The investigation of lithium extraction by roasting with sulfating agent and water leaching from nepheline syenite rocks

Zeynep Üçerler, Ali Güney

Istanbul Technical University, Faculty of Mines, Mineral Processing Engineering Department, Istanbul, Turkey, 34469

Corresponding author: ucerler@itu.edu.tr (Zeynep Üçerler)

Abstract: In this study, the extraction of lithium from zinnwaldite concentrate containing 0.25% Li was investigated. The run-of-mine ore originated from nepheline syenite rocks in Kırşehir, Turkey, and contained 216.3 ppm Li. Firstly, the ore was beneficiated by a flotation process to increase the lithium content. Then, it was subjected to roasting and water leaching processes, respectively. In the roasting process, calcite and gypsum were used as additives to form dissoluble lithium sulfate for the next process. Additionally, the effect of roasting temperatures (750, 850, 950, and 1000°C) and times (30, 60, 90, 120, and 240 min) was examined along with different ratios of additives to concentrate to find the optimal conditions. Accordingly, the calcined product from the roasting process was dissolved in water by determining the optimal leaching temperature, time, and water/solid ratio. Consequently, a lithium product was obtained from the concentrate with 93.3% extraction efficiency. Finally, the mother liquor contained 30 mg/dm^3 Li, the production of Li_2CO_3 from mother liquor will be investigated in case of production of the sample at the optimal conditions of roasting and leaching in further studies.

Keywords: zinnwaldite, water leaching, roasting, lithium extraction

1. Introduction

Lithium has been listed as a critical or close to a critical element in various researches from the point of view of the importance of green technology. Moreover, it was included in a list of 15 important minerals with the participation of several countries at the International Strategic Minerals Inventory (ISMI) in the 1980s and 1990s (Anstett et al., 1990). Lithium can be commercialized as ore, concentrate, lithium compounds, or metal lithium for the market in different usage areas. While LiOH with a 25% ratio of lithium or lithium compounds is used on the market, Li_2CO_3 has a ratio above 50%, and other lithium compounds and metal lithium have ratios of almost 20–25% (Yıldız, 2016). Moreover, Li_2CO_3 has various usage areas, but usage in the production of batteries for electrical vehicles is the most important in recent years (Akgök and Şahiner, 2017). In 2008, due to awareness of the requirement for Li_2CO_3, research was carried to determine whether or not the known and existing lithium deposits were sufficient for usage in electrical vehicles and electrical machines such as computers and cell phones in which lithium is still being used (Yıldız, 2016). Consequently, it was found that the reserves were sufficient for use in many types of electric vehicles such as HEVs (hybrid electrical vehicles), PHEVs (plug-in hybrid electric vehicles), BEVs (battery electrical vehicles), and EVs (electrical vehicles), and electrical machines (Yıldız, 2016). Spodumene ($LiAlSi_2O_6$), lepidolite ($LiKAl_2F_2Si_3O_9$), petalite ($LiAlSi_4O_{10}$), zinnwaldite ($LiKFeAl_2F_2Si_3O_{10}$), hectorite ($Na_{0,3}(Mg,Li)_3Si_4O_{10}(F,OH)_2$), and amblygonite ($LiAlFPO_4$) have commercial value for beneficiation although there are many lithium-bearing minerals in the world (Jandova et al., 2010; Meshram et al., 2014).

In Table 1, the beneficiation methods have been shown for certain lithium minerals bearing economic value. These methods are applied depending on the properties of the minerals and the concentrates contain between 4.5 and 7.8% Li_2O depending on the types of minerals (Tadesse et al., 2019).

Zinnwaldite is generally found in granitic pegmatite rocks and contains more impurities and higher

Table 1. Some examples of beneficiation methods for lithium minerals

	Beneficiation Methods	
Spodumene	**Flotation** (Banks et al. (1953), McVay and Browning (1962), Zhu et al. (2015), Li et al. (2017), Tian et al. (2018))	**Dense Media Separation** (Munson and Clarke (1955), Redeker (1979), Amarante et al. (1999), Aghamirian et al. (2012))
Lepidolite	**Flotation** (Choi et al. (2012), He et al. (2013), Vieceli et al. (2016))	-
Zinnwaldite	**Flotation** (Siame and Pascoe (2011))	**Magnetic Separation** (Bale and May (1989), Botula (2005), Siame and Pascoe (2011), Leißner et al. (2016))

iron content compared with lepidolite (Paukov et al., 2010). The biggest known deposits of zinnwaldite are in Cinovec, Zinnwald, at the boundary between the Czech Republic and Germany (Martin et al., 2017). To produce final products such as Li_2CO_3, LiCl, LiOH, roasting, and leaching processes are generally applied on lithium concentrates such as spodumene (Chen et al., 2011; Barbosa et al., 2015), lepidolite (Yan et al., 2012a; Yan et al., 2012b; Yan et al., 2012c; Luong et., 2013; Luong et al., 2014; Hien-Dinh et al., 2015;), hectorites from boron wastes in Turkey (Mordoğan et al., 1995) or Nevada clays in the USA (Crocker et al., 1987), petalite (Sitando and Crouse, 2012), and zinnwaldite (Jandová et al., 2007; Jandová et al., 2009; Jandová et al., 2010; Siame and Pascoe, 2011; Vu et al., 2013).

