

Characterization and treatment of clayey waste using a sulfuric acid roasting-water leaching process for the extraction of lithium

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Abstract: In this study, a detailed characterization of the clayey waste of the Kırka boron plant was undertaken before the development of a sulfuric acid roasting-water leaching process for the extraction of lithium from this waste. The effects of roasting temperature (650-800°C) and sulfuric acid/waste ratio (90-260 kg H₂SO₄/1000 kg waste on a dry basis) on the extraction of lithium were investigated. By roasting the waste sample, which contained 0.37% Li₂O with dolomite, smectite and borax as the main phases, at temperatures between 650°C and 800°C in the absence of sulfuric acid as the additive, CaMgSiO₄ was found to form as the dominant phase after the decomposition of dolomite and smectite present in the sample. On the other hand, the X-ray diffraction analyses of the waste sample subjected to sulfuric acid treatment without roasting showed the in-situ formation of various hydrated calcium sulfate phases for all sulfuric acid/waste ratios tested. Besides, at the highest acid/waste ratio of 260, a hydrated magnesium sulfate phase was also identified in the sample. The application of the sulfuric acid roasting-water leaching process under the optimum roasting temperature of 750°C and the acid/waste ratio of 180 was found to lead to a lithium extraction of 85.7%. The applied sulfuric acid roasting-water leaching process appeared to be an attractive process with its attributes including low roasting temperature, high extraction percentage and no requirement for gypsum as the external sulfation agent.

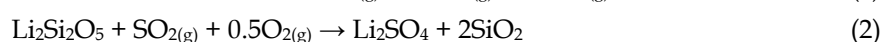
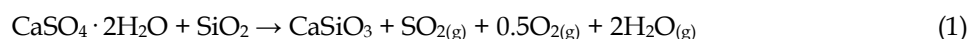
Keywords: Kırka boron plant, lithium, smectite, sulfuric acid roasting, water leaching

1. Introduction

As the lightest metallic element, lithium is the 25th most abundant element in the earth's crust and due to its high reactivity, it does not exist in its native form in nature. Lithium is mainly used in battery, glass, ceramic and lubricant industries, and may also be used in air treatment, metallurgy and rubber industries. Lithium is widely found within the compositions of various silicate and phosphate minerals. Lithium can also occur at low concentrations in various brines distributed around the world. Industrial lithium production, mostly as lithium carbonate and lithium hydroxide, is mainly secured from two different sources, e.g. the brines and the pegmatites. Another potential resource is lithium-containing clays, especially smectites (Kesler et al., 2012; Meshram et al., 2014; Swain, 2017; Meng et al., 2019).

Most of the studies seem to focus on the extraction of lithium using acidic and alkaline chemical processing methods from pegmatites containing spodumene, lepidolite, petalite, amblygonite or zinnwaldite (i.e., Ellestad and Clarke, 1955; Colton, 1957; Averill and Olson, 1978; Meshram et al., 2014; Choubey et al., 2016; Li et al., 2019; Karrech et al., 2020; Salakjani et al., 2021). But, the extraction of lithium from lithium-bearing smectites has received less interest (May et al., 1980; Edlund, 1983; Lien, 1985; Crocker et al., 1988; Amer, 2008; Zbranek et al., 2013; Western Lithium, 2014; Bacanora Minerals, 2018; Gu et al., 2020; Zhu et al., 2021). Lien (1985) proposed a treatment process for montmorillonite-type clays (0.6% Li), which involved roasting of the clay in the presence of limestone and gypsum as additives above 900°C, to transform the contained lithium into water-soluble lithium sulfate (solubility:

