

TECHNOLOGY OF LITHIUM EXTRACTION FROM HARD ROCK LITHIUM ORES AND ENVIRONMENT IMPACT

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Abstract: This paper presents the methods of lithium extraction from ores and their impact on the environment. The dominant process of industrial lithium extraction from spodumene is carried out using sulfuric acid and is characterized by high energy consumption and large release of waste residues – gases and water. An attempt to apply the same method in the extraction of lithium from lepidolite had difficulties. Other methods – Alkaline methods and the salt chlorination method have lower energy consumption, but it is still necessary to research the optimal reaction conditions so that they can be applied in industry. The salt roasting method is used industrially in the extraction of lithium from lepidolite, but like the sulfuric acid method, it is characterized by high energy consumption and high material flow. However, it is considered that these methods have possibility for optimization in order to be applied in the industrial process of lithium extraction. What all methods of lithium extraction from ores have in common is that they require a large amount of energy and resources, resulting in a large emission of pollutants and an unfavorable impact on the environment. The impact of these pollutants on the environment is 9.3–60.4 times higher than the lithium extraction technology from salt lakes.

Key words: Lithium, Acid method, Alkali method, Salt roasting method, Chlorination method, Environmental impact

1. INTRODUCTION

Lithium has become a very sought-after metal in the world because it is the basic component for the production of batteries (Li-ion) that are used for many consumer devices: mobile phones, laptops, electric vehicles (cars, bicycles and scooters) and others. Special interest in this metal arose in the Republic of Serbia due to the "Jadar" project implemented by the company Rio Tinto. The company's website [1] states:

"If realized, "Jadar" will produce lithium carbonate of a quality suitable for making batteries for electric cars and batteries for storing energy from renewable sources. In addition, "Jadar" would also produce borates used in the development of equipment for renewable energy sources such as solar panels and wind turbines.

The proposed development of the project includes the construction of an underground mine with associated infrastructure and equipment, including electric powered trucks, as well as an ore processing plant to produce battery-grade lithium carbonate.

If the project receives all the necessary approvals and permits, in full production. "Jadar" will annually produce about 58,000 tons of lithium carbonate, 286,000 tons of boric acid and 255,000 tons of sodium sulfate, which will place Rio Tinto among the top ten lithium producers in the world. According to these data, "Jadar" would produce 2.3 million tons of lithium carbonate during the mine's expected lifetime of 40 years" [1].

Interest in lithium – Li (Greek: lithos – stone) came about because of its unique physical and chemical properties: it is the lightest of all known metals; its specific weight is 534 kg/m³ (at 20 °C), which is only about half of the specific weight of water [2]. It has the highest heat capacity of all solid materials, 3.58 kJ/kgK, which is why lithium was often used, before Li-ion batteries, in coolants for heat transfer [3]. It is characterized by great reactivity and flammability and is not found in nature in an elemental state. Pure lithium must be stored in a vacuum, an inert atmosphere, or under an inert liquid such as purified kerosene [4] or mineral oil.

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The largest lithium ore deposits in the world are located in Bolivia, Chile, Argentina, China and Australia, and the minerals that contain it are spodumene ($\text{AlLi}(\text{SiO}_3)_2$), lepidolite ($\text{K}(\text{Li},\text{Al})_3(\text{Al},\text{Si},\text{Rb})_4\text{O}_{10}(\text{F},\text{OH})_2$), zinnwaldite ($\text{KLiFeAl}(\text{AlSi}_3)\text{O}_{10}(\text{OH},\text{F})_2$), and petalite ($\text{LiAlSi}_4\text{O}_{10}$) [5]. In November 2004, a unique mineral containing lithium was discovered in Serbia – jadarite ($\text{LiNaSiB}_3\text{O}_7(\text{OH})$), named after the locality where it was found. It was confirmed and registered as a unique mineral by the scientists of the Natural History Museum in London and the National Research Council of Canada [6].