A zinnwaldite concentrate obtained from magnetic separation contains 2.7% Li_2O, and 90% of the passing material is under 100 μm in size. In the research by Siame and Pascoe, $CaSO_4.2H_2O$ (> 98% purity) and Na_2SO_4 (> 99.5% purity) were used as additives separately with concentrates in ratios of 1:2 and 1:5, respectively. The roasting process was realized with gypsum at 1050°C and with Na_2SO_4 at 850°C. Additionally, the water leaching conditions were a leaching temperature of 85°C during 3 h with a water-to-solid (w/s) ratio of 10:1. The highest extraction efficiencies for the experiments with two different additives were 84% and 89%, respectively (Siame and Pascoe, 2011). In a study, zinnwaldite concentrate (1.21% Li) obtained by magnetic separation from waste Sn-W in the Czech Republic was used to take lithium ions into solution. The experiments were carried out by roasting at 825°C for 1 hour with a 1:5 ratio of concentrate: $CaCO_3$ (size below 100 μm) and water leaching at a temperature of 90–95°C for 30 min with a mixing rate of 400 rpm and a w/s ratio of 10:1. Lithium was extracted with 90% efficiency (Jandová et al., 2007). In subsequent work (Jandová et al., 2010), even though 10:1 had been previously chosen as the optimal w/s ratio, a further study was carried out with a w/s ratio of 5:1 to make the leach solution more saturated. CO_2 gas was fed into the solution at room temperature with a flow rate of 40 dm^3/s to carbonize the rubidium and impurities such as metal hydroxides at pH 6.8. As the impurities were precipitated and filtrated, the temperature was increased to 90–95°C, and 85, 95, and 98% of the total volume of the leach liquor was fractionally evaporated. Moreover, the precipitates were separated by filtration in every step, washed with water, and then dried. The purities of Li_2CO_3 obtained in three steps were 99.5, 99.7, and 99.8%, respectively.

Jandová et al. (2009) researched the precipitation of Li_2CO_3 by using the same zinnwaldite concentrate as in their previous studies. The concentrate was roasted with additives like $CaSO_4$ and $Ca(OH)_2$ in a ratio of 6:4.2:2. The process was carried out at 950°C for 60 min. The calcine obtained from the roasting was subjected to leaching at 90°C for 10 min. The l/s ratio was 10:1. Lithium was taken into solution with an extraction efficiency of 96%. Before Li_2CO_3 was precipitated with high purity, some impurities such as Ca^{2+} ions were precipitated by K_2CO_3 at 20°C and separated from the solution by filtration. As the temperature increased, the solubility of Li_2CO_3 decreased; consequently, the leach liquor was heated to 90°C and purified; accordingly, the solution contained 9 g/dm^3 Li before precipitation. K_2CO_3 was added into the solution in a stoichiometric ratio and Li_2CO_3 started to precipitate incrementally. The purity of the washed Li_2CO_3 was 99%. Another study examined the extraction of lithium from zinnwaldite concentrate containing 1.29% Li from Sn-W waste in the Czech

Republic, and a lithium extraction efficiency of 84% was reached at a roasting temperature of 835°C, a roasting time of 60 min, a 1:5 ratio of $CaCO_3$ additive to concentrate, and leaching of the calcined product at 95°C during 60 min; in addition to these optimal conditions, the l/s ratio was 10:1 (Vu et al., 2013). The studies mentioned above are shown in Table 2.

The main objective of this study was to recover lithium with the highest extraction efficiency from zinnwaldite concentrate enriched by the flotation process from poor lithium-bearing nepheline syenite rocks. The optimal conditions for the roasting and water leaching processes were established systematically. Consequently, the new resource from nepheline syenite rocks for the production of lithium-derived compounds was determined and investigated for the first time.

Table 2. Studies on zinnwaldite concentrate

References	Method	Roasting Temperature (°C)	Roasting Time (min)	Additives /Ratio	Leaching Temperature (°C)	Leaching Time (min)	w/s Ratio	Ext.Eff. (%)
Siame and Pascoe (2011)	Roasting/ Water Leaching	1050	60	Conc:$CaSO_4$. $2H_2O$ 1:2	85	30	10:1	84
		850		Conc:Na_2SO_4 1:5				89
Jandová et al. (2007)	Roasting/ Water Leaching	825	60	Conc:$CaCO_3$ 1:5	90-95	30	10:1	90
Jandová et al. (2009)	Roasting/ Water Leaching	950	60	Conc:$CaSO_4$: $Ca(OH)_2$ 6:4.2:2	90	10	10:1	96
Vu et al. (2013)	Roasting/ Water Leaching	835	60	Conc:$CaCO_3$ 5:1	95	60	10:1	84

2. Materials and methods

2.1. Materials

The zinnwaldite concentrate containing 2500 ppm Li was derived from the nepheline syenites rocks (216.3 ppm Li) in Kırşehir-Turkey. The size of run-of-mine ore was below 2 mm. To prepare the materials, the ore was ground below 212 μm by a ball mill and then subjected to the flotation process including rougher, scavenger, and cleaning circuits to increase the lithium content in the ore. The optimal collector and depressant dosages were determined to obtain the best recovery and grade combination. Figure 1 shows the X-ray diffraction (XRD) pattern of run-of-mine ore, revealing the peaks of biotite, albite, nepheline, and K-feldspar. Moreover, according to the modal mineralogy analysis demonstrated in Table 3, the ore consisted of Na-feldspar (28.85%), K-feldspar (29.72%), nepheline (35.42%), biotite (2.71%), and others (3.3%). Magnetic separation was performed to separate the biotite to prove that zinnwaldite was found with mica. Figure 2 shows the XRD pattern of the magnetic product.