34.2 g/100 g H₂O^{25°C}; Lide, 2010) according to Equations (1) and (2), followed by water leaching of the calcine. To increase the concentration of lithium, the leaching solution was evaporated before the subsequent recovery of lithium (80%) as Li₂CO₃ (99% purity) by precipitation with the addition of Na₂CO₃. Lien (1985) also demonstrated the effects of various parameters including gypsum and limestone dosages, roasting time and temperature. In this regard, the addition of gypsum and limestone appeared to enhance the extraction of lithium with an optimum clay:limestone:gypsum ratio of 5:3:3. Increasing the temperature from 750°C up to 1000°C was found to improve the extraction of lithium, which was adversely affected beyond 1000°C. In a similar study, Crocker et al. (1988) tested various treatment options including direct acid and water leaching, pressure leaching, acid curing followed by water leaching, and roasting with carbonates and chlorides. They found that high lithium recoveries could be achieved by acid-based tests at the expense of high acid consumption and extensive dissolution of impurities such as aluminium and iron. These researchers identified selective chlorination and, in particular, sulfation roasting in the presence of gypsum and limestone as the most promising option for the effective extraction of lithium from montmorillonite type-clays.



A large amount of lithium-bearing clayey (smectite) waste has already been generated over the years in the boron ore processing plants in Turkey. The wastes of these processing plants offer significant resource potential for lithium. Therefore, the treatment of these clayey waste products of the boron processing plants for the recovery of lithium has received great interest over the years (i.e., Beskardes et al., 1992; Mordogan et al., 1994; Mordogan et al., 1995; Buyukburc and Maraslioglu, 2003; Buyukburc and Koksall, 2005; Buyukburc et al., 2006; Ulusoy and Gulmez, 2012; Akyildiz, 2015; Eti Maden, 2016; Lee et al., 2016; Karakas et al., 2019; Ozbas, 2019; Ozbas and Derun, 2021). Mordogan et al. (1995) reported water leaching, acid leaching and water leaching after roasting of the clay sample (Li₂O content: 0.56%; main phases: dolomite, montmorillonite and hectorite) obtained from the Kirka deposit. These researchers observed a limited extraction of lithium (only 2.4%) in the water leaching while almost complete leaching of lithium (99%) was achieved in the acid leaching under suitable conditions (80°C, 10% solids, -500 µm and 160 g/L H₂SO₄). They also found that acid leaching was not selective in that 43.0% of iron, 58.1% of magnesium and 35.0% of calcium were also dissolved. Roasting of the sample in the presence of gypsum (17%) as an additive for 2 h at 900°C led to the extraction of 77% Li in the subsequent water leaching. Buyukburc and Koksall (2005) investigated in detail the effects of various parameters including gypsum to waste ratio, limestone to waste ratio, temperature and roasting time on the subsequent water leaching of lithium from Bigadiç clay samples. They achieved an 88% extraction of lithium under the optimum conditions. It can be seen that these studies are mainly based on the roasting-water leaching of clayey waste of boron processing plants in Turkey using gypsum as the external sulfation agent.

In this study, following detailed identification, the extraction possibility of lithium from the clayey waste of the Kirka boron processing plant was investigated using a roasting-water leaching process, which utilizes sulfuric acid as the only sulfation agent. A detailed physical, chemical and mineralogical characterization of the waste sample, the sulfuric acid-treated waste samples and the calcines were carried out to provide a deeper insight into the sulfuric acid roasting-water leaching process applied at different temperatures (650-800°C) and acid/waste ratios (90-260 kg H₂SO₄/1000 kg waste on a dry basis).

2. Materials and methods

2.1. Reagents

In the experimental studies; reagent-grade concentrated (95-97% H₂SO₄) sulfuric acid, distilled water and classical laboratory porcelainware/glassware were used. A synthetic lithium metasilicate (Li₂SiO₃) and a hand-picked sample of natural calcium sulfate dihydrate (gypsum, CaSO₄·2H₂O) were used in the studies to provide an insight into the mechanism of sulfation of lithium present in the waste sample. The former was prepared in the laboratory from reagent-grade lithium carbonate and silicon dioxide using a high-temperature solid-state synthesis method.

2.2. The clayey waste sample

The clayey waste sample used in this study was obtained from Kırka Boron Plant (Eskişehir, Turkey). The as-received waste sample was dried under atmospheric conditions and then reduced in size using a laboratory type jaw crusher and a disc mill prior to use in tests. The particle size distribution of the ground waste sample (Fig. 1), determined by Malvern-Mastersizer 3000, indicated that the 100%, 80%, 50% and 20% of the sample was found to be finer than 665.8, 80.2, 14.8 and 1.7 μm , respectively.

