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Extraction of Lithium from Spodumene by Alkali fusion

알칼리 용융법을 이용한 스포듀민에서의 리튬 추출

2018년 8월

서울대학교 공과대학원

에너지시스템공학부

이 수 경

Abstract

Extraction of Lithium from Spodumene by Alkali Fusion

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The most common process of extracting lithium from spodumene is the sulfuric acid roasting process. In this process, spodumene is roasted with sulfuric acid at 250 °C followed by leaching with water to extract lithium in the solution. However, this process is preceded by a calcination step at a temperature of over 1000 °C to transform α–spodumene to β–spodumene before the roasting stage. This calcination step consumes a large amount of energy. Many studies have been conducted to develop a novel process for extracting lithium from spodumene, however, most studies only dealt with β-spodumene formed after the transformation stage. Only a few studies made use of α-spodumene.

Hence, in this study, lithium was extracted from α-spodumene directly without the phase-transformation at temperature over 1000 °C. For this process, the alkali fusion method was chosen because it is the typical pre-treatment method for silicate minerals. This study is divided into two parts: (1) sodium hydroxide (NaOH) fusion, (2) sodium carbonate (Na_2CO_3) fusion. Experiments

were conducted at various conditions to determine the optimum condition for extracting lithium.

In the NaOH fusion test, the optimum fusion conditions were 600 °C fusion temperature, 60min fusion time, and 1.5:1 NaOH/sample ratio; furthermore, the leaching conditions were 5min leaching time and 25 °C leaching temperature. The extraction efficiency of lithium under these conditions was 63.88%.

In the Na_2CO_3 fusion test, the fusion temperature was fixed at 850 °C. At this fusion temperature, the optimum fusion conditions for were 60 min fusion time and 1:1 Na_2CO_3/sample. The leaching conditions were 5 h leaching time and 1.5 M sulfuric acid concentration. The results of the sodium carbonate fusion test under these conditions show that 99.98% of the lithium in the samples was extracted. However, all the silicon and 75% of the aluminum in the sample was extracted along with lithium. After leaching with 1.5M hydrochloric acid under the same fusion conditions, the lithium extraction was lower than sulfuric acid. However, it was possible to remove silicon and aluminum by adding Na_2CO_3 into the leachate.

In summary, the optimum fusion and leaching conditions were investigated to extract a high percentage of lithium from spodumene by the alkali fusion method. The results show that almost of the 100% lithium in the samples was extracted with Na_2CO_3 fusion and sulfuric acid leaching. However considering impurities, the optimum conditions were using 1.5M of hydrochloric acid in the leaching stage followed by removal of Si and Al by adding Na_2CO_3. This experiment was conducted at a lower temperature than that of the existing processes with no phase-conversion stage. Therefore, it is a better process in terms of the energy consumption and simplicity of the process.

Keywords: Alkali fusion, Leaching, Spodumene, Lithium

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1. Introduction

1.1. Research background

Lithium, the third element in the periodic table (Figure 1), belongs to Group 1, which includes typical metallic elements such as sodium and potassium. Being in the second period with an atomic weight of 6.94, it is the lightest metal. Lithium contains three electrons: two electrons are located in the inner shell (1s) and one electron is in the outer shell (2s). Due to this atomic structure, lithium can lose an electron from the shells easily, thus possessing good electrical conductivity (Jessica Elzea Kogel, 2006). Hence, lithium is widely used in various products, such as batteries, glass, ceramics, and aluminum (Jaskula, 2013). Its largest use (46%) is in lithium batteries, because of its unique properties of low density and high conductivity (USGS, 2018). Lithium batteries are extensively used for a wide variety of electronic devices, vehicles, and other applications. As the demand for these products increases, the use of lithium is also expected to increase continually. World lithium production increased by 13% in 2017 from the previous year and the use of lithium also increased from 36,700 tons to 41,500 tons in 2017. The demand for lithium is likely to continue increasing as shown in Figure 2 (Statista, 2018). Therefore, there is an urgent need to produce more lithium from various natural resources and improved methods for producing lithium need to be developed.

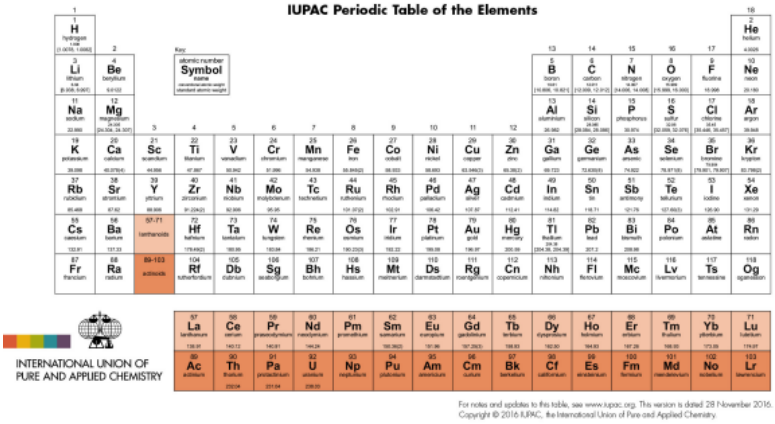


Figure 1. Periodic table

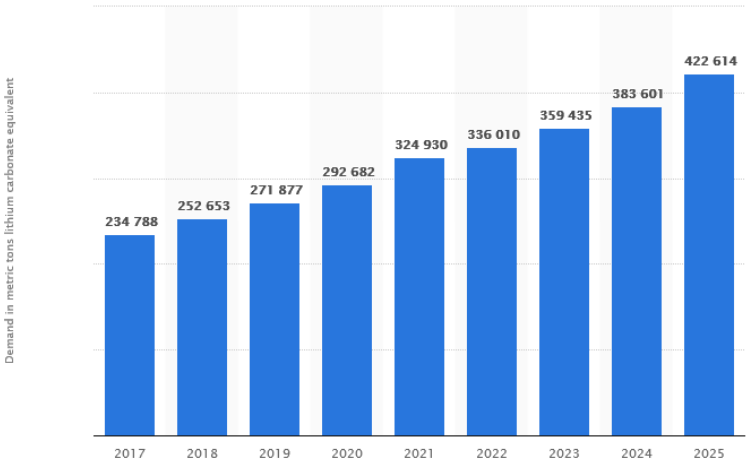


Figure 2. Projection of lithium demand

The sources of lithium include brine, pegmatite, and clays. The production from brine accounts for 46% of the total global production (Figure 3) (Talens Peiró, Villalba Méndez, and Ayres, 2013) and it is concentrated in South America. Salar de Atacama in Chile has the most lithium, which is estimated to be 35.7 Mt (Dinh, 2015). In addition, Salar de Uyuni in Bolivia has an estimated resource of 5.5 - 10.2 Mt of lithium. Additionally, brines in Argentina, and USA also contain lithium. The typical process of lithium extraction from brine includes evaporation and subsequent precipitation with various precipitants. However, this process requires 12 - 24 months and large spaces to remove impurities, such as Ca, Mg, Na and K (Chagnes, 2015). In addition, the concentration of lithium in brine can be influenced by rain, thus climate is a very important factor in the production cost.

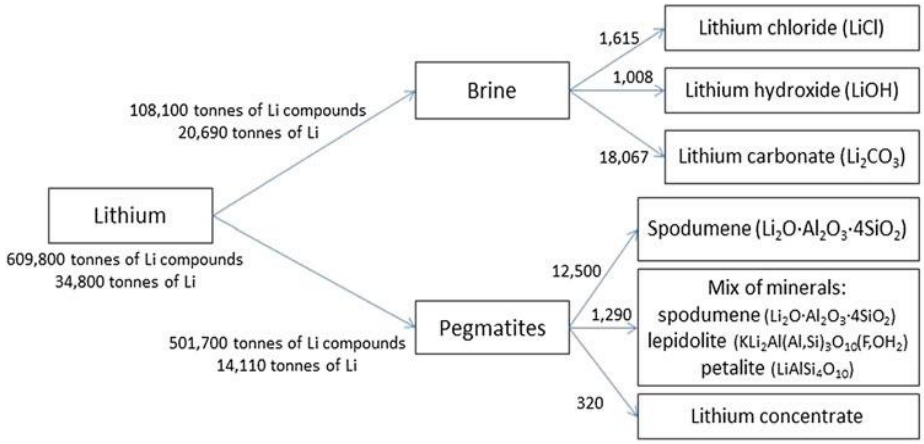


Figure 3. Resources of lithium

Pegmatite is the second largest sources of lithium, and currently 40% of lithium comes from pegmatite. The pegmatites which contain lithium include spodumene ($LiAlSi_2O_6$), lepidolite ($KLi_2Al(Al,Si)_3O_{10}(F,OH_2)$), and petalite ($LiAlSi_4O_{10}$) (Table 1). Among these, spodumene which contains 3.83% lithium, comprises 88% of lithium production from pegmatite (Dinh, 2015) (Figure 3).

Table 1. Type of pegmatite mineral

Lithium sources	Minerals	Formula	Li content (wt. %)
Pegmatites	Spodumene	$LiAlSi_2O_6$	3.73
	Lepidolite	$K(Li,Al)_3(Si,Al)_4O_{10}(F,OH)_2$	3.58
	Zinnwaldite	$KLiFe^{2+}Al(AlSi_3O_{10})(F,OH)_2$	1.59
	Petalite	$LiAlSi_4O_{10}$	2.09
	Amblygonite	$LiAlPO_4F$	3.44
	Eucryptite	$LiAlSiO_4$	5.51

Many companies produce lithium from minerals. Extracting lithium from minerals requires three stages: (i) concentration (comminution and floatation), (ii) extraction by hydrometallurgy method, and (iii) precipitation. Figure 4 shows the complete process of producing lithium from minerals before precipitation stage (William A. Averill, 1978).