2.2. Methods

Following various researches in the literature (Crocker et al., 1987; Jandová et al., 2007; Jandová et al., 2009; Jandová et al., 2010; Siame and Pascoe, 2011; Luong et al., 2013; Vu et al., 2013; Luong et al., 2014), the parameters to be determined were the roasting temperature and time, and the ratio of the two additives which were mixed with the zinnwaldite concentrate (concentrate: calcite: gypsum) and leaching parameters (temperature, time, and water/solid ratio). Each parameter of two processes was examined individually by keeping all of the other conditions constant.
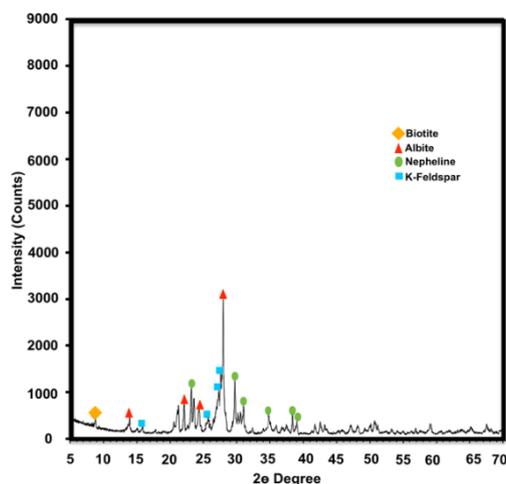
Fig. 1. XRD pattern of ore
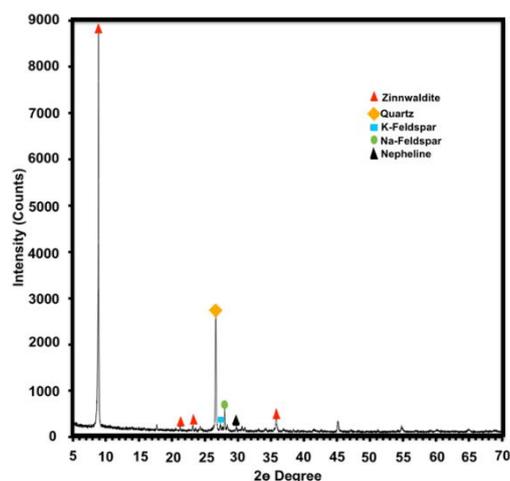
Fig. 2. XRD pattern of the magnetic product

Table 3. The contents of minerals according to modal mineralogy analysis

Mineral	Content (%)
K-feldspar	29.72
Albite	28.85
Biotite	2.71
Nepheline	35.42
Others	3.3

2.2.1. Roasting experiments

Roasting is a process that is widely used for altering the chemical structure of a mineral at a high temperature. Since high temperatures are involved, it is one of the costly methods in terms of plant operations. A lithium-bearing mineral cannot naturally be dissolved in water; thus, the structure of the mineral can be transformed into a soluble form by the roasting using gypsum (sulfating agent) as an additive. Roasting experiments were conducted in an oxygen purged ash furnace. The mixed materials were fed into the furnace in ceramic crucibles. The calcined product obtained from the roasting process was then leached. In each experiment, the roasting process was conducted using a 22-g sample including 10 g of concentrate and additives in different ratios. The 90% passing sizes of $CaCO_3$ (Merck KGaA, 99.5% purity) and $CaSO_4.2H_2O$ (Eczacıbaşı-ESAN, 99.7% purity) were 48 and 93 μm, respectively.

In Table 4, the parameters of roasting experiments are given. While studying on roasting, all of the leaching conditions (T: 60ºC, t: 60 min, w/s ratio: 10:1) were kept constant as below. In meantime, each condition of roasting was observed individually and respectively.

Table 4. The variable parameters of roasting

Roasting (Variable parameters)		Temperature (ºC)	Time (min)	Ratio of additives (concentrate: $CaCO_3$: $CaSO_4.2H_2O$)
	1	750-850-950-1000	60	5:3:3
	2	1000	30-60-90-120-240	5:3:3
	3	1000	90	5:0:6, 5:1:5, 5:2:4, 5:3:3, 5:4:2, 5:5:1, 5:6:0
Leaching (Constant conditions)				
Temperature (ºC)		60		
Time (min)		60		
w/s ratio		10:1		
Stirring rate (rpm)		500		

2.2.2. Leaching experiments

In each experiment, the calcined product obtained from the roasting process conducted under the optimal conditions (T: 1000ºC, t: 90 min, ratio of additives: 5:0:6) was exposed to the leaching process to take lithium into solution. For this purpose, the optimal conditions for the leaching process were individually examined, such as the leaching temperature and time, and the w/s ratio. Leaching parameters have been chosen according to previous studies (Jandová et al., 2007; Jandová et al., 2009; Vu et al., 2013; Siame and Pascoe, 2011). A stirring rate of 500 rpm was applied in each experiment. In Table 5, the variable parameters of leaching are presented.

Table 5. The variable parameters of leaching

Roasting (Constant conditions)				
Temperature (ºC)		1000		
Time (min)		90		
The ratio of additives		5:0:6		
Leaching (Variable Parameters)		Temperature (ºC)	Time (min)	w / s Ratio
	1	25-40-60-90	60	10:1
	2	40	30-60-90-120	10:1
	3	40	90	10:1-5:1-3:1

To perform liquid/solid separation, the leach liquor was filtrated by vacuum filtration and was transferred to a 250 cm³ flask for chemical analysis with Atomic Absorption Spectroscopy (AAS). However, the residue was washed with distilled water several times to achieve the maximum recovery and then was dried at approximately 100ºC for 12 h for chemical analysis. After obtaining the lithium contents of both solid and liquid as ppm, the extraction was calculated as Eq. 1:

$$Extr. Eff. (\%) = \frac{Liquid\ Li\ content}{Liquid\ Li\ content + Solid\ Li\ content} . 100 \qquad (1)$$

All tests were conducted only once, however, they were repeated twice or three times if inconsisted results were obtained. On the other hand, chemical analyses of the samples from each experiment were replicated three times to assure the accuracy. Consequently, error estimation related to chemical analysis was calculated approximately as ±1% for each result. Accordingly, it was calculated the arithmetical mean of three extraction values from analysis, hence the possible error factor was measured. The flowsheet of the process is shown in Fig. 3.
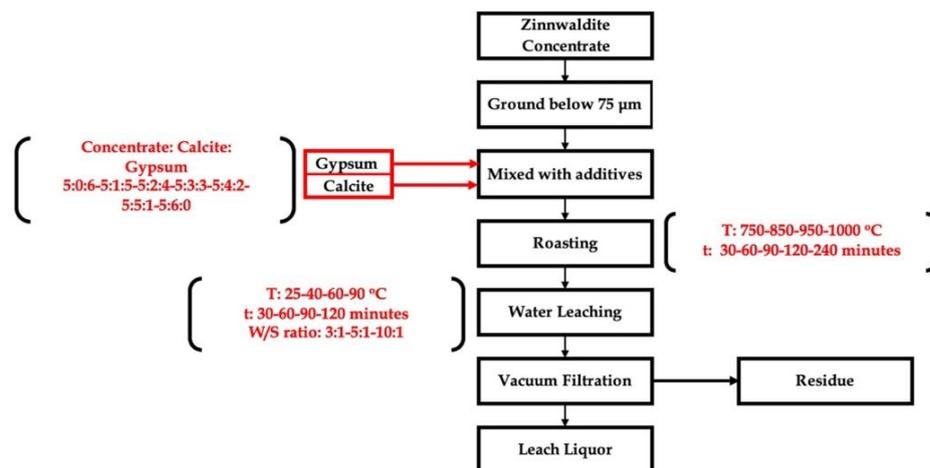
Fig. 3. Schematic flow diagram of the process