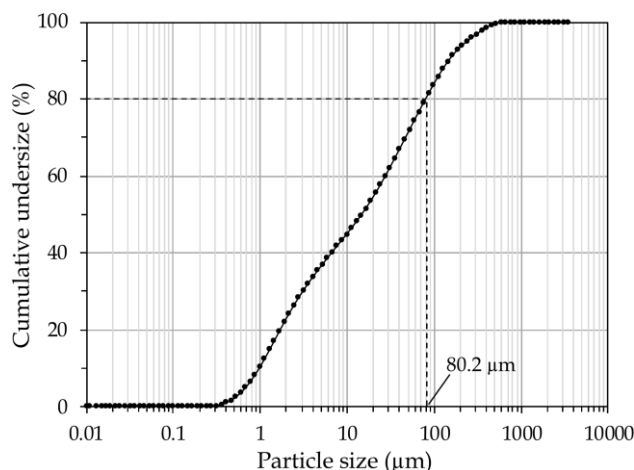


Fig. 1. Particle size distribution of the waste sample

The detailed chemical composition of the ground waste sample determined by different analytical techniques was given in Table 1. The main chemical components of the waste sample in decreasing abundance are CaO, MgO, SiO₂, B₂O₃ and Na₂O (Table 1). The lithium content of the waste sample is 0.37% Li₂O.

Table 1. Chemical composition (wt.%) of the waste sample

CaO*	17.51	Na ₂ O*	4.42	F**	0.61	TiO ₂ *	0.04
MgO*	17.09	Al ₂ O ₃ *	1.35	SO ₃ *	0.55	MnO*	<0.01
SiO ₂ *	16.61	SrO*	1.19	Li ₂ O****	0.37	P ₂ O ₅ *	<0.01
B ₂ O ₃ ***	8.34	K ₂ O*	0.76	Fe ₂ O ₃ *	0.34	LOI*,*****	31.40

*by X-ray fluorescence (XRF) (AcmeLabs/Bureau Veritas).

**by specific ion electrode (AcmeLabs/Bureau Veritas).

***by titration (Eti Maden)

****by inductively coupled plasma emission spectrometer (ICP-ES) (TENMAK, BOREN).

*****Loss on ignition.

2.3. Characterization of samples

A detailed X-ray diffraction (XRD) analysis (PANalytical-Empyrean, CuK α radiation) of the waste sample was carried out to determine its mineralogical composition with particular emphasis on the clay fraction as the lithium-bearing phase. Air-dried, glycolated and heated clay fractions were also prepared from the waste sample as described by Gundogdu and Yilmaz (1984) for the XRD analyses. Furthermore, the XRD analysis was also exploited as an analytical tool to identify the changes in the phase composition of the waste sample in response to acid- and heat-treatments. In addition, Fourier-transform infrared (FT-IR) analysis was also carried out using a Varian 660-IR equipment to provide a further insight into the phases present in the waste sample. The thermal (TG/DTA) analyses were also carried out using a Netzsch-STA 449 equipment at a heating rate of 10°/minute in the temperature range of ambient to 1000°C to characterize the thermal behaviour of the waste sample before and after acid-treatments.

2.4. Sulfuric acid roasting-water leaching

Sulfuric acid+waste mixtures prepared at three different acid/waste ratios were subjected to roasting at different temperatures and then water leached to reveal the extraction behaviour of lithium from the waste sample. In the sulfuric acid roasting-water leaching experiments, firstly, the waste sample (32 g) was wetted by a small amount of distilled water before the addition of the calculated amounts of concentrated sulfuric acid at the selected acid/waste ratios of 90, 180 and 260. The acid was added dropwise to the moistened waste and the obtained mixture was hand-mixed for five minutes in a porcelain crucible. Then, the crucible containing the acid and waste mixture was heated for one hour in a furnace (Protherm-PLF 110) maintained at the selected roasting temperatures of 650, 700, 750 and 800°C. After cooling the crucible to room temperature, the roasted mixture was hand-ground and leached with 100 mL of water for 30 minutes at room temperature. Following filtration, washing and drying, the lithium content of the undissolved residue was determined (Thermo Scientific-iCAP 7000 ICP-ES) for calculating the extent of lithium extraction.