2. METHODS OF OBTAINING LITHIUM CARBONATE FROM ORES

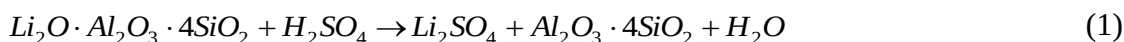
The majority of today's commercial lithium production is from extracting lithium from underground brine reservoirs (salars). Most takes place in the so-called Lithium Triangle, high-up in the Andes, where the borders of Bolivia, Argentina and Chile meet, and also in China. Salt-rich water is pumped to the surface and into a series of evaporation ponds. Over a period of months, the water slowly evaporates and a variety of salts precipitate out, leaving a brine with an ever-increasing concentration of lithium. When lithium concentration reaches a certain point, the brine is pumped to a recovery facility to extract the metal. The extraction of lithium from solid rocks is a more complex and energy-demanding process. Although there are over 145 minerals that contain lithium, only five are used for commercial lithium extraction: spodumene, lepidolite, petalite, amblygonite, and eucryptite [7]. Processes of lithium extraction from ores can be divided into the following methods: acid methods, alkaline methods, salt baking method and chlorination method [8].

2.1. Acid method

The acid process can be divided into sulfuric acid [9], [10] hydrofluoric acid [11], hydrochloric acid [12], etc. The process of using sulfuric acid is dominant in the process of lithium extraction from spodumene ore, while the use of other acids is still in the research phase.

2.1.1. Sulfuric acid method

The use of sulfuric acid in the lithium extraction process has been in development for a long time and is now a method that is easy to control and gives consistent quality [13]. The technological process includes calcination, then acid roasting, washing, purification, evaporation, deposition of lithium carbonate, release of anhydrous sodium sulfate and crystallization. Crushed $\square$ -spodumene concentrate is calcined at 950–1100°C and converted to $\square$ -spodumene, and then acidified with excessively concentrated sulfuric acid (1.4 times) [14] in a rotary kiln at 250–300°C to form water-soluble sulfate (Equation 1). It is then washed with water at 90°C, the excess sulfuric acid is neutralized with lime and the pH value is adjusted to 7–10 in order to remove most impurities such as iron and aluminum. A crude lithium sulfate solution containing about 10% lithium oxide is obtained [15]. Then milk of lime is added to the lithium solution, in order to remove most of the magnesium and adjust the alkaline environment of the solution (pH=11–12) [16]. The removal of the remaining calcium, magnesium, etc. is done by introducing sodium carbonate, followed by evaporation and concentration of the solution in order to obtain a purified solution of lithium sulfate with a lithium content of more than 20%. Finally, lithium carbonate is precipitated by adding sodium carbonate (Equation 2), then centrifuged, dehydrated and finally dried. The separated mother liquor is concentrated and crystallized to produce anhydrous sodium sulfate, and the excess water is returned to the leaching process (Figure 1). In early research, the calcination temperature and acid consumption using the sulfuric acid method were significantly higher. Thus, the calcination temperatures were 1000–1350°C, the acid concentration was in the interval 1.3–2.4, and the acid baking temperature was 250–300°C. Under the optimum water leaching conditions (solid to liquid (S/L) ratio 1:1.85, reaction at room temperature for 15 minutes), the lithium leaching rate was 96.93%.



Scientists have also studied the possibility of extracting lithium from lepidolite using the sulfuric acid method. However, this method has drawbacks such as large acid residue and long reaction time [17].

Despite the failure when it comes to the extraction of lithium from lepidolite, the extraction process using sulfuric acid has a wide adaptability to raw materials. Its main disadvantage is the high consumption of sulfuric acid, while sodium carbonate has low values of sodium sulfate. The intensity of energy consumption and release of waste residues of lithium extraction using the sulfuric acid method (SO₂ waste water and sulfuric acid fog and leached residue) are high. Therefore, scientists are investigating possibilities to reduce sulfuric acid concentrations and optimize acid exposure conditions, which would improve the efficiency of lithium leaching and reduce the consumption of raw chemical materials. In addition, how to efficiently extract silicon and aluminum from lithium ores as well, which would reduce resource consumption and waste discharge [9].