2.2.3. Analytical methods

The lithium extraction efficiency was determined according to leach residue and leach liquor. In every step of the research, the leach residue was filtrated and dried after leaching and the leach liquor was analyzed by Atomic Absorption Spectroscopy (AAS) (Varian AA24FS) by using standard solutions of 0.5 ppm Li, 1 ppm Li and 2 ppm Li to define the extraction efficiency. The XRD (PANalytical X'Pert Pro) method was used to analyze the leach residue. An X-ray diffraction (XRD) analysis was conducted with a copper X-ray-sourced Panalytical X'Pert Pro diffractometer (Malvern Panalytical Ltd., Malvern, UK). PDF4/Minerals International Centre of Diffraction Data (ICDD) software (PDF-4/Minerals, ICDD, Delaware County, PA, USA) was used for mineral characterization. Moreover, differential thermal analysis and thermogravimetric analysis (DTA/TGA) (Netzsch-STA 449 F3-Jupiter) was used to determine the thermal properties of zinnwaldite concentrate and the mixture that would be subjected to the roasting process. Also, Malvern 2000 Mastersizer was used to determine the size of additives.

3. Results and discussion

3.1. Roasting experiments

3.1.1. Effect of roasting temperature

Roasting temperatures of 750, 850, 950, and 1000°C were tested, while ~~the~~ other parameters were kept constant as shown in Table 4. DTA/TGA anaylses of zinnwaldite concentrate and the mixture of concentrate and gypsum in the ratio of 5/6 were used to assess the roasting temperature and the results are shown in Figs. 4 and 5.

The curves of DTA/TGA in Fig. 5 show that approximately 4% loss occurs in the zinnwaldite concentrate between 100 and 950°C. It is understood that this slight loss in the sample is because it contains small amounts of carbonates. Moisture loss occurs at about 100-150°C, while at 800°C low structural degradation is encountered. The DTA curve reveals that the main endothermic peak forms at about 860–870°C, which represents the structural degradation of the mixture, and the TGA curve indicates that a moisture loss of 4.84% occurs at about 200°C.

The results of lithium extraction at different roasting temperatures (Fig. 6) show that the lithium extraction was lower at a roasting temperature of 750°C compared to the other temperatures. Accordingly, it could be understood that the formation of lithium sulfate at 750°C had not reached a sufficient level. As the temperature increases, the efficiency increases proportionally. The highest and optimal result was obtained at 1000°C, with a lithium extraction efficiency of 48.5%. It was aimed to increase this value by optimizing the other parameters. Unlike this study, Jandovà et al. (2007) determined that the optimal roasting temperature was 825°C. The difference between the roasting temperature in their study and ours arose from the type of additive. In their study, calcite was used as an additive, and it is known that the degradation of calcite occurs at about 600°C.
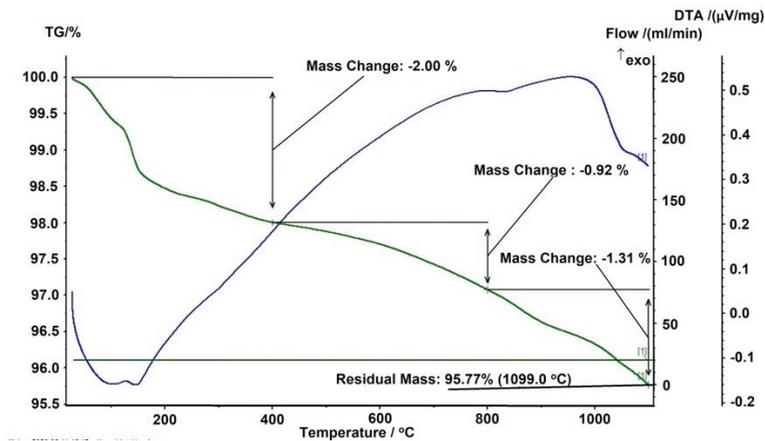
Fig. 4. DTA-TGA curve of zinnwaldite concentrate
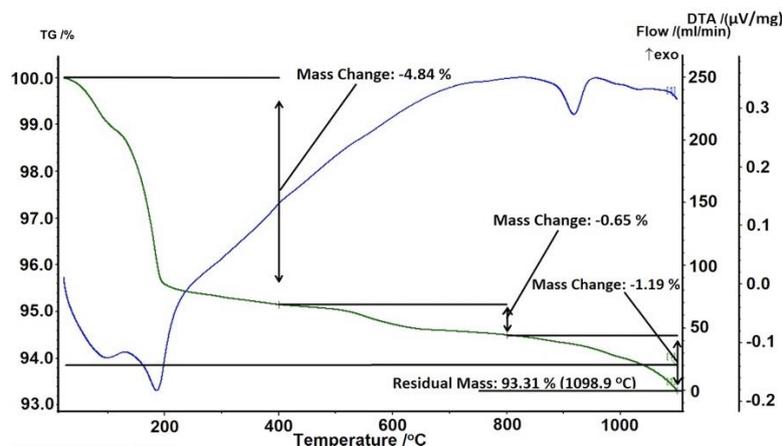
Fig. 5. DTA-TGA curves of the mixture of concentrate and gypsum in a ratio of 5:6

3.1.2. Effect of roasting time

In the series of experiments in which the effect of roasting time was examined, the constant conditions were the same as in the previous experiments. The roasting times which were examined were 30, 60, 90, 120, and 240 min, and results of lithium extraction are shown in Fig. 7. According to the results, the highest lithium extraction was obtained with a roasting time of 120 min and was 66.4%. It is seen that the extraction efficiency increased as the duration increased at high temperatures. Although there was a 10% of extraction difference between 90 and 120 min, 90 min was chosen as the optimal roasting time so as to decrease the operation costs.