3. Results and discussion

3.1. Characterization of the clayey waste sample

The XRD pattern, together with the patterns of air-dried, glycolated and heated clay fractions of the ground waste sample, indicated that the sample was composed of dolomite, smectite and borax as the major phases, with tinalconite, calcite and quartz being present as the minor phases (Fig. 2). The expansion of the basal spacing (1.77 nm) following ethylene glycol treatment and the contraction of the basal spacing (1.02 nm) following heat-treatment at 500°C in comparison to the basal spacing (1.54 nm) of the air-dried clay fraction (see inset of Fig. 2) indicated that the dominant clay mineral(s) in the waste sample belong to the smectite group (Brindley and Brown, 1980). Besides, the very low-intensity XRD peak observed approximately at 1 nm in the patterns of air-dried and glycolated clay fractions probably indicate the presence of other clay mineral(s) in the waste sample. The mineralogical composition of the waste sample is consistent with the chemical composition (Table 1) and also the TG/DTA curves (see Fig. 3) of the sample.

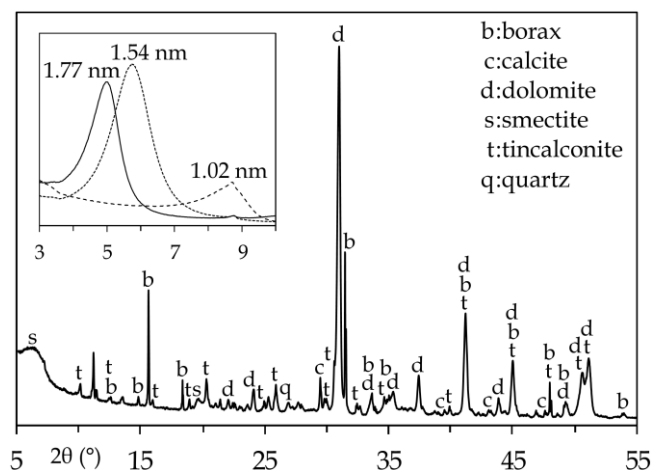


Fig. 2. XRD pattern of the waste sample (Inset: air-dried (dotted-line), glycolated (full-line) and heated (dashed-line) patterns of clay fractions of the sample)

The low-temperature endothermic peaks appeared at 98°C and 141°C (Fig. 3) are probably caused by the removal of moisture, and the water in smectite and borate minerals in the waste sample (Allen, 1957; Earnest, 1983; Waclawska, 1995; Kurama et al., 2006; Onal and Sarikaya, 2007). The very low-intensity exothermic peak at 333°C, corresponding to a mass loss of approximately 1.4%, may indicate the presence of organic matter in the Kırka borate ore. This exotherm may also be related to the organic chemicals used during the processing of Kırka borate ore in the boron derivatives plant (Simsek, 2006; Cai et al., 2007; Ma et al., 2016; Panna, 2016). The high-intensity endothermal and exothermal events observed at 608°C and 672°C may be related to the decomposition of major dolomite and smectite

phases and probably also minor phase calcite (either present in the waste sample or neoformed by the decomposition of dolomite in the waste sample), and the formation of dominant CaMgSiO_4 silicate and minor CaMgB_2O_5 borate phases (see also Fig. 5). The endotherm that belongs to the decomposition of dolomite and smectite and the exotherm that belongs to the formation of CaMgSiO_4 (monticellite) phase occurred at lower temperatures when compared to the literature that studied the decomposition of dolomite and smectites separately, and that synthesized monticellite from corresponding oxides and/or carbonates (Kulp et al., 1951; Grim, 1968; Earnest, 1983; Strandkvist et al., 2015), probably due to the presence of high amounts of fluxing components, i.e. Na_2O , B_2O_3 , MgO and CaO , formed in-situ during the heating of the waste sample, as also found by Trindade et al. (2010) and Koroglu and Ayas (2018).