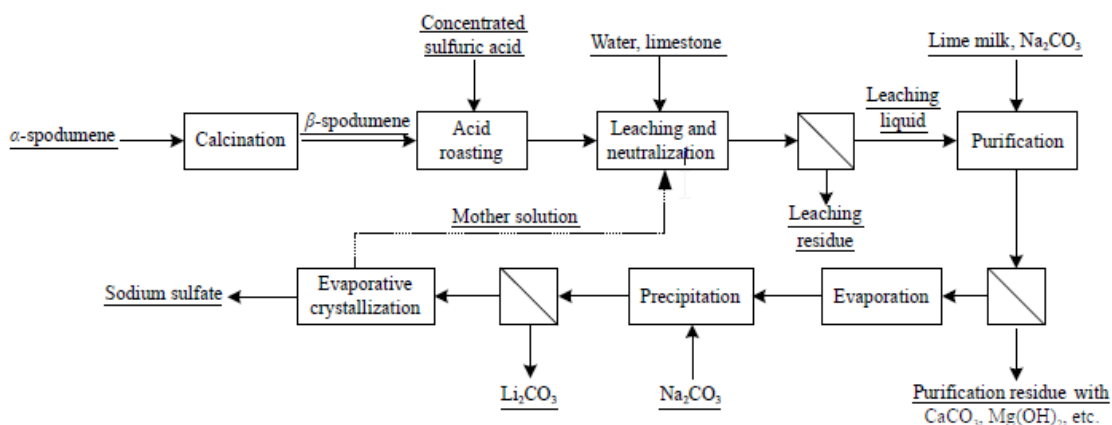


Fig. 1 Process flow sheet for extracting lithium from spodumene by the sulfuric acid method [9]

2.2. Alkaline method

In order to reduce the consumption necessary for the extraction of lithium using the sulfuric acid method, scientists are trying to carry out the same process using alkaline substances – sodium hydroxide, calcium hydroxide and sodium carbonate. Alkaline substances, mainly sodium hydroxide, can react directly with lithium minerals or calcined lithium minerals [9].

2.2.1. Sodium hydroxide method

The alkaline method with sodium hydroxide involves hydrothermal alkaline treatment of α -spodumene, which forms hydroxysodilite and zeolite, and lithium from the ore is released into the solution from which it precipitates (Figure 3). The reaction rate of α -spodumene with sodium hydroxide solution at 500°C was very slow, after three days only a part of α -spodumene decomposed into sodalite and lithium carbonate. After those results, the influence of temperature, time and particle size on the rate of extraction of lithium carbonate was analyzed [18]. Under the optimized conditions, the leaching rate was low (40%). According to research by a group of authors [19], this is due to the low concentration of sodium hydroxide. They increased the concentration up to 600 g/L, reaction time was 2 h, temperature 250°C and mixing speed of 500 rpm, the leaching rate of lithium from spodumene can reach 95.8%.

The same procedure was applied to lepidolite, [20] proposed a new procedure for lithium extraction using the sodium hydroxide method and studied the effects of alkali concentration, S/L1 ratio, reaction temperature and time on the lithium conversion rate. Under optimal conditions, they managed to achieve a conversion rate of 98.2%.

The application of the alkaline method simplifies the washing of lithium and the process of removing impurities, reduces chemical raw materials and energy consumption, and also reduces the emission of sulfur, chlorine, etc. The purified solution is suitable for the evaporation and crystallization of lithium hydroxide and the precipitation of lithium carbonate. Currently, only China

ENFI Engineering Co., Ltd has conducted a pilot test using the sodium carbonate autoclave method, and the result has shown that the technology is feasible and meets the conditions for conducting extended tests and semi-industrial trials [9].

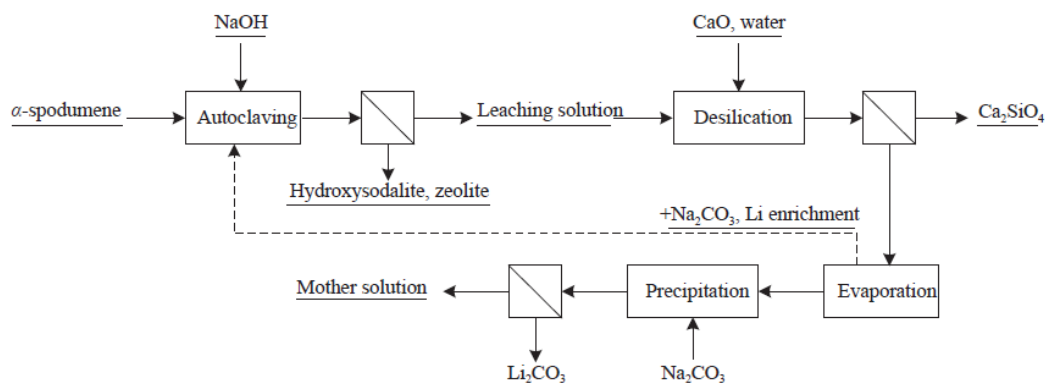


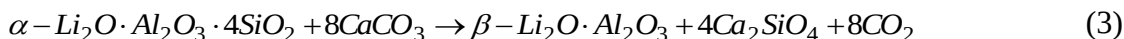
Fig. 2 Process of lithium tracting from spodumene by sodium hydroxide metod [9]

2.3. Salt roasting method

Salt reagents used by scientists generally include carbonates (calcium carbonate and sodium carbonate) and sulfates (potassium sulfate, sodium sulfate, and calcium sulfate). Only the carbonate method will be presented in the paper.