3.1.3. Effect of different ratios of additives with concentrate

In the series of experiments aimed at optimizing the roasting temperature and time, the ratio of concentrate:calcite:gypsum was set as 5:3:3.

While the main objective of using gypsum as a primary additive was to alter the structure of mineral to obtain lithium sulfate, calcite was used as a secondary additive was to prevent the reversal of the reaction at high temperatures. The ratios of concentrate:calcite:gypsum tested were 5:0:6, 5:1:5, 5:2:4, 5:3:3, 5:4:2, 5:5:1, and 5:6:0. The test results were presented in Fig. 8.

The highest lithium extraction was obtained at a ratio of concentrate: $CaCO_3:CaSO_4.2H_2O$ of 5:0:6 and was 93.1%. It was observed that the use of calcite had no influence on lithium extraction and the use of gypsum was necessary and sufficient to form Li_2SO_4. Unlike our study, Siame and Pascoe (2011) obtained a lithium extraction of 84% at 1050°C, even though gypsum was used as an additive in a ratio of 2:1. This value of ratio was approx. two and a half times higher than the ratio of concentrate to gypsum investigated in our research. However, a higher lithium extraction value was achieved in this
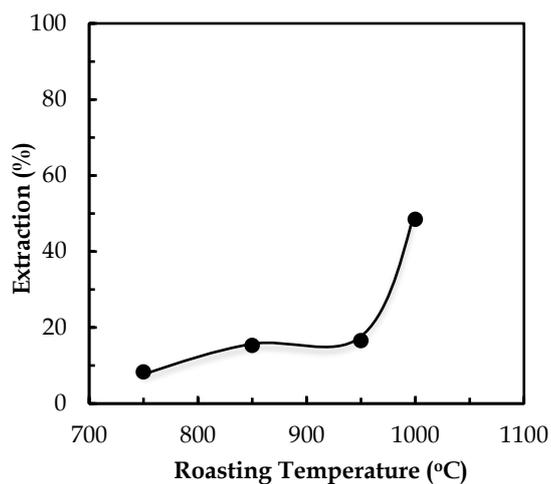
Fig. 6. Effect of different roasting temperatures on lithium extraction. Calcines from roasts for 60 min using concentrate: $CaCO_3:CaSO_4.2H_2O$ ratios of 5:3:3. Leaching at 60°C for 1 h using water/solid mass ratio of 10:1
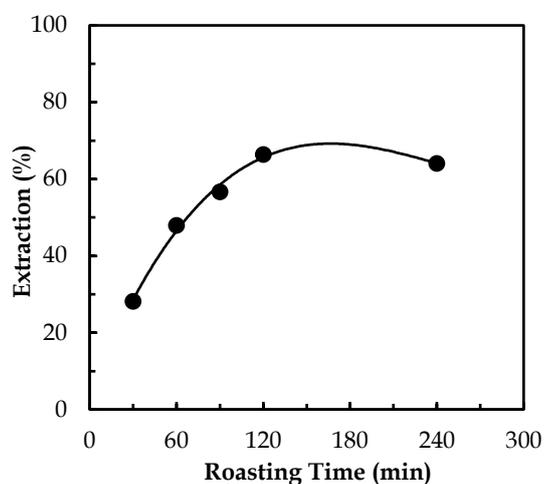
Fig. 7. Effect of different roasting times on lithium extraction. Calcines from roasts at 1000°C using concentrate: $CaCO_3:CaSO_4.2H_2O$ ratios of 5:3:3. Leaching at 60°C for 1 h using water/solid mass ratio of 10:1
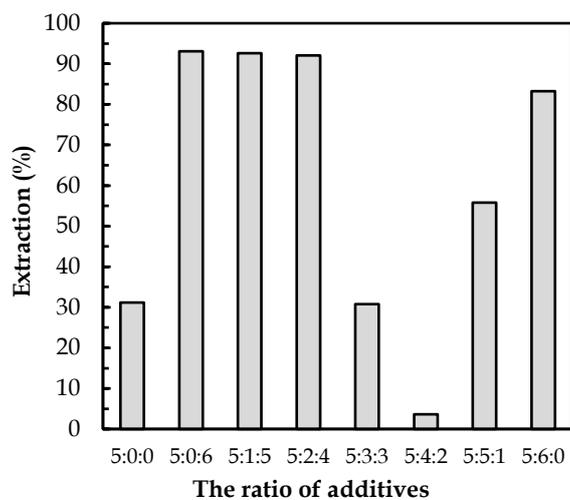
Fig. 8. Effect of different ratios of additives to concentrate on lithium extraction. Calcines from roasts at 1000°C for 90 min. Leaching at 60°C for 1 h using water/solid mass ratio of 10:1

investigation comparing two studies. The difference in lithium extraction efficiencies might be attributed to the usage of high calcium-bearing additive. It was clearly seen that high dosage of calcium adversely affected the leaching.

Moreover, in a study examined by Jandová et al. (2007), calcite was used as an additive along with zinnwaldite concentrate at the roasting temperature of 825°C for 60 min and 90% lithium extraction was achieved. The amount of calcite was almost 5 times higher than our study. However, the ratio of concentrate to $CaCO_3$ in the study of Vu et al. (2013) did not compare to the ratio in the study of Jandová et al. (2007). Jandová et al. (2007) obtained much higher lithium extraction values in spite of employing lower calcite dosages.

The reason for the higher roasting temperature compared with our study must have been the different ratios of zinnwaldite concentrate and gypsum.

However, as the ratio of calcite:gypsum changed from 0:6 to 4:2, it was seen that there was an instantaneous decline in the lithium extraction. Therefore, the leaching residues were subjected to the XRD analyses after the roasting experiments which were conducted at ratios of 5:0:6, 5:4:2, 5:5:1, and 5:6:0. The XRD patterns of these ratios are shown in Fig. 9.