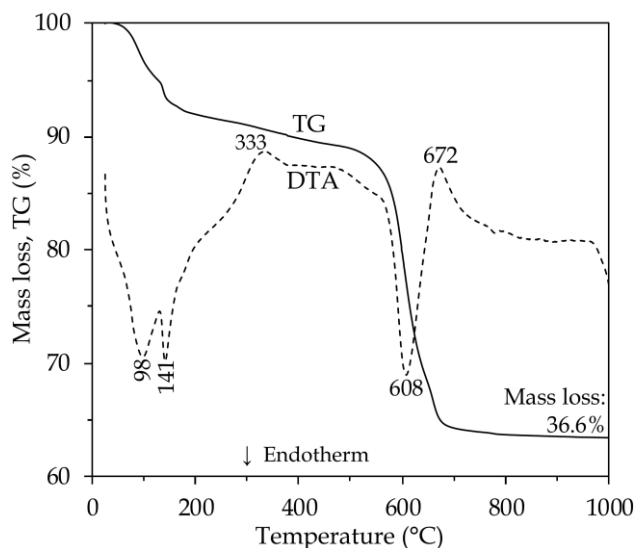


Fig. 3. TG/DTA curves of the waste sample

According to the XRD pattern (Fig. 2), the waste sample contained mainly dolomite, smectite and borax, and the absorption peaks of these phases mostly overlap as seen in FT-IR spectrum of the waste sample (Fig. 4). The very low-intensity absorption peak at 1633 cm^{-1} and high-intensity absorption peaks at 3365 and 3498 cm^{-1} may be attributed, respectively, to H-O-H bending and O-H stretching modes, showing the presence of water in the waste sample. The absorption bands for planar bending of carbonate groups characteristic for major dolomite and minor calcite phases were observed at 729 and 710 cm^{-1} , respectively. The high-intensity sharp peak for out-of-plane bending of carbonate groups centred at 883 cm^{-1} belongs to dolomite in the waste sample. The broad and very high-intensity absorptions found at 1453 and 1439 cm^{-1} may be assigned to antisymmetric stretching of carbonate groups in dolomite and calcite phases, respectively (Weir and Lippincott, 1961; Adler and Kerr, 1963). On the other hand, according to the literature (Mordogan et al., 1994; Helvacı et al., 2004; Lee et al., 2016), the smectite present in the Kırka deposit was mostly hectorite. Therefore, the low-intensity absorption band seen at 463 cm^{-1} could be assigned to the in-plane bending of Si-O bonds in the smectite phase. The shoulder near 532 cm^{-1} may probably be related to Si-O-Al vibrations and Mg-O stretching in the smectite phase. The low-intensity absorption peak observed at 648 cm^{-1} may be attributed to R-O-Si bonds ($\text{R}=\text{Mg, Al, Fe}$) in the smectite. The strong broad absorption centred at 1001 cm^{-1} may be related to in-plane Si-O stretching vibrations whereas the band at 1066 cm^{-1} may be caused by the out-of-plane stretching vibrations of Si-O bonds in the smectite structure (Komadel et al., 1996; Steudel et al., 2009). Also, the main borax ($\text{Na}_2[\text{B}_4\text{O}_5(\text{OH})_4] \cdot 8\text{H}_2\text{O}$) and minor tincalconite ($\text{Na}_2[\text{B}_4\text{O}_5(\text{OH})_4] \cdot 3\text{H}_2\text{O}$) minerals in the waste sample contained the same fundamental borate anion of $[\text{B}_4\text{O}_5(\text{OH})_4]^{2-}$ structure, which formed from two $\text{B}_{(4)}\text{-O}$ tetrahedrons and two $\text{B}_{(3)}\text{-O}$ planar triangles. These two minerals also contained B-O-H bonds in their structures (Christ and Clark, 1977). The absorptions, which overlap with the absorptions of carbonate groups in the carbonate minerals, at 1439 and 1257 cm^{-1} may be attributed to the asymmetric stretching of B-O whereas the shoulder near 950 cm^{-1} may be assigned to symmetric stretching of B-O bonds in trigonal $\text{B}_{(3)}\text{-O}$ in borate minerals in the waste sample. The bands, that overlapped with Si-O bonds in the smectite structure, at 1066 and 1001 cm^{-1} may be due to asymmetric