2.3.1. Carbonate method

The limestone roasting method has been successfully applied to the industrialized lithium extraction process. Its reaction is shown by Equation 3. The flow of the process is as follows: Spodumene and limestone are mixed into the sludge in a certain proportion for baking, then water is washed and calcium, aluminum and other impurities are removed, and finally lithium carbonate is deposited (Fig. 3). [21].



The ratio of limestone and rate of lithium recovery is still in the research phase. Research shows that the lower the level of spodumene, the higher the consumption of limestone; when $\text{CaO}:\text{SiO}_2$ 2.4–2.6, the lithium recovery rate is the highest and reaches 92.14%.

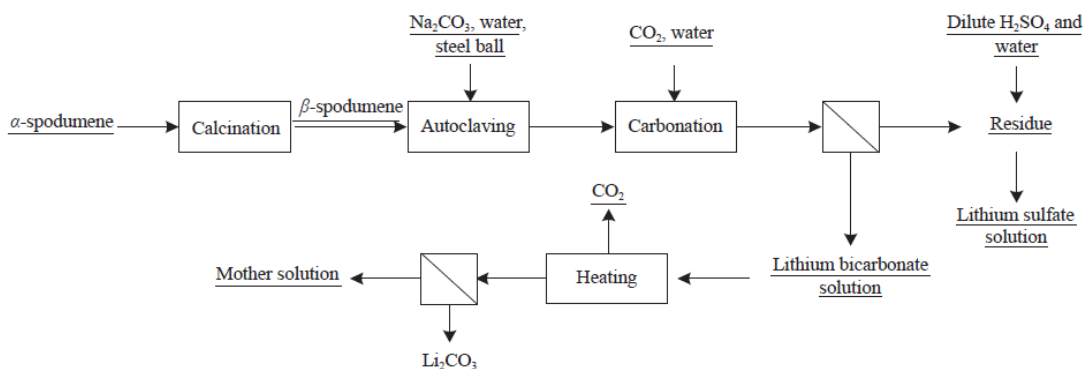


Fig. 3 Process of recovery lithiumby sodium caarbonate metod [9]

The method of calcining limestone can also be used to extract lithium from lepidolite [22], of course under different mass ratios, firing temperature and firing time, particle size and other factors. Under optimal conditions, the lithium leaching rate from lepidolite is above 89.6%.

3. ENVIRONMENTAL IMPACT

Of all the mentioned methods of lithium extraction from rocks, the sulfuric acid method is the most commonly used industrial process, especially for the extraction of lithium from spodumene because it can be used when the lithium content in the ore is both low and high. The following raw materials are required for the application of this method: spodumene concentrate, sulfuric acid, sodium hydroxide, calcium hydroxide, sodium carbonate, water, etc. Consumption of the mentioned raw materials is typically 8.67 t/t, 3.02 t/t, 0.55 t/t, 0.65 t/t, 2.26 t/t, and 49.46 t/t, respectively [23]. The pollutants that occur during the extraction process are mainly NO_x, SO₂ and sulfuric acid mist (which is formed during calcination and acidification), as well as the rest of the waste generated during the leaching and purification stages. The emission intensity is for NO_x – 6.67 kg/t, SO₂ -7.52 kg/t, sulfuric acid mist – 0.90 kg/t, and the rest of the waste – 10.93 t/t [24]. Due to the different types of fossil fuels used (coal/natural gas) and research limits, the emission intensity of these pollutants are somewhat different in Jiang SI [23] and Gu GZ [24], Figure 4..