The calcined product obtained from the roasting process performed at a ratio of 5:0:6 was subjected to the leaching process. After the filtration, it was found that the residue did not consist of a compound with lithium content. Moreover, the highest lithium extraction was obtained at the ratio of 5:0:6, which had been already chosen as the optimal condition.

The XRD pattern of the calcined product under optimal conditions shown in Fig. 11(b) indicates that the formation of $KLiSO_4$ was achieved. However, when the effect of the ratio of additives is examined it is seen that the ratio of 5:4:2 caused a reduction in the lithium extraction efficiency. According to the XRD patterns demonstrated in Fig. 9(b), it is clear that the formation of jarosite ($KFe_3(SO_4)_2(OH)_6$) led to decreased lithium extraction values.
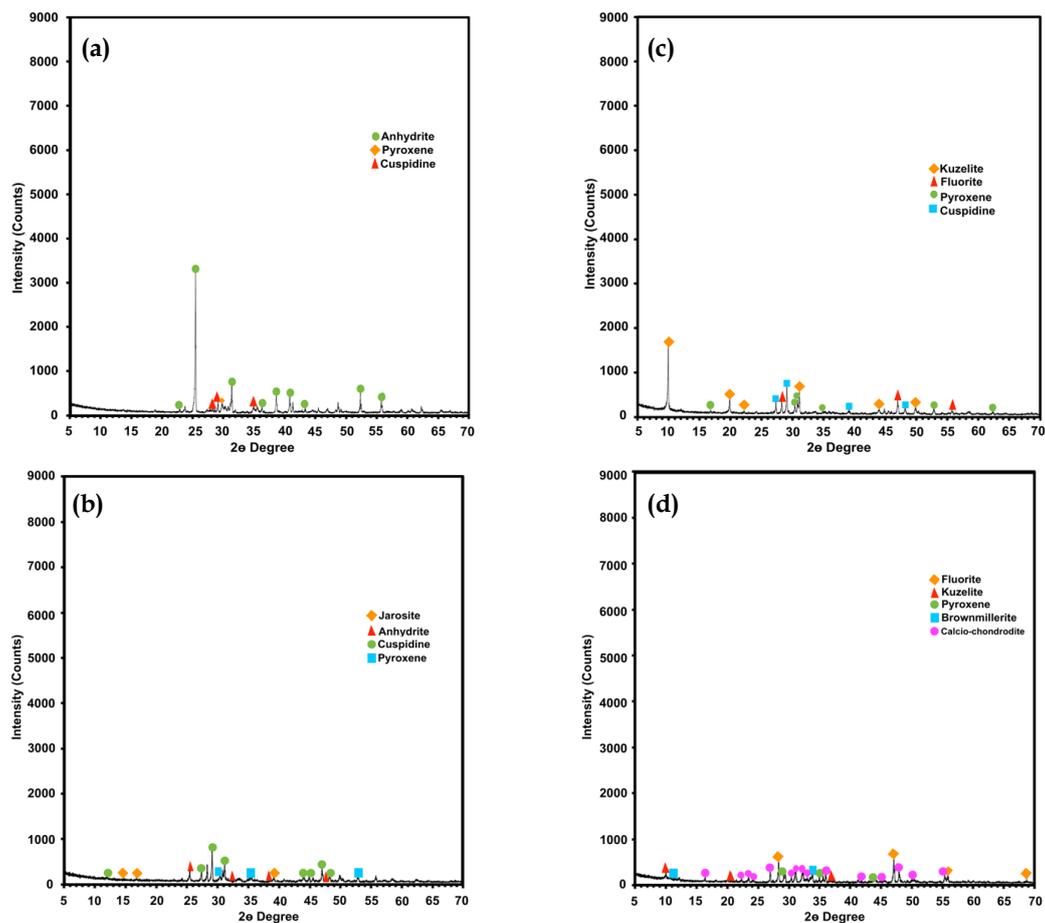
Fig. 9. XRD patterns of leach residue obtained after the roasting process realized at a concentrate:$CaCO_3$:$CaSO_4.2H_2O$ ratio of a) 5:0:6, b) 5:4:2, c) 5:5:1, d) 5:6:0

Figures 9(c) and (d) show that while neither residue from the leaching process consisted of a compound with lithium content, both residues consisted of compounds with high calcium contents for both additive ratios examined. Since a compound with lithium content was not found, neither the 5:5:1 nor the 5:6:0 ratio was chosen as the optimal ratio according to the lithium extraction.

3.1.4. Comparison of roasting times of 90 and 120 min

In the previous studies, a roasting time of 90 min and the roasting temperature of 1000ºC was chosen as the optimal conditions for the roasting process, and the optimal ratio of additives was determined depending on these conditions. It was aimed to decrease the 10% efficiency difference between the roasting times of 90 and 120 min by determining the other roasting conditions. The experiments were conducted twice in the conditions determined as optimal. The results related to lithium extraction efficiency are shown in Fig. 10. According to the results, 10% extraction difference shown in Fig. 7, diminished to approximately 1%. 94.1% and 95.3% lithium extraction values were achieved for 90- and 120-minutes roasting durations, respectively. In conclusion, the roasting time of 90 min continued to be chosen as the optimal one.