stretching and the band at 827 cm^{-1} may be due to symmetric stretching of B-O bonds in four-coordinate $B_{(4)}\text{-O}$ in the structure of borate minerals. In addition, the low-intensity peak at 1130 cm^{-1} may belong to the bending mode of B-O-H bonds (Jun et al., 1995; Goel et al., 2013). On the other hand, the weak intensity peak observed at 3025 cm^{-1} and the very weak intensity peaks at 2933 and 2904 cm^{-1} (not shown in Fig. 4), which may respectively be attributed to C-H groups, probably be related to the organic matter in the waste sample (Ribeiro et al., 2001; Tatzber et al., 2007; Zhang and Zhao, 2020).

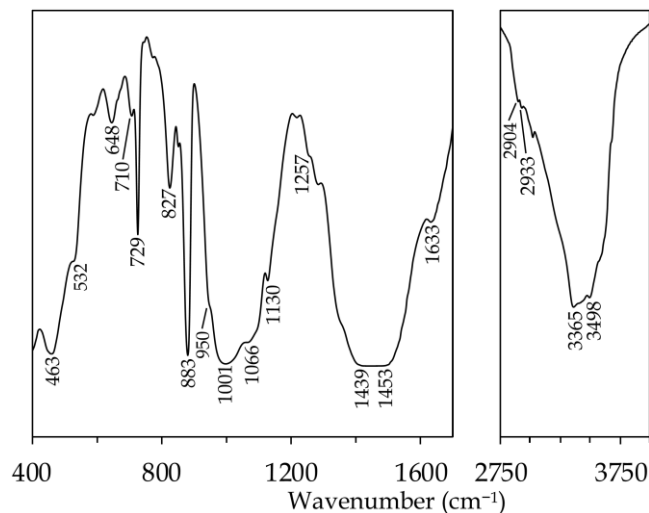


Fig. 4. FT-IR spectrum of the waste sample

3.2. Effect of heating on the waste sample in the absence of sulfuric acid

The XRD patterns of the waste sample were determined before and after heat-treatment in the absence of sulfuric acid for one hour at temperatures of 500, 600, 650, 700 and 800°C (Fig. 5), selected according to the DTA curve given in Fig. 3. These patterns (Fig. 5) allowed the identification of phase changes that occurred under the effect of heat-treatment, because the destruction of smectite as the lithium-bearing phase (Mordogan et al., 1994; Helvacı et al., 2004; Lee et al., 2016) is required for the extraction of lithium. As illustrated in Fig. 5, dolomite, present as the most abundant phase in the waste sample, appeared to decompose partially at 600°C to yield magnesium oxide and neofomed calcium carbonate phases, and completely at 650°C by forming calcium and magnesium oxide phases. The main basal XRD peak belonging to the abundant smectite phase in the waste sample near 2θ value of 6.1° observed at higher angle values (near $2\theta=8.9^\circ$) after high-temperature heating, i.e. 500°C, due to the removal of interlayer water and the collapse of the smectite layers. Further heating at 650°C and over, the basal XRD peak completely disappeared from the patterns of heated samples because of the decomposition of the smectite phase in the waste sample. Increasing the temperature in the range of 650°C to 800°C was observed to lead to almost complete decomposition of the most abundant dolomite and smectite phases resulting in the formation of CaMgSiO_4 (monticellite) as the main phase. Consistent with these findings, Koroglu and Ayas (2018) also reported the formation of the monticellite phase during the production of ceramic materials from the boron plant waste. The very large endothermic peak at 608°C and the following exothermic peak centred at 672°C (Fig. 3) may be related to the decomposition and formation of the aforementioned phases.