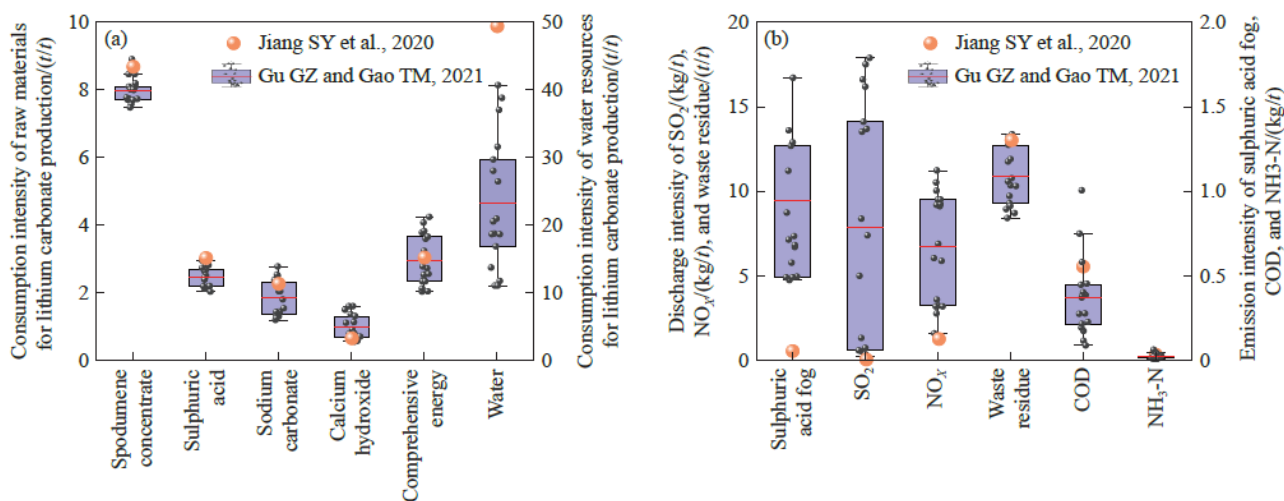


Fig. 4 Resource consumption (a) and pollutant emission (b) of lithium extraction from spodumene by the sulfuric acid method [9]

Unlike spodumene, in lepidolite, sulfuric acid extraction gives a low yield of lithium, where it is difficult to purify the leaching solution and the generated silicon-aluminum slag is difficult to use. Therefore, the sulfate process is commonly used in China for the extraction of lithium from lepidolite [9]. According to the survey data of Lepidolite Enterprise in Jiangqi Province, China, the consumption intensity of lepidolite concentrate produced from lithium carbonate is 17.86 t/t, potassium sulfate, calcium carbonate, and sodium sulfate 1.43 t/t, 3.03 t/t and 16,3 kg/t, and natural gas and electricity 2952 m³/t and 767 kWh/t, respectively. The emission intensity of pollutants such as NO_x and SO₂ in this process are lower than those of spodumene by the sulfuric acid method with an intensity of 12.70 kg/t and 23.22 t/t, respectively[9].

In general, the extraction of lithium from ores requires a large amount of energy and resources, resulting in large emissions of pollutants. The impact of these pollutants on the environment is 9.3–60.4 times greater than the extraction of lithium from salt lakes. Observing the emission of CO₂, it can be seen that its emission during the extraction of lithium from ore is 15.69 tCO₂ek/t, 47.7 times more than salt water (0.33 tCO₂ek/t) [23].

4. CONCLUSION

Analyzing the methods of lithium extraction from ores (mainly spodium and lepodolite), the following is observed:

- The sulfuric acid process is the dominant process for the extraction of lithium from spodumene, but has disadvantages when applied to lepidolite. During the extraction process, this method has a high energy consumption, and a large discharge of waste residues – waste gas and waste water;
- Alkaline and salt chlorination methods reduce energy consumption and have a high recovery rate of lithium, but the optimal reaction conditions, equipment and safe operation are still being investigated in order to be used in industry;
- The salt roasting method has an industrial application in the extraction of lithium from lepidolite, but it is characterized by a large flow of material and high energy consumption. Therefore, it is necessary to optimize the process, which would lead to greater efficiency and reduction of production costs;

The various technologies for the extraction of lithium from lithium ores have their advantages and disadvantages, but what is important is the room for improvement. Therefore, it is necessary to strengthen research on the process of extracting lithium from ores in order to save energy, improve the extraction of lithium and all valuable metals from lithium ores..

Which process of lithium extraction from jadarite ore would the company Rio Tinto use, one of the above or a completely new method is not known to the public.

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