concentrate grinding before the sulfatization process in a planetary mill to increase the area of the reacting surface may face the problem of filtration on an industrial scale.
Lithium extraction from brines is rapidly developing through the development of selective membranes, ion sieves, and technological modes of lithium separation from impurities.

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