The formation of a different silicate phase, i.e. CaMgSiO_4 , by the decomposition of the smectite component of the waste sample is very important for the extraction of lithium because it is alleged to exist in the structure of smectite (Mordogan et al., 1994; Helvacı et al., 2004; Lee et al., 2016). According to the literature (Edlund, 1983; Lien, 1985), in the initial clay-containing mixture, there must be enough calcium oxide that must combine with free silicon dioxide (to form different calcium silicates) originating from the decomposed smectite. Otherwise, lithium released from the decomposed smectite may combine with free silicon dioxide to form water-insoluble lithium silicate(s). For this purpose, Edlund (1983) and Lien (1985) used limestone (CaCO_3) in their lithium extraction studies. In this study, no extra calcium-containing additive was used. The main dolomite ($\text{CaMg}(\text{CO}_3)_2$) phase originally

present in the waste sample was utilized for this purpose. According to the chemical composition of the waste sample, the theoretical chemical formula of the calcium magnesium silicate phase that may form is $1.13\text{CaO} \cdot 1.53\text{MgO} \cdot \text{SiO}_2$, in which the molar amounts of CaO and MgO in comparison to SiO_2 are much higher when compared to the formed dominant phase, i.e., CaMgSiO_4 or $\text{CaO} \cdot \text{MgO} \cdot \text{SiO}_2$. This was also substantiated by free CaO and MgO peaks observed in XRD patterns of the heated samples (Fig. 5).

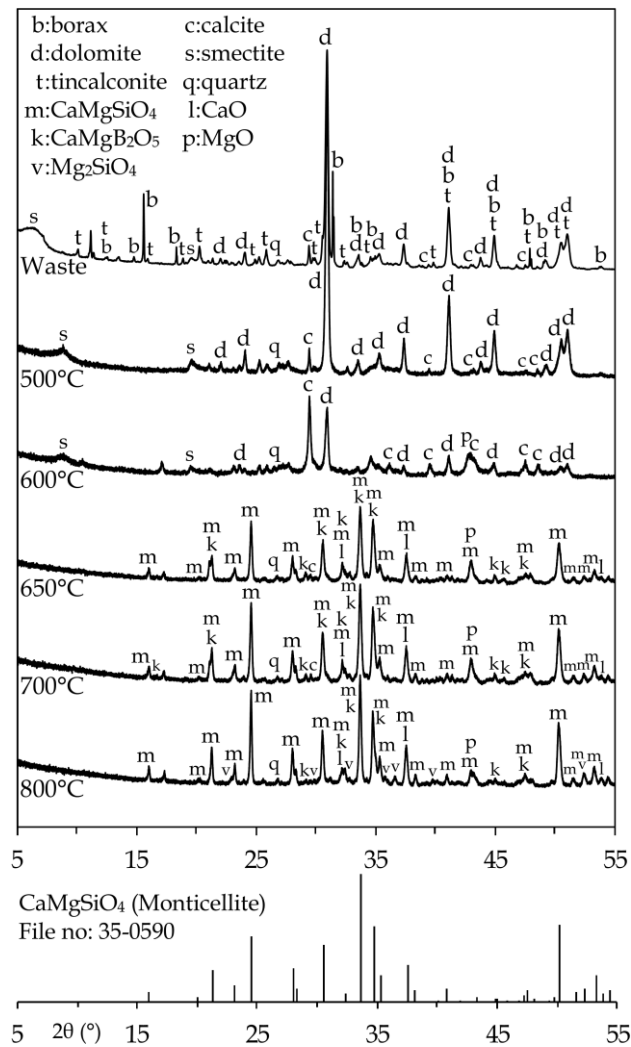


Fig. 5. XRD patterns of the waste sample and the waste samples heated in the absence of sulfuric acid at indicated temperatures.