The final optimal conditions for the roasting process were determined as a roasting temperature of 1000ºC, roasting time of 90 min time, and the ratio of concentrate to additives of 5:0:6. In order to show the effect of the roasting process, the XRD analyses were realized for the sample before being exposed to the roasting process and the calcined product. The XRD patterns of samples are shown in Fig. 11.
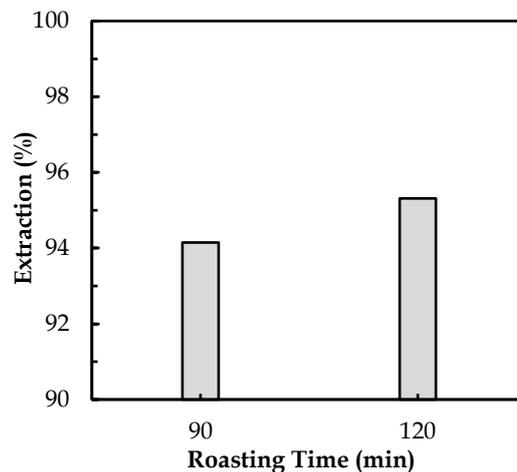
Fig. 10. Comparison of roasting times of 90 and 120 min depending on lithium extraction
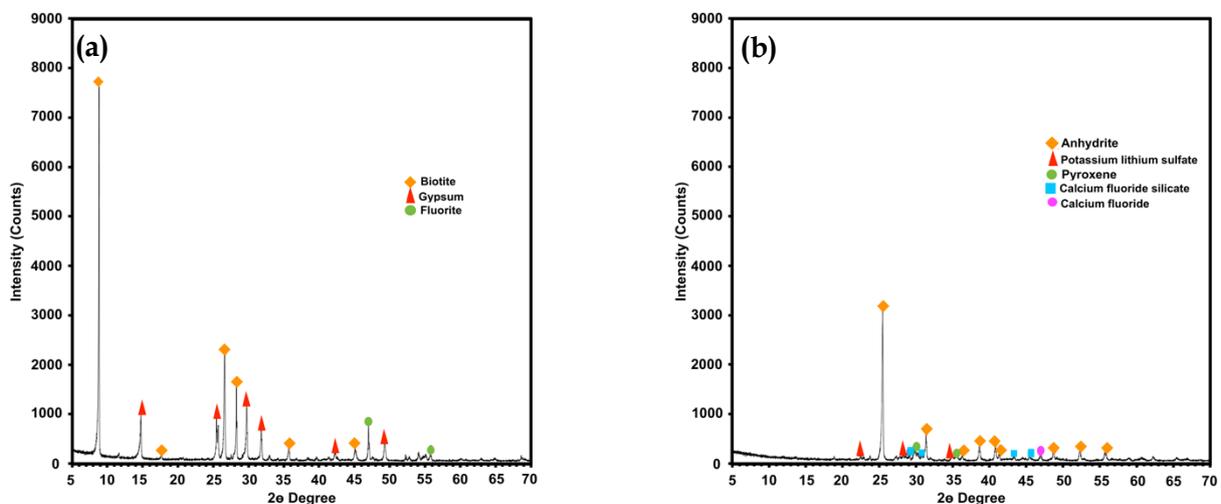
Fig. 11. XRD patterns of a) the sample which was prepared with a ratio of 5:0:6 before being exposed to the roasting process, b) the calcined product

Figure 11(a) proves that biotite and gypsum were found in the sample which was prepared for exposure to the roasting process. It was observed that potassium lithium sulfate was formed after the roasting process in Fig. 11(b). The reaction between zinnwaldite concentrate and gypsum is shown in Eq.2:

$$KLiFeAl(AlSi_3)O_{10}(OH,F)_2 + 3CaSO_4.2H_2O \rightarrow KLiSO_{4\ (s)} + CaSO_{4\ (s)} + CaF_{2\ (s)} +$$
$$+ CaFeAl_2Si_2O_{6\ (s)} + SiO_{2\ (s)} + 3H_2O_{(g)} + SO_{2\ (g)} + 3/2\ O_{2\ (g)} \qquad (2)$$
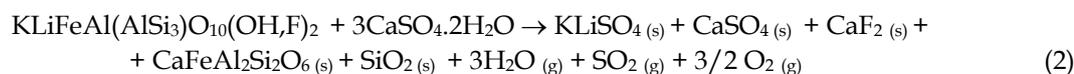
Figure 12 shows the comparison of XRD patterns of the calcined product and the leach residue. The dissolving of potassium lithium sulfate in the calcined product by the leaching process was certainly proved by the XRD analyses. The chemical reaction of potassium lithium sulfate during leaching was shown in Eq.3:

$$KLiSO_{4\ (s)} \rightarrow K^+_{(aq)} + Li^+_{(aq)} + SO4^{-2}_{(aq)} \qquad (3)$$
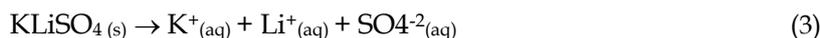
In contrast to our study, Jandovà et al. (2009) used gypsum and calcium hydroxide as additives in a ratio of 6:4.2:2. It was seen that the influence of calcium hydroxide was lower than that of gypsum and similar to that of calcite, which was used in our study during the roasting process. However, it was understood and predicted that calcite was not necessary for our study, because of the high amount of gypsum. The Ca^{2+} ions were sufficient because of the presence of gypsum.
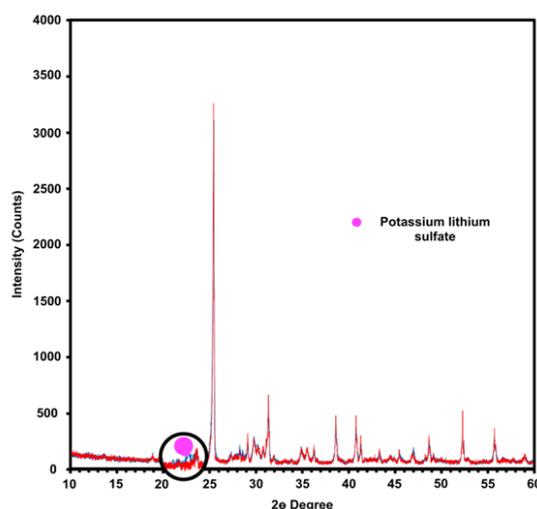
Fig. 12. Comparison of XRD patterns of the calcined product after the roasting process and the leach residue

3.2.   Leaching experiments

3.2.1. Effect of leaching temperature

To determine the optimal leaching temperature, the temperatures of 25, 40, 60, and 90°C were investigated. The results of lithium extraction are shown in Fig. 13. The highest lithium extraction was reached at a leaching temperature of 40°C and was 96.7%. Unlike our study, Jandovà et al. (2007) determined that the optimal leaching temperature was 90–95°C, which was higher than the result of our study. The reason for the higher leaching temperature was the lower leaching time used compared to our study.

3.2.2. Effect of leaching time

To reach the optimal conditions for leaching time, experiments were conducted at a leaching temperature of 40°C, w/s ratio of 10:1, and stirring rate of 500 rpm while leaching times of 30, 60, 90, and 120 min were investigated. The results of lithium extraction for each experiment are given in Fig. 14. It can be seen that while the leaching time increased, the lithium extraction efficiency tended to increase and the highest lithium extraction values of 95% was obtained during 90 min leaching time. However, the test results show that as the leaching time increased, lithium extraction figures started to reduce. Accordingly, 90 min agitation duration was chosen as the optimal leaching time.

3.2.3. Effect of water/solid ratio during leaching

For each experiment, the w/s ratio was stabilized at 10:1 during the leaching process. However, the w/s ratio is a crucial parameter from the perspective of wastewater emergence. Therefore, w/s ratios of 3:1, 5:1, and 10:1 were investigated to diminish water usage. The results of lithium extraction for the three parameters are shown in Fig. 15.

Although the highest lithium extraction was obtained at a w/s ratio of 10:1, the ratio of 5:1 was determined as the optimal condition because the difference in efficiency was small. Similar to our study,
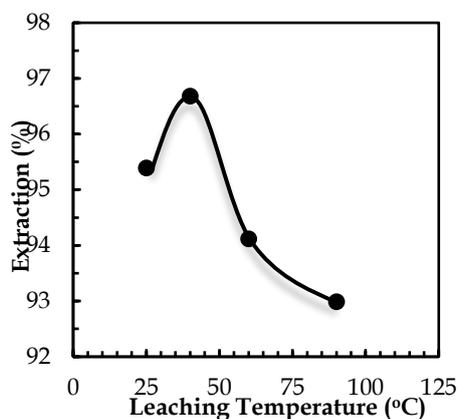
Fig. 13. Effect of leaching temperature on lithium extraction. Calcines from roasts at 1000°C using concentrate: $CaCO_3:CaSO_4.2H_2O$ ratios of 5:0:6. Leaching for 1 h using water/solid mass ratio of 10:1
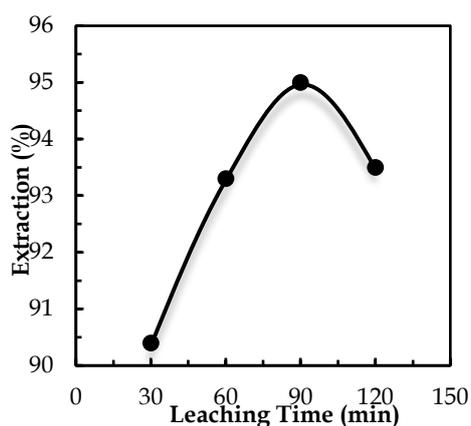
Fig. 14. Effect of leaching time on lithium extraction. Calcines from roasts at 1000°C using concentrate: $CaCO_3:CaSO_4.2H_2O$ ratios of 5:0:6. Leaching at 40°C using water/solid mass ratio of 10:1
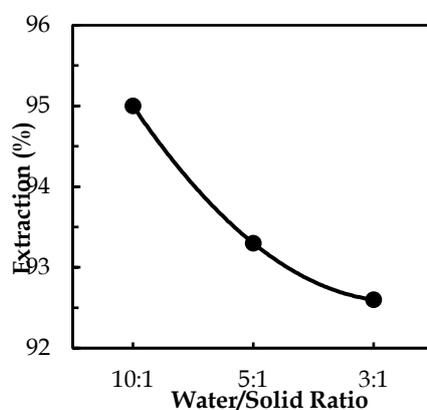
Fig. 15. Effect of w/s ratio on lithium extraction. Calcines from roasts at 1000°C using concentrate: $CaCO_3:CaSO_4.2H_2O$ ratios of 5:0:6. Leaching at 40°C for 90 min

Jandovà et al. (2007) found that the optimal w/s ratio was 5:1, although a higher lithium extraction was provided by a w/s ratio of 10:1. According to AAS analysis, the leach liquor obtained under the optimal roasting (at 1000°C for 90 minutes by using concentrate:CaSO$_4$.2H$_2$O ratio of 5:6) and leaching conditions (at 40°C for 90 minutes using w/s ratio of 5:1) contained 30 mg/dm^3 Li. Other impurities in the solution and their contents (0.036 mg/dm^3 Fe, 26.7 mg/dm^3 Al, 1.235 mg/dm^3 Mg, 144.4 mg/dm^3 Ca, 76.9 mg/dm^3 Na and 142.1 mg/dm^3 K) are also presented in Table 6.

Table 6. Elemental content of final mother liquor. Calcined from roasts at 1000°C for 90 minutes using concentrate: CaSO$_4$.2H$_2$O ratios of 5:6. Leaching at 40°C for 90 minutes using water/solid ratios of 5:1

Elemental	Content(mg/dm^3)
Li	30
Fe	0.036
Al	26.7
Mg	1.235
Ca	144.4
Na	76.9
K	142.1

4. Conclusions

In summary, the zinnwaldite concentrate with an Li content of 2500 ppm obtained from the flotation process was subjected to roasting and leaching processes, respectively. In the study, it was observed that the ratio of additives to concentrate became more important to reach a high lithium extraction. Finally, among all the parameters which were observed, a lithium extraction of 93.3% was achieved with a roasting temperature of 1000°C, roasting time of 90 min, and the ratio of 5:6 (zinnwaldite concentrate:gypsum) followed by a leaching temperature of 40°C, leaching time of 90 min, and w/s ratio of 5:1. In conclusion, the leach liquor obtained after filtration contained some impurities such as Fe, Al, Mg, Ca, Na, and K. The precipitation of impurities and purification of the solution to obtain a lithium-rich solution should be investigated in further studies.

Acknowledgments

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