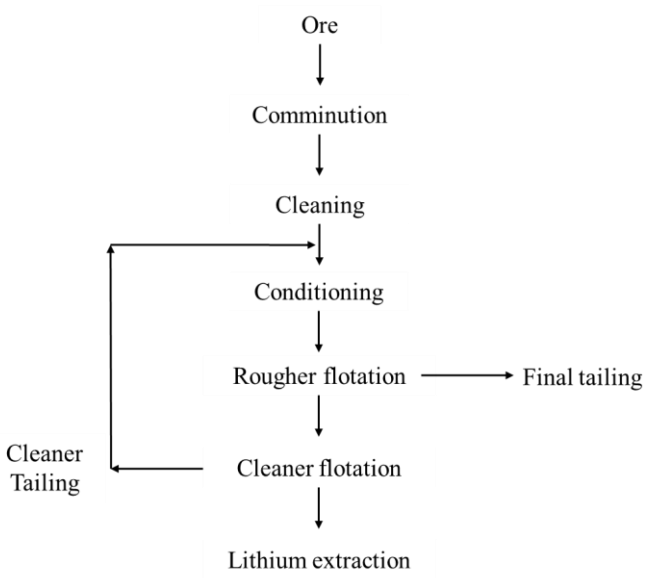


Figure 4. Process of producing lithium from minerals

The most common method for producing lithium from spodumene is the sulfuric acid method. This process is used by several companies, e.g., Galaxy Resources Ltd. in Australia and Nemaska Lithium Inc. in Canada. In addition to the sulfuric acid method, roasting with lime is also applied to the extraction of lithium from spodumene. This process consists of the roasting stage with lime and the leaching stage. This process is employed by the Foote Mineral Company (Dinh, 2015). In addition to these methods, other methods have been proposed for producing lithium from spodumene, with studies being actively performed. The natural state of spodumene is α-spodumene, which is less reactive and thus, its conversion to β-spodumene at a temperature over 1050 °C is required to increase its reactivity. However, this process consumes a considerable amount of energy because of the high temperature required. Hence, the conversion stage is a major factor in the production cost. Therefore, it would be better if this high-temperature conversion step could be eliminated.

Other natural sources of lithium are the clay minerals, hectorite and montmorillonite (Table 2) (Dinh, 2015). For producing lithium from clay minerals, their conversion in the presence of sulfate or carbonate is a typical method. This process also uses the roasting stage at 1000 °C, similar to the extraction process from spodumene. i.e., roasting with calcium sulfate or lime stone, followed by the leaching stage.

Table 2. Clay minerals of lithium

	Mineral	Formula	Li content (wt. %)
Clays and others	Hectorite	$Na_{0.3}(Mg,Li)_3Si_4O_{10}(OH)_2$	0.54
	Montmorillonite	$(Na,Ca)_{0.3}(Al,Mg)_2Si_4O_{10}(OH)_2 \cdot n(H_2O)$	

1.2. Recent studies

The most common method of extracting lithium from spodumene used in the industry is the sulfuric acid method. In this method, heating is performed in two stages. The first heating stage is for the transformation of the spodumene structure at 1050 °C and; the second stage is roasting the transformed β-spodumene with sulfuric acid at 250 °C. During the second-stage heating, spodumene reacts with sulfuric acid and produces lithium sulfate (Li_2SO_4) (Ellestad, 1950). Another industrial process is the lime-roasting process. In this process, α-spodumene is roasted with lime and transformed to $Li_2O{\cdot}Al_2O_3$ and $CaO{\cdot}SiO_2$. After this process, water leaching is conducted and high-purity lithium hydroxide (LiOH) can be obtained.

For lithium extraction from spodumene, other processes and reagents have been investigated. Some researchers used an autoclave for lithium extraction (Chen et al. 2011; Kuang et al. 2018). Kuang et al. (2018) used sodium sulfate solution with calcium oxide (CaO) and sodium hydroxide (NaOH) as an additive to increase the extraction efficiency. In this study, the effect of additives was investigated and found that the use of CaO as an additive resulted in a higher extraction efficiency (93.3%) than the use of NaOH (90.70%). Calcination was conducted at 1100 °C for 1 h, and the leaching temperature was also high. Extraction by HF leaching has been conducted after conversion to β-spodumene (Rosales, Ruiz, and Rodriguez, 2014). The optimum conditions in this study achieved over 90% recovery, obtaining lithium as lithium carbonate (Li_2CO_3). The methods of chlorination roasting using chlorination gas (Cl_2) and calcium chloride ($CaCl_2$) were studied (Barbosa et

al., 2014; Barbosa, González, and Ruiz, 2015). The roasting process with Cl_2 gas was first investigated at various conditions, and the reaction products and residues were analyzed using XRD, XRF, AAS, SEM, and EPMA. The results showed that the lithium in spodumene was conducted to lithium chloride (LiCl). Si and Al did not react with Cl_2 and remained in the solid residues. The second experiment used $CaCl_2$ at various conditions. The roasting temperature and time were chosen as variables and the optimum roasting condition was found.

Most techniques for extracting lithium from spodumene require the conversion of α-spodumene to β-spodumene at a high temperature. Only a few studies have used the natural state of spodumene without phase-transformation. Enhanced leaching using a mixture of hydrofluoric acid and sulfuric acid without undergoing a transformation to change the structure of spodumene was studied (Guo et al. 2017).

In summary, studies of lithium extraction have been actively performed because of the importance of lithium; most studies showed a high lithium extraction efficiency. However, most studies required the roasting stage for the phase transformation to β-spodumene at 1000 °C.

1.3. Research objectives

In this study, the extraction of lithium from spodumene without the high-temperature conversion stage was investigated for reducing the energy consumption and decreasing the number of stages. With this objective, the optimum fusion and leaching conditions were investigated. The experiments in this process were divided into two parts: fusion with NaOH and with Na_2CO_3. Each process consists of three stages: fusion, leaching, and separation. Each stage was performed at various conditions to investigate its effects on lithium extraction. In the NaOH fusion stage, the factors studied were the fusion time, temperature, and NaOH: spodumene ratio; the leaching conditions considered were time and temperature. The factors considered in the Na_2CO_3 fusion stage were the fusion time and Na_2CO_3/spodumene ratio. Subsequently, the effect of leaching time, leaching temperature, and concentration of acid solutions (hydrochloric acid and sulfuric acid) were investigated.

By conducting the experiments above, the optimum conditions for fusion and leaching were identified and using these conditions, the separation stage was conducted to obtain high-purity lithium.

2. Background

2.1 Properties of lithium and spodumene

In natural, lithium exists in brine and minerals. The commercial lithium minerals are Spodumene ($LiAlSi_2O_6$), Lepidolite ($K(Li,Al)_3(Si,Al)_4O_{10}(F,OH)_2$), Petalite ($LiAlSi_4O_{10}$), Amblygonite ($LiAlPO_4F$), and Eucryptite ($LiAlSiO_4$), among which spodumene is the main lithium mineral. Spodumene is a peroxene lithium mineral and the chemical formula is $LiAl(SiO_3)_2$. Typically, it contains 3.73% of lithium (8.03% of lithium oxide, Li_2O) and other major elements are silicon and aluminum (Table 3) (Garrett, 2007).

Table 3. Contents of spodumene

Formula	**wt.%**
Li (Li_2O)	3.73 (8.03)
Si (Si_2O)	30.18 (64.58)
Al (Al_2O_3)	14.50 (27.40)

The natural state of spodumene is α-spodumene in the monoclinic system (Deer 1997). This structure can be transformed to β-spodumene and γ-spodumene at high temperatures (Peltosaari et al. 2015). Each type of spodumene shows different crystal structures (Salakjani, Singh, and Nikoloski 2016) (Figure 5).

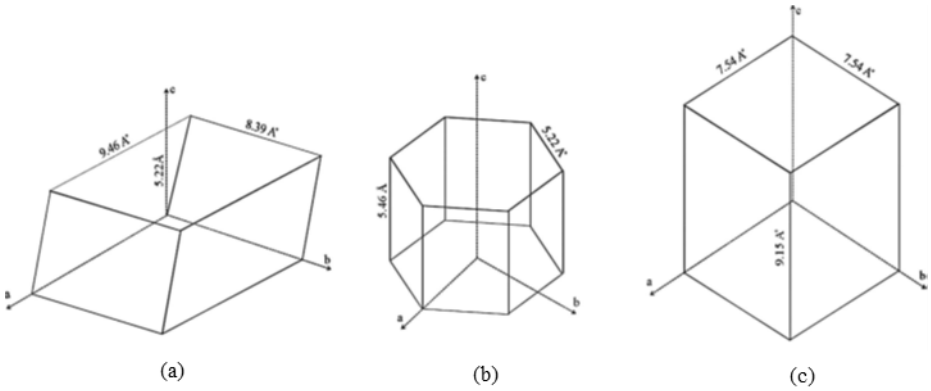


Figure 5. Structures of spodumene

(a) α-spodumene, (b) β-spodumene, and (c) γ-spodumene

The specific gravities of the natural state of spodumene, α-spodumene, and β-spodumene are 3.15 g/cm^3 and 2.4 g/cm^3, respectively (Habashi 1986). Figure 6 shows the optical structure of spodumene.

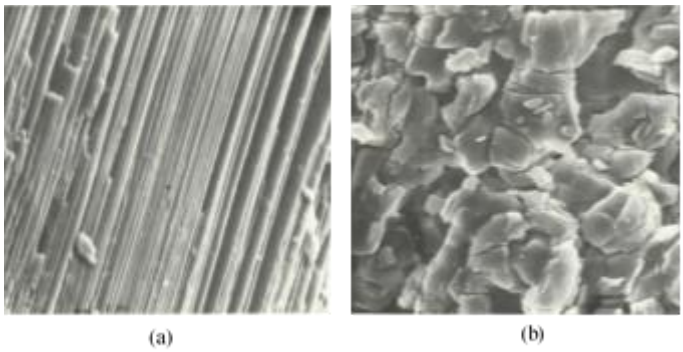


Figure 6. Spodumene crystal (a) α-spodumene and (b) β-spodumene

2.2 Alkali fusion method

Alkali fusion is one of the treatment methods, however alkali fusion for extraction lithium from spodumene has not been reported. This method invloves heating ore with alkali reagents, such as sodium hydroxide, sodium carbonate, calcium oxide, and others. Especially, sodium carbonate and sodium hydroxide are commonly used in that minerals. Sodium hydroxide is used for beryl, Nb-Ta ores, and zircon sand and sodium carbonate is fused with bauxite, clays, beryl, chromite, and wolframite (Habashi 1986).

For zirconium extraction, zirconium silicate ore is reacted with sodium hydroxide at 650 °C to convert into more soluble form. This reaction is followed by the equation:

$$\mathrm{ZrSiO_4} + 4NaOH \rightarrow Na_2ZrO_3 + Na_2SiO_3 + 2H_2O \qquad (1)$$

Reginaldo et al. (2012) studied alkali fusion and leaching of a zircon concentrate with sodium hydroxide. In this study, water and sulfuric acid leaching were conducted after NaOH fusion and 91.5 % of zircon was extracted as zirconium sulfate compound.

The alkali fusion process using sodium carbonate is applied to bauxite, clays, beryl, chromite, and wolframite. Bauxite ($Al(OH)_3$) is reacted with sodium carbonate and fused with CaO. By this process, $Al(OH)_3$ is transformed to $NaAlO_2$ and SiO_2 is changed to Ca_2SiO_4 according to the following equation:

$$2\mathrm{Al(OH)_3} + Na_2CO_3 \rightarrow 2NaAlO_2 + CO_2 + 3H_2O \qquad (2)$$

$$2CaO + SiO_2 \rightarrow Ca_2SiO_4 \quad (3)$$

For beryllium extraction, beryl is heated with sodium carbonate at 1000 °C and decomposed to be leached with acid according to the following equation:

$$3\mathrm{BeO} \cdot \mathrm{Al}_2O_3 \cdot 6SiO_2 + 6Na_2CO_3 \rightarrow 3BeO + 3Al_2O_3 \cdot 6Na_2SiO_3 + 6CO_2 \quad (4)$$

After the fusion process, BeO is extracted as Beryllium sulfate ($BeSO_4$) by sulfuric acid leaching (Anil Kumar De 2007).

3. Materials and methods

3.1 Sample characteristics

The spodumene sample for this experiment was from Australia and was in the powder state. Therefore, additional grinding was not conducted for this sample.

The size distribution of the sample is shown in Figure 7 and Table 4. As shown, 90% of the particles were under 0.26 mm in size.

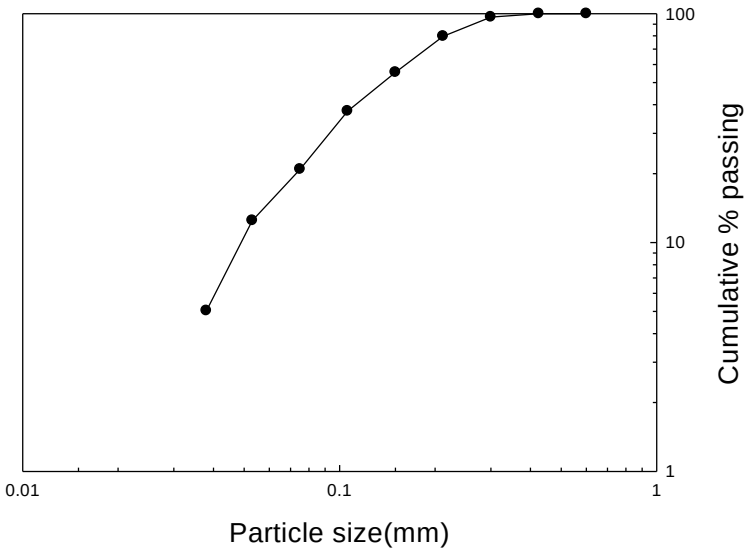


Figure 7. Cumulative size distribution of spodumene sample

Table 4. Size analysis of spodumene sample

Mesh	Size(mm)	Wt.(g)	Cumulative wt. (g)	Cumulative % passing
30	0.6	0.03	226.98	100.00
40	0.425	7.7	226.95	99.99
50	0.3	38.67	219.25	96.59
70	0.212	54.8	180.58	79.56
100	0.15	40.6	125.78	55.41
140	0.106	37.76	85.18	37.53
200	0.075	19.12	47.42	20.89
270	0.053	16.87	28.3	12.47
400	0.038	11.43	11.43	5.04
Total		226.98		

Figure 8 shows the XRD analysis results of the spodumene sample, which revealed rethat the sample is mainly composed of spodumene.

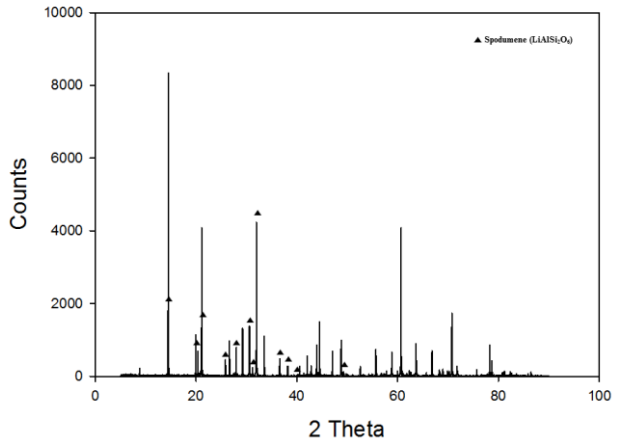


Figure 8. Result of XRD analysis of the spodumene sample

Table 5 shows the analysis results from ICP-OES. The sample contained 3.60% lithium, 29.29% silicon, 13.88% aluminum, and a small amount of other impurities. This means that this sample contained over 95% spodumene.

Table 5. Chemical contents of spodumene sample by ICP-OES

element	wt. %
Li	3.60
Si	29.29
Al	13.88
K	0.52
Mg	0.27
Ca	0.22
Fe	0.22

3.2 Experimental methods

Alkali fusion and leaching experiments were conducted to optimize the conditions for high extraction efficiency. The main step involves fusion, leaching, and separation (Figure 9).

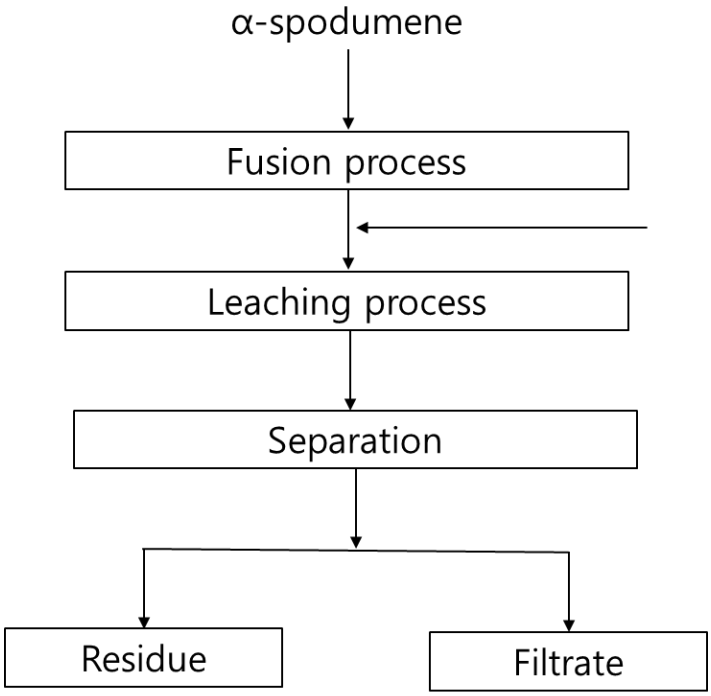


Figure 9 Alkali fusion process

3.2.1 Fusion experiment

The spodumene sample was mixed with NaOH and Na_2CO_3 and fused in an electric furnace (Figure 10). In all the experiments, 5g of the spodumene sample was used. The mixture was placed in a nickel crucible and fused under various conditions. The variables in the NaOH fusion were time, temperature, and NaOH/spodumene ratio; the variables in the Na_2CO_3 fusion were time and Na_2CO_3/spodumene ratio. The fusion with NaOH was conducted at 400–600 °C and the fusion with Na_2CO_3 was performed at a fixed temperature (850 °C). The fusion time was 15–60 min and the ratios of the reagent to the spodumene sample were 1:0.5, 1:1, 1:1.5, and 1:2. After preparing the sample, the furnace temperature was increased to the target temperature and maintained during the specified time. After the fusion, the sample was cooled in the furnace to room temperature, and the crucible was removed from the electric furnace.

Figure 10. Electric furnace

Table 6. Fusion conditions of NaOH fusion

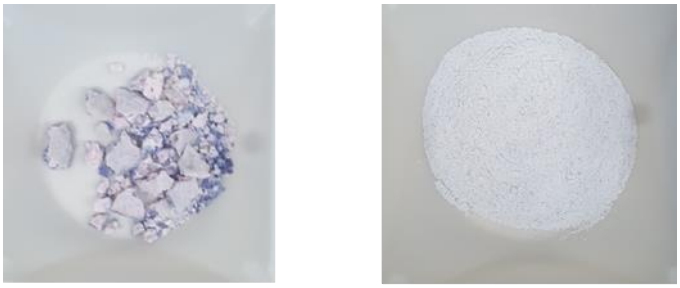
Fusion conditions – NaOH fusion	
Temperature (°C)	400/500/600
Time (min)	15/30/60
NaOH : Sample	0.5:1/1:1/1.5:1

Table 7. Fusion conditions of Na_2CO_3 fusion

Fusion conditions – Na_2CO_3 fusion	
Temperature (°C)	850
Time (min)	15/30/60
Na_2CO_3 : Sample	1:1/1.5:1/2:1

It was observed that the product state differed depending on the reagent used. While the samples that fused with NaOH were powders, the products of fusion with Na_2Co_3 were of mass state. Therefore, the mass-state products were pulverized to yield the powder state to reduce the particle size for the leaching test. To pulverize the mass-state samples, a hydraulic lab press (HLP-12) was used (Figure 11). The mixture was pulverized under 10 MPa force and compression was performed several times. The pulverized mixtures were sieved with 50-mesh sieves at each compression process (Figure 12).

Figure 11. Hydraulic lab press (HLP-12)



(a) (b)

Figure 12. (a) Before pressing, (b) After pressing

3.2.2 Leaching experiment

Leaching tests were conducted differently in the two fusion methods. The samples fused with NaOH were leached with only D.I water, but the samples fused with Na_2CO_3 were leached with D.I water and an acid solution. In this leaching test, sulfuric acid and hydrochloric acid at various concentrations (0 M–1.5 M) were used as the leaching reagents. Table 8 shows the NaOH leaching conditions and Table 9 shows the Na_2CO_3 leaching conditions. The fused sample was added to a 200 ml beaker and stirred in water, at 800 rpm. In addition, the leaching test was conducted at various temperatures (25 °C, 40 °C, and 70 °C). Sampling was conducted at various time periods to investigate the effect of leaching time. The collected leaching solution sample was filtered using a filter paper. After filtering, the solution sample was diluted 10 times and 100 times for ICP-OES analysis (Figure 13).

Figure 13. ICP-OES

Table 8. Leaching conditions of NaOH fusion

Leaching conditions - NaOH	
Temperature (°C)	25/40/70
Time (min)	5/10/15/30/45/60

Table 9. Leaching conditions of Na_2CO_3 fusion

Leaching conditions – Na_2CO_3	
Time(h)	1/2/3/4/5
Acid concentration (HCl/H_2SO_4) (M)	0.5/1/1.5

3.2.3 Separation

The leachate contained other impurities such as silicon and aluminum. Thus, increasing the purity of the lithium separation process was required. In particular, the concentration of Si was very high; therefore, the removal of Si was the major issue. Solvent extraction, ion exchange, adsorption, and precipitation methods have been used for separation (Free, 2013). For this purification, the precipitation method was used. The precipitation method is adding sodium carbonate and stirring for 1 h to mix the leachate with sodium carbonate. After the precipitation process, the precipitates were filtered using a filter paper and the solution was analyzed using ICP.

4. Results and Discussion

4.1. NaOH fusion method

To determine the optimum fusion and leaching conditions, experiments were conducted at various conditions such as fusion time, fusion temperature, NaOH/sample ratio, leaching time, and leaching temperature.

The equation for this reaction is given in eq. (5):

$$4\mathrm{NaOH} + \mathrm{LiAl}(SiO_3)_2 \rightarrow 2Na_2SiO_3 + LiOH + Al(OH)_3 \qquad (5)$$

Figure 14 showed the result of XRD analysis after NaOH fusion and confirmed that the sodium silicate was produced. The effect of the variables was studied by changing each condition. The results are as follows.

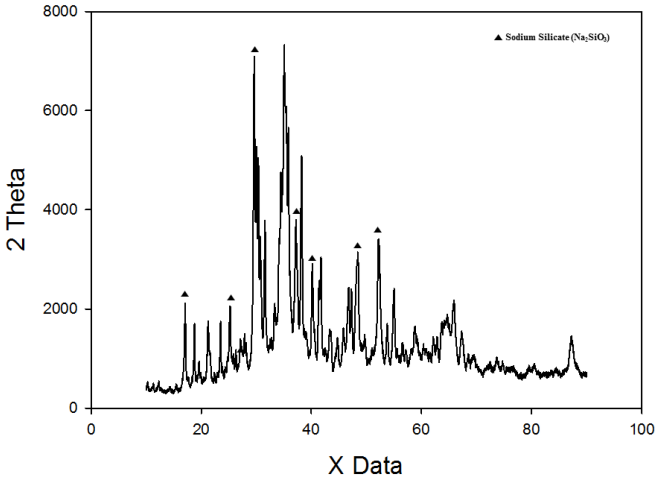


Figure 14. XRD analysis of the fused sample with NaOH

4.1.1. Effect of fusion time and temperature

The melting point of sodium hydroxide (NaOH) is 318 °C. Therefore, the fusion experiment was conducted at over 318 °C. Leaching with water at room temperature and 800 rpm of stirring speed was performed. The NaOH/sample ratio was fixed at 1.5:1.

The effect of fusion time was studied first. For the tests, the fusion temperature and NaOH/sample ratio were kept constant. The fusion and leaching conditions were as listed in Table 10.

Table 10. Conditions of leaching and fusion experiments for the effect of fusion time

Content	Condition
Reagent	Sodium hydroxide (NaOH)
Ratio of NaOH/Sample	1.5:1
Fusion temperature	600°C
Leaching time	5min
Leaching temperature	25°C
Agitation speed	800 rpm
L/S ratio	20/1

When the fusion time was 60 min, the extraction efficiency of lithium was the highest (63.88%). However, 61.21% and 58.33% of lithium were also extracted at 15 min and 30 min, respectively (Figure 15). These values did not show a significant difference. Thus, the fusion time did not significantly affect the extraction efficiency of lithium when the fusion time exceeded 15 min. In consideration of the energy efficiency, 15min of fusion time is the optimum condition.

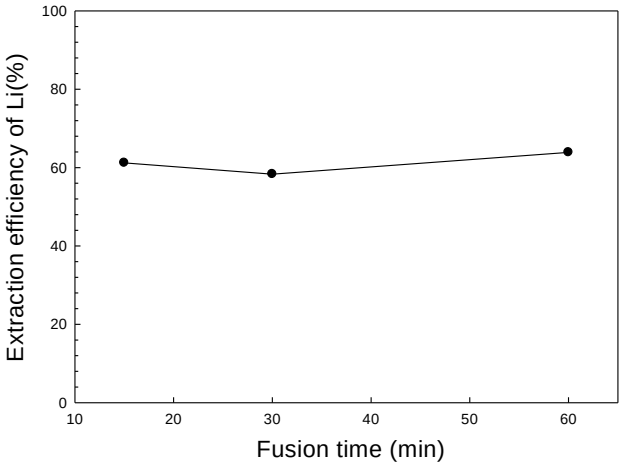


Figure 15. Extraction efficiency of lithium at various fusion time

Subsequently, the effect of fusion temperature was studied. In this test, fusion temperature were 400, 500, and 600 °C. Table 11 shows the detailed experimental conditions to investigate the effect of fusion time.

Table 11. Conditions of fusion and leaching for the effect of fusion temperature

Content	**Condition**
Reagent	Sodium hydroxide (NaOH)
Ratio of NaOH/sample	1.5:1
Fusion time	15min
Leaching temperature	25 °C
Agitation speed	800 rpm
L/S ratio	20/1

Figure 16 and Table 12 show that the extraction efficiency of lithium was 61.21%, when the fusion temperature was 600 °C and the leaching time was 5 min. However, the efficiencies at various fusion temperature did not differ significantly for each leaching time. This result means that the fusion temperature over 400 °C did not affect the extraction efficiency of lithium. In addition, as the leaching time increased, the extraction efficiency of lithium decreased. This trend of decreasing lithium recovery was due to precipitation of lithium as insoluble compounds with increasing leaching time.

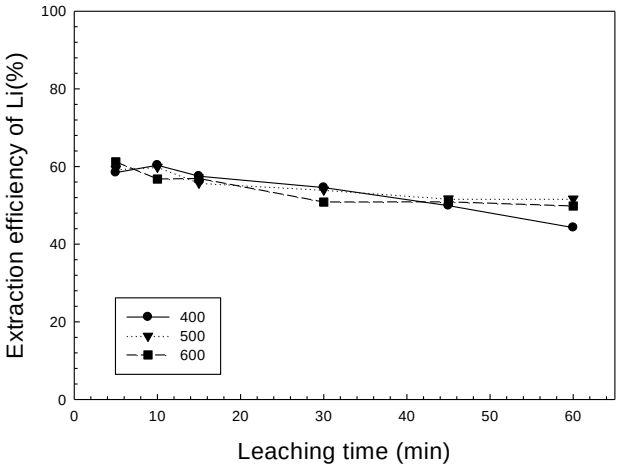


Figure 16. Extraction efficiency of lithium at various fusion temperature

Table 12. Extraction efficiency of lithium at various fusion temperature

	400°C	500°C	600°C
5 min	58.45	59.37	61.21
10 min	60.32	59.87	56.77
15 min	57.52	55.78	56.91
30 min	54.56	54.00	50.84
45 min	49.91	51.71	50.89
60 min	44.26	51.69	49.83

Figure 17 shows the extraction efficiency of Li, Si, and Al as compared with that of lithium. When the leaching time was increased, the extraction of Si also increased from 88% to 99%, while that of Al did not show a significant difference. Therefore, the amount of extracted lithium and the purity of lithium decreased as the leaching time increased.

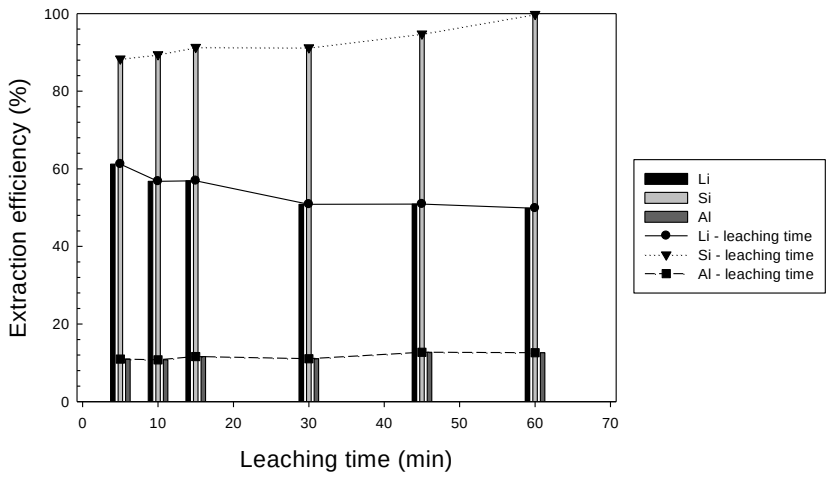


Figure 17. Extraction efficiency of Li, Si, and Al at different leaching time

4.1.2. Effect of NaOH/sample ratio

Experiments at various NaOH/sample ratios were conducted and the effect of the fusion ratio was investigated. For this test, the fusion time and temperature were fixed at 15 min and 600 °C, respectively. Other leaching conditions were fixed. In Table 13, the detailed fusion and leaching conditions are stated.

Table 13. Conditions of fusion and leaching experiment for the effect of ratio

Content	Condition
Reagent	Sodium hydroxide (NaOH)
Fusion time	15min
Fusion temperature	600 °C
Leaching time	5min
Leaching temperature	25 °C
Agitation speed	800 rpm
L/S ratio	20/1

Figure 18 shows the result of this test. As the amount of NaOH increased, the extraction efficiency of lithium also increased. When the NaOH/sample ratio was 0.5:1, only 14.53% of lithium was extracted. This is because not all of the sample reacted with NaOH. As the amount of NaOH increased, the extraction efficiency of lithium increased significantly up to a ratio of 1.5:1. However, when the ratio was increased from 1.5:1 to 2:1, there was only a 2% increase in the extraction efficiency. This result shows that adding NaOH at 1.5:1 ratio is sufficient to react with spodumene.

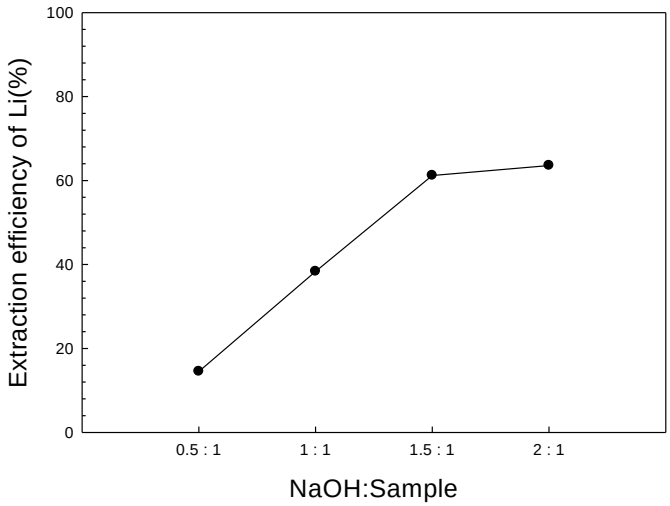


Figure 18. Extraction efficiency of lithium at various NaOH/sample ratios

The extraction of other elements at various NaOH/sample ratios is shown in figure 19. When the ratio was increased, the amount of Si and Al elements also increased. In addition, when the ratios were 0.5:1 and 1:1, the extraction efficiencies of Li and Si were similar. As the amount of NaOH increased to 1.5:1, a larger percent of Si was extracted than that of Li. In addition, when the NaOH/sample ratio was increased from 1.5:1 to 2:1, the extraction of Si was 12%, while that of lithium increased slightly. When the amount of NaOH was increased from 1.5:1 to 2:1, lithium purity was reduced. Hence, 1.5:1 was the optimum condition of fusion.

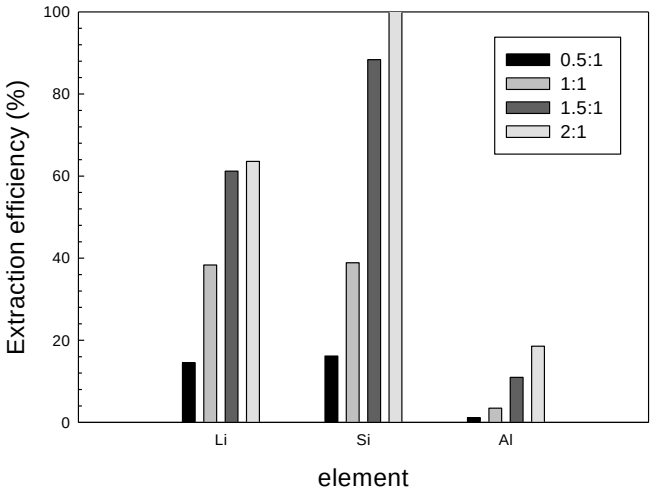


Figure 19. Extraction efficiency of Li, Si, and Al at various NaOH/sample ratios

4.1.3 Effect of leaching temperature

To investigate the effect of the leaching temperature, leaching was performed at 25, 40, and 70 °C. The fusion conditions were fixed at 15 min fusion time and 600 °C fusion temperature. In these experiments, other conditions were fixed and the detailed conditions are shown in Table 14.

Table 14. Conditions of fusion and leaching for the effect of leaching temperature

Content	Condition
Reagent	Sodium hydroxide (NaOH)
Fusion time	15min
Fusion temperature	600℃
Ratio of NaOH/Sample	1.5:1
Leaching time	5min
Agitation speed	800 rpm
L/S ratio	20/1

Figure 20 shows the results of the leaching test at 25, 40, and 70 °C. As the leaching temperature increased, the amount of extracted lithium decreased. This result means that extraction of lithium process is an exothermic reaction.

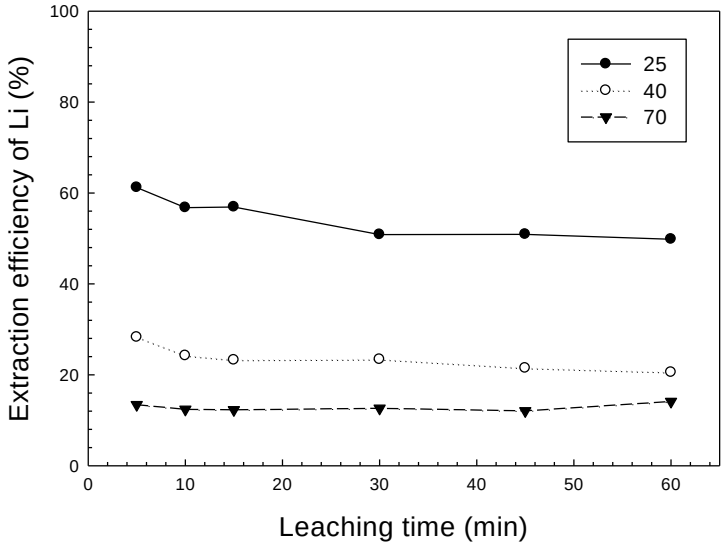


Figure 20 Extraction efficiency of lithium at various leaching temperatures

The extraction efficiencies of Li, Si, and Al are shown in Figure 21. Al extraction did not change significantly with the leaching temperature, while the extraction efficiency of Li increased. In addition, the amount of silicon did not be affected by the leaching temperature. This result shows that the only lithium was highly influenced by the temperature change.

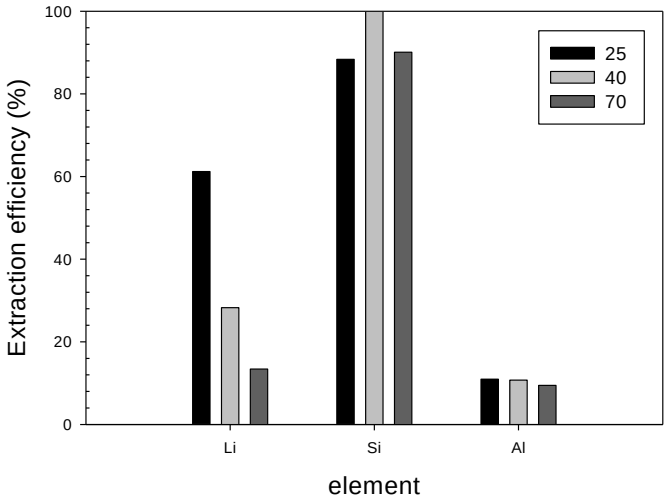


Figure 21. Extraction efficiency of Li, Si, and Al at different leaching temperatures

The maximum extraction efficiency of Li was relevantly low (63.88 %). Therefore, the residue was analyzed by XRD. Figure 22 shows the result of the XRD analysis of the residue after water leaching. The residue was composed of lithium aluminum oxide, which is insoluble in water. This product was produced when spodumene sample partially reacted with sodium hydroxide. Consequently, the extraction of lithium was inhibited by formation of the insoluble compound.

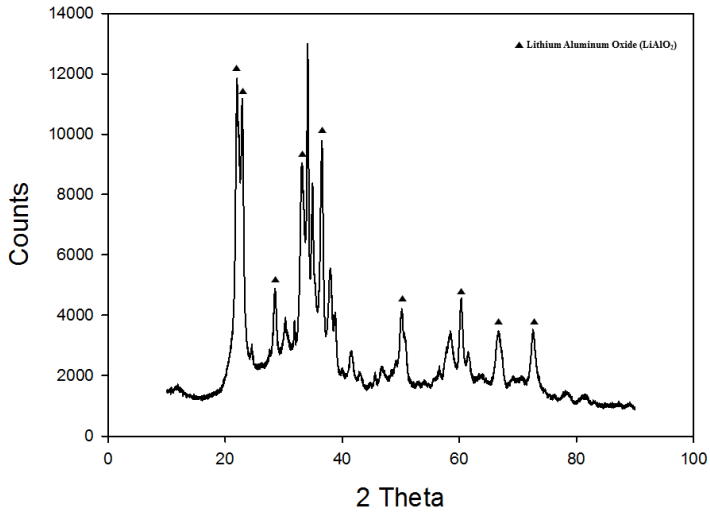


Figure 22. Result of XRD analysis of the residue after water leaching

4.2. Na_2CO_3 fusion method

The second fusion experiment was the Na_2CO_3 fusion method. In this test, the fusion time and Na_2CO_3/sample ratio were selected as the variables. In the leaching stage, the leaching time and acid (HCl/H_2SO_4) concentrations were chosen as the variables. The reaction in this method is as follows:

$$\mathrm{Na}_2CO_3 + 2LiAl(SiO_3)_2 \rightarrow Li_2CO_3 + Na_2O \cdot Al_2O_3 \cdot 4SiO_2 \quad (6)$$

When the fusion was conducted below 850 °C, the reaction did not occur. In this experiment, fusion was conducted only at 850 °C and the effect of fusion temperature was not investigated. Since, this temperature was already high, additional fusion tests at temperatures over 850 °C were not conducted.

Figure 23 shows the result of the XRD analysis of the spodumene sample after the fusion with Na_2CO_3. Sodium aluminum silicate and sodium silicate were produced in the Na_2CO_3 fusion.

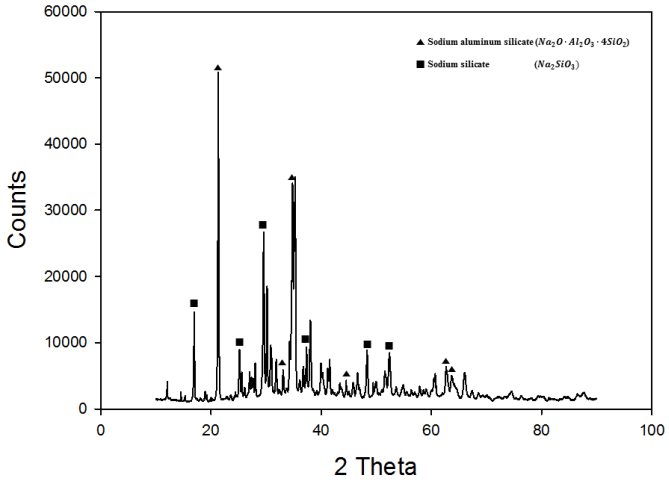


Figure 23. Result of XRD analysis of the fused sample with Na_2CO_3

4.2.1. Effect of fusion time

The effect of fusion time on lithium extraction was studied in the Na_2CO_3 fusion experiment at fixed fusion and leaching conditions. In this test, the fusion time was 15, 30, and 60min. Table 15 shows the detailed conditions of this experiment.

Table 15. Conditions of fusion and leaching experiments for the effect of fusion time

Content	Condition
Reagent	Sodium carbonate (Na_2CO_3)
Fusion time	60min
Fusion temperature	850 °C
Ratio of Na_2CO_3/sample	1:1
Leaching temperature	25 °C
Agitation speed	800 rpm
Acid concentration	HCl 1.5M
L/S ratio	20/1

Figure 24 shows the trend of extraction efficiency with the fusion time. When the fusion time was 30 min, the extraction efficiency was the highest at 1 h and 2 h of leaching time. However, when the leaching time was increased to more than 3 h, almost the same amount of lithium was extracted for 30 min and 60 min of fusion time. This result means that the fusion time over 30min did not have an effect on the extraction efficiency of lithium. However, 15min of fusion time was not enough to react with Na_2CO_3 and spodumene.

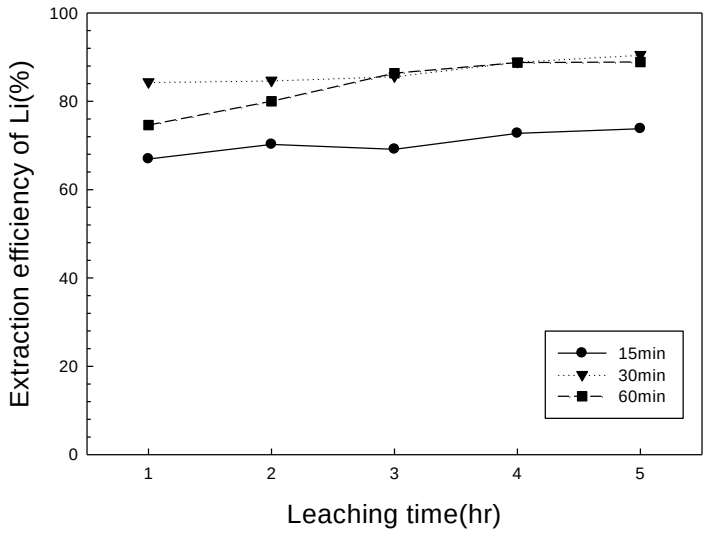


Figure 24. Extraction efficiency of lithium at various fusion times

4.2.2. Effect of Na_2CO_3/sample ratio

To investigate the effect of the Na_2CO_3/sample fusion ratio, fusion experiments were conducted at mass ratios of 1:1, 1.5:1, and 2:1. The fusion test was performed under other fusion conditions of fusion time 60 min and fusion temperature 850 °C. After the fusion, the samples were leached with 1.5 M of hydrochloric acid. The other conditions are shown in Table 16.

Table 16. Conditions of fusion and leaching

Content	Condition
Reagent	Sodium carbonate (Na_2CO_3)
Fusion time	60min
Fusion temperature	850℃
Ratio of Na_2CO_3/Sample	1:1/1.5:1/2:1
Leaching temperature	25℃
Agitation speed	800 rpm
Acid concentration	HCl 1.5M
L/S ratio	20/1

Figure 25 shows the effect of mass ratio between Na_2CO_3 and the sample at each leaching time. The extraction efficiency of lithium at the 2:1 mass ratio was markedly lower than that at 1:1 and 1.5:1. The amount of extracted lithium at 1:1 and 1.5:1 were similar before 2 h of leaching time. However, the extraction efficiency of lithium at 1:1 mass ratio was larger than that at 2:1 after 3 h of leaching time. Consequently, the largest amount of lithium was extracted at mass ratio 1:1. This indicates that the extraction performance improves as the Na_2CO_3/sample ratio decreases.

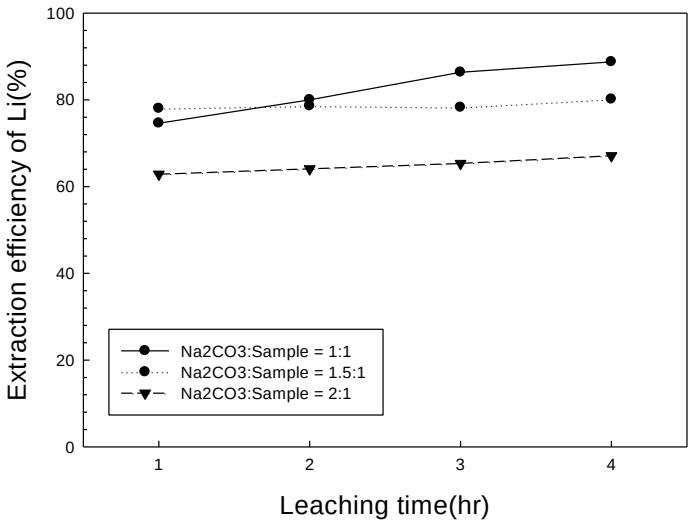


Figure 25. Extraction efficiency of lithium at various Na_2CO_3/sample ratios

4.2.3. Effect of leaching time

The effect of leaching time was studied by comparing the results of the experiments with various leaching times. The fusion conditions were constant: fusion temperature of 850 °C, fusion time of 60 min, and Na_2CO_3/sample ratio 1:1. The leaching conditions other than the leaching time were also fixed. Table 17 shows the other conditions.

Table 17. Conditions of leaching and fusion for the effect of leaching time

Content	Condition
Reagent	Sodium carbonate (Na_2CO_3)
Fusion time	60min
Fusion temperature	850 °C
Ratio of Na_2CO_3/Sample	1:1
Leaching temperature	25 °C
Agitation speed	800 rpm
Acid(HCl/H_2SO_4) concentration	0/0.5/1.0/1.5
L/S ratio	20/1

To investigate the leaching time effect, the leaching results of each acid reagent, hydrochloric acid and sulfuric acid, were compared. In addition, the leaching was conducted with 0, 0.5, 1, and 1.5 M concentrations.

When water is used as leaching agent, only approximately 12% of lithium was extracted (Figure 26) over at 5hr of leaching time because the solubility of lithium carbonate in water is low.

At 0.5 M of acid concentration, the extraction efficiency of leaching with hydrochloric acid changed slightly. In other words, the amount of extracted lithium increased as the leaching time increased for 0.5 M sulfuric acid (Figure 26). From this result, the leaching time with sulfuric acid correlated with the amount of extracted lithium. However, the amount of lithium did not show the difference when 0.5M of hydrochloric acid was used for leaching.

At 1.0 M acid concentration, both the HCl and H_2SO_4 leaching efficiencies increased with increasing leaching time. In addition, leaching with HCl showed a larger increase than that of H_2SO_4 (Figure 26). In comparison to 0.5M of acid leaching, leaching with sulfuric acid at 1.0M showed a slight increase as increasing the leaching time. This result shows that the reaction time is shortened from 0.5M to 1M.

At 1.5 M acid concentration, the amount of extracted lithium increased as the leaching time increased. In addition, the extraction efficiency of leaching with H_2SO_4 was larger than that with HCl and all of the lithium was extracted with 1.5M of the sulfuric acid for 5h of leaching time (Figure 26). Hence, 1.5M of sulfuric acid was the optimum condition in terms of the recovery of lithium.

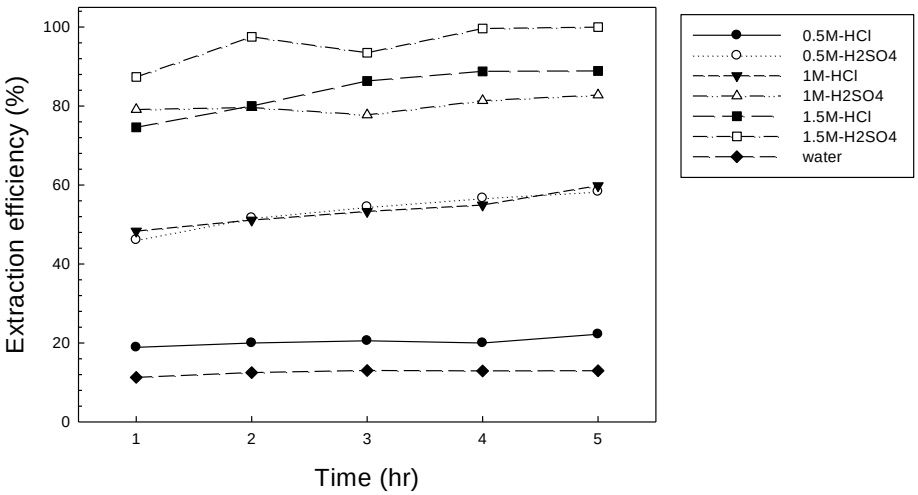


Figure 26. Extraction efficiency of lithium at various leaching time and acid (HCl/H_2SO_4) concentration

4.2.4 Effect of acid (HCl/H_2SO_4) concentration

To investigate the effect of acid concentration, leaching experiments were performed with two kinds of acid solutions: HCl and H_2SO_4. The fusion and leaching conditions other than acid concentrations were constant. The detailed conditions are shown in table 18.

Table 4. Conditions of leaching and fusion for the effect of acid concentration

Content	Condition
Reagent	Sodium carbonate (Na_2CO_3)
Fusion time	60min
Fusion temperature	850 °C
Ratio of Na_2CO_3/Sample	1:1
Leaching temperature	25 °C
Agitation speed	800 rpm
Acid(HCl/H_2SO_4) concentration	0.5/1.0/1.5
L/S ratio	20/1

Figure 27 shows the results of the leaching test with hydrochloric and sulfuric acid solutions at various concentrations. The results show that the amount of extracted lithium increased as the concentration of acid increased. This trend applied to both HCl and H_2SO_4. However, when H_2SO_4 was used as the reagent, a larger amount of lithium was extracted than HCl.

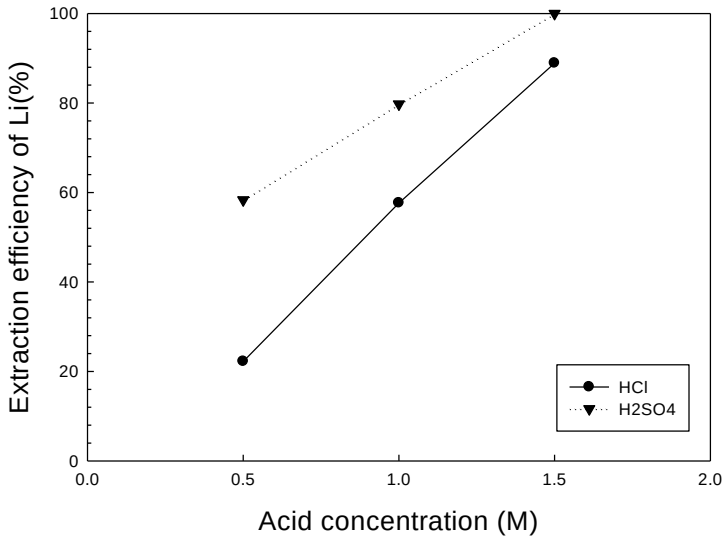


Figure 27. Extraction efficiency of lithium at various acid concentration

In addition, the extraction efficiency of lithium with 1.5 M of hydrochloric acid was less than 90%; thus, an additional experiment was conducted with 2.0 M of hydrochloric acid under the same conditions. Figure 28 shows the result of this experiment. The highest extraction efficiency of lithium was 87.09% and it is similar to the extraction efficiency with 1.5 M of hydrochloric acid. This indicates that further lithium extraction did not occur above 1.5 M HCl concentration.

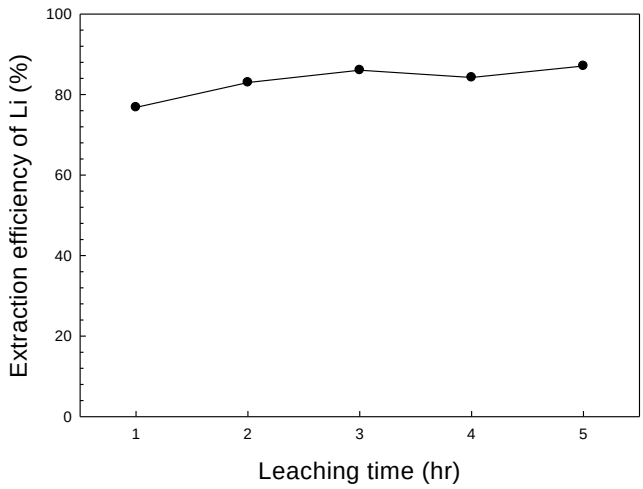


Figure 28. Extraction efficiency of lithium at various leaching times with 2M HCl

After leaching with 1.5 M of H_2SO_4, 99.98% of lithium was extracted. However, other elements were also extracted along with lithium; Figure 29 shows the extraction efficiencies of Li, Si, and Al. All the Si and 75% of Al was extracted. This shows that the lithium purity was low and an additional process for removing impurities was required.

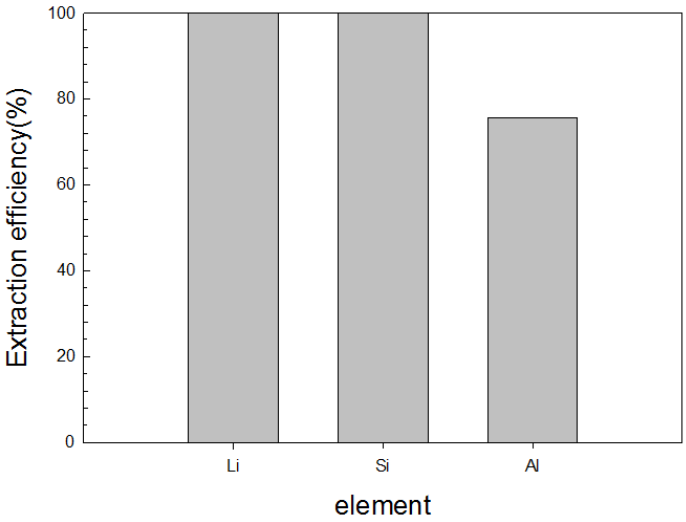


Figure 27. Extraction efficiency of Li, Si, and Al with 1.5M of sulfuric acid leaching

4.3 Separation

After leaching, the amount silicon and aluminum were also high, thus an additional process for removing impurities was needed. For separation of silicon and aluminum from lithium, precipitation method was used. In this study, adding sodium carbonate (Na_2CO_3) were chosen for precipitation.

When adding sodium carbonate and mixing the leachate with Na_2CO_3 for 1 h, leachate leaching with hydrochloric acid showed the change of the amount of element for 12 h. The amount of all elements decreased as increasing the time in the leachate. As a result, all of Si was precipitated and the amount of aluminum showed 5% after 12 h (Figure 30). Lithium was also precipitated but over 50% of lithium still remained in the leachate after precipitation.

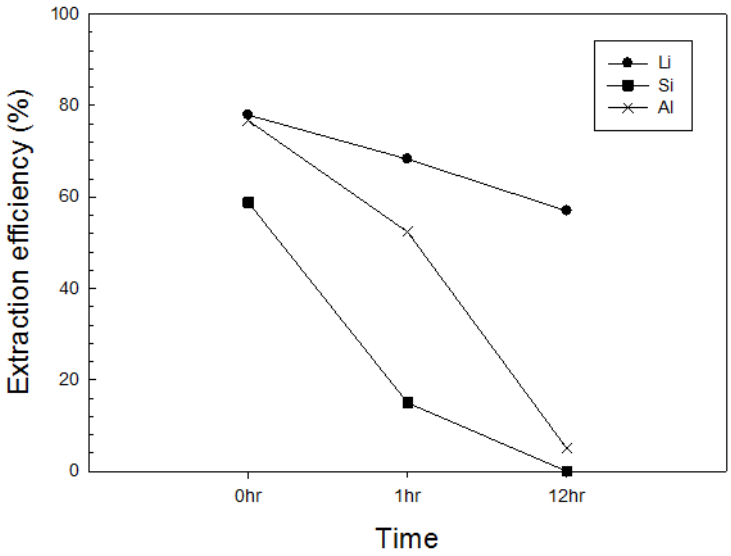


Figure 30. Extraction efficiency of Li, Si, and Al after separation

However, the amount of Si and Al in the leachate with sulfuric acid leaching did not decrease after adding sodium carbonate.

5. Conclusion

Alkali fusion with NaOH and Na_2CO_3 was studied to obtain the optimum fusion and leaching conditions for a high extraction efficiency of lithium from spodumene. In the NaOH fusion test, the fusion time, temperature, and NaOH/sample ratio were varied. In the leaching experiment, water leaching was conducted and the leaching time and temperature were chosen as the variables. The fusion with Na_2CO_3 was conducted only at 850 °C, and the fusion time and Na_2CO_3/sample ratio were varied. In the leaching stage, the effects of leaching time and acid concentrations were investigated.

The effect of various conditions in NaOH fusion was studied. The results of the effect of fusion time show that the extraction efficiency at 60 min fusion time is the highest. However, the extraction efficiency of lithium did not show a significant difference as the fusion times were varied. When the experiments were conducted at various fusion temperatures, the largest amount of lithium was extracted at 600 °C at 5 min leaching time. However, the extraction efficiency did not change considerably. These results imply that the fusion time and temperature did not affect the extraction efficiency of lithium in NaOH fusion. The NaOH/sample ratio was changed from 0.5:1 to 2:1. At the 0.5:1 ratio, only 14.53% of lithium was extracted, while over 60% of lithium was extracted at 1.5:1 and 2:1. The amount of lithium increased with the increasing ratio, but Li extracted was not significantly higher beyond the 1.5:1 ratio.

The effect of the leaching conditions after the NaOH fusion were studied. Leaching was conducted with only water. By increasing the leaching time from 5 min to 60 min, the extraction efficiency of lithium showed a decreasing trend. Additionally, approximately 12% of lithium decreased in the solution for 55 min. The leaching temperature was varied to 25 °C, 40 °C, and 70 °C. At 25 °C, approximately 60% of lithium was extracted. However, the amount of extracted lithium decreased rapidly with increasing leaching temperature from 25 °C to 40 °C. The extraction efficiency of lithium was lower at 70 °C than at 25 °C.

The optimum conditions in the NaOH fusion are 600 °C, 60 min, and 1.5:1 NaOH/sample; additionally, the leaching conditions were 5 min and 25 °C.

The Na_2CO_3 fusion test was conducted under various conditions. Lithium extraction was lesser in 15 min compared with that in 30 min and 60 min; further, the extraction efficiencies of lithium were almost the same at 30 min and 60 min of fusion. This indicates that the fusion time after 30 min does not affect the amount of extracted lithium. The extraction efficiency of lithium decreased with increasing amount of Na_2CO_3.

The leaching time, acid concentrations, and acid reagents were varied in leaching experiments conducted after Na_2CO_3 fusion. The leaching time did not influence the extraction efficiency of lithium when the leaching was conducted with water. However, the results of leaching at 0.5 M, 1 M, and 1.5 M of acid concentration showed that the amount of extracted lithium increased with the leaching time. As the acid concentration increased, the extraction efficiency of lithium increased significantly. In addition, leaching with H_2SO_4 extracted more lithium than with HCl at all concentrations. The extraction efficiency of lithium did not increase when the leaching was conducted with

only water. This indicates that the leaching time did not influence the extraction of lithium. However, when leaching was conducted with acid, the extraction efficiency of lithium showed an increase. In this case, the leaching time affected the extraction efficiency of lithium. Therefore, spodumene fused with sodium carbonate was not extracted with only water but extracted with acid. In addition, the amount of lithium extracted depended on the leaching time.

The highest amount of lithium (99%) was extracted when fusion was conducted for 60 min with 1:1 of Na_2CO_3/sample ratio and when leaching was conducted for 5 h with 1.5 M H_2SO_4. However, a large amount of silicon and aluminum was also extracted along with lithium.

After leaching separation process by precipitation was conducted. Si and Al contents were not decreased after the separation stage in the H_2SO_4 leaching. However, Si and Al in leachate with HCl leaching was precipitated after the separation process. As a result, Si was removed and the amount of Al decreased from 76% to 5%.

The optimum method for the high extraction efficiency of lithium was Na_2CO_3 fusion with H_2SO_4 leaching. However, considering the purity of lithium, Na_2CO_3 fusion with HCl leaching was the optimum condition for extracting lithium from spodumene.

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초 록

리튬은 가장 가벼운 금속이자 높은 전기 전도성을 가지는 물질로 산업의 다양한 곳에서 활용되어 특히 배터리, 세라믹, 유리 등에 많이 사용된다. 또한 오늘날 전자기기의 사용이 증가함에 따라 배터리의 소비 역시 증가하여 리튬의 수요는 계속해서 늘어날 것으로 예측된다. 리튬을 생산하는 주요 자원은 염수이지만 페그마타이트로부터 생산되는 리튬의 양 역시 많은 양을 차지한다. 리튬을 포함하고 있는 주요 페그마타이트 광물로는 스포듀민, 레피돌라이트, 페탈라이트 등이 있으며 그중에서도 페그마타이트로부터 생산된 리튬의 약 80%를 스포듀민에서 생산하고 있다. 따라서 스포듀민은 리튬 생산에 빼놓을 수 없는 광물이며 증가하는 리튬 수요에 맞춰 스포듀민에서의 리튬 생산을 위한 연구는 계속해서 이루어져야 한다.

산업 공정에서 사용되는 가장 대표적인 스포듀민에서의 리튬 추출 공정은 황산 배소법을 이용한 공정이다. 이 공정은 황산과 함께 약 250도에서 배소된 스포듀민을 물을 이용한 침출을 통해 리튬을 수용액 상으로 침출한다. 하지만 이 공정은 배소 단계 이전에 1000도 이상의 고온에서 하소를 수행하여 α-스포듀민에서 β-스포듀민으로 구조를 변경하는 단계를 거친다. 이 과정은 매우 높은 온도에서 진행되므로 많은 양의 에너지를 소모한다는 단점을 가지고 있다. 위 공정 이외에도 스포듀민에서 리튬을 추출하기 위한 많

은 연구들이 이루어지고 있지만 대부분의 연구가 마찬가지로 β-스포듀민에서의 리튬 추출 연구를 수행하고 있으며 자연 상태인 α-스포듀민에서 리튬 추출하는 방법에 대한 연구는 매우 적은 편이다.

본 연구에서는 1000도 이상의 고온에서 상변화하는 과정을 거치지 않고 α-스포듀민에서 바로 리튬을 추출하는 연구를 수행하였으며 실리케이트 광물의 전처리에 많이 사용되는 알칼리 용융법을 사용하였다. 본 연구는 (1) 수산화나트륨을 이용한 용융, (2) 탄산나트륨을 이용한 용융으로 나누어 리튬 추출의 최적 조건을 찾기 위해 다양한 조건하에서 수행되었다.

수산화나트륨 용융 실험에서 최적 조건은 용융 온도 600도, 용융 시간 60분, 1.5:1의 수산화나트륨과 시료의 질량비로 나타났고, 침출 최적 조건의 경우 침출 시간 5분, 침출 온도 25도로 나타났다. 최종적으로 위 조건하에서 수행한 실험 결과 63.88%의 리튬이 추출되는 것을 확인하였다.

탄산나트륨을 이용한 용융 실험에서는 용융 온도를 850도 고정한 후 실험을 진행하였다. 위 용융 온도 하에서 용융 최적 조건은 용융 시간 60분 탄산나트륨과 시료의 질량비 1:1이었고, 침출 최적 조건의 경우 1.5M의 황산을 이용하여 5시간 침출했을 때 가장 높은 리튬 추출 효율을 나타내었다. 실험 결과로 얻은 최적 조건하에서 99.98%의 리튬이 추출되었다. 이 효율은 매우 높지만 100%의 규소와 75%의 알루미늄이 리튬과 함께 추출된다는 단점을 가진다. 같은 조건에서 염산 1.5M을 이용한 침출 실험 결과 추출된 리튬의 추출 효율은 황산을 이용한 침출보다 더 적었으나 규소와 알

루미늄 또한 적게 추출되었다. 그러나 이 역시 높은 농도이므로 리튬의 순도를 높이기 위하여 추가적인 분리를 수행하였고 분리 결과 염산을 이용한 침출액에서 규소가 모두 제거되었으며 알루미늄의 침출률이 5%로 줄어드는 결과를 확인하였다.

본 연구에서는 스포듀민에서 많은 양의 리튬을 추출하기 위한 최적 용융, 침출 조건을 찾는 연구를 알칼리 용융법을 이용하여 수행하였다. 실험 결과 대부분의 리튬이 탄산나트륨을 이용한 용융과 황산을 이용한 침출에서 추출되는 결과를 얻었다. 하지만 불순물을 함께 고려했을 때 1.5M의 염산을 이용한 침출이 최적 조건을 가진다는 결론을 얻었다. 이 실험은 상변화 단계를 거치지 않아 기존의 공정보다 낮은 온도에서 수행되었다. 그러므로 본 연구는 새로운 공정에 대한 가능성을 제시하였고 에너지 소비와 리튬 생산 공정 단계를 줄였다는 점에서 큰 의의를 가진다.

주요어: 알칼리 용융법, 침출, 스포듀민, 리튬

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