3.3. Effect of sulfuric acid treatment on the waste sample in the absence of heating

The effect of sulfuric acid treatment on the phase composition of the waste sample was studied at acid/waste ratios of 90, 180 and 260 kg H_2SO_4 /1000 kg waste on a dry basis, which were selected based on the results of preliminary tests. Following sulfuric acid treatment (with no high-temperature heating), the XRD patterns of the dried (at 40°C) waste samples were determined (Fig. 6). Most of the studies on the extraction of lithium from silicates reported the use of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) as the sulfation agent. However, the findings of this study indicated that the external gypsum additive is not required in that the $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ phase is formed in-situ in the waste sample through the reaction of the concentrated sulfuric acid added with dolomite and/or calcite for all of the tested acid/waste ratios. In this regard, as shown in Fig. 6, the highest intensity XRD peaks belonging to $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ phase were observed only at an acid/waste ratio of 180. At higher acid/waste ratios, the XRD peak intensities of the $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ phase decreased and those of the $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ (bassanite) phase increased. In addition, at an acid/waste ratio of 260, additional XRD peaks of different phases, such as $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$

(hexahydrate), $\text{Na}_2\text{Ca}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ and $\text{Na}_2\text{Ca}_5(\text{SO}_4)_6 \cdot 3\text{H}_2\text{O}$, were observed to form, which, together with $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$, simultaneously reduced the amount of in-situ formed $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ phase in the sample. According to the theoretical calculations, at an acid/waste ratio of 180, the amount of added sulfuric acid could only convert approximately 58% of the total calcium component in the sample to calcium sulfate, i.e. the sulfuric acid did not totally react or consume all the dolomite and calcite phases present in the sample, which was substantiated by the existence of XRD peaks of both dolomite and calcite as shown in Fig. 6. In conclusion, based on these findings, the optimum acid/waste ratio was selected as 180. On the other hand, the small intensity peaks in the complex XRD pattern obtained at acid/waste ratios of 180 and 260 given in Fig. 6 may belong to unidentified phases of hydrated sodium, calcium and/or magnesium borates or sodium, calcium, magnesium, aluminium and/or iron sulfate phases.

The concentrated sulfuric acid added was also found to react with smectite phase in the waste sample as revealed by the shift in the position of main basal peak of acid-interacted smectite that was observed at a higher angle (2θ) of near 6.68° . Besides, a new, low-intensity peak located at 8.5° , probably linked with the smectite phase, also appeared in the patterns of sulfuric acid-treated waste samples, especially at acid/waste ratios of 180 and 260 (Fig. 6). These changes may be attributed to the partial dehydration of smectite interlayers, the penetration of hydrogen ions by cation exchange into smectite interlayers and/or partial dissolution smectite phase in the waste sample. The latter two processes might facilitate the extraction of lithium from the waste sample.

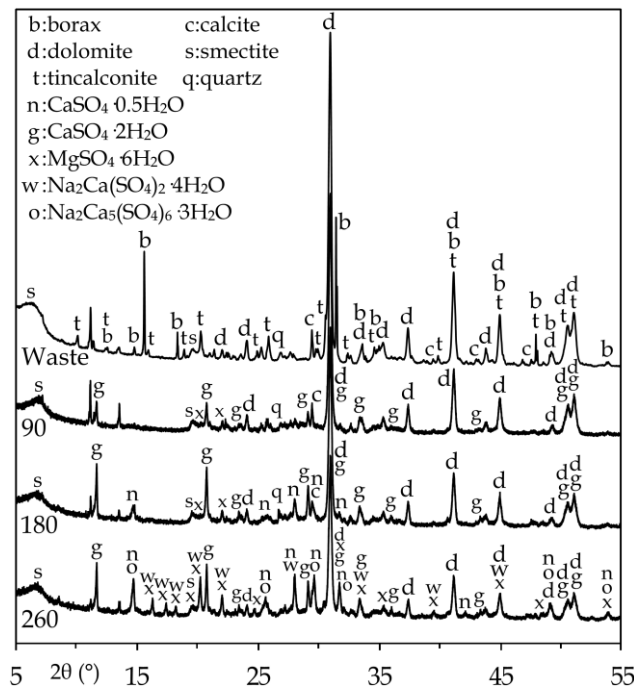


Fig. 6. XRD patterns of the waste sample and the dried waste samples (no high-temperature treatment) containing sulfuric acid at indicated acid/waste ratios

Although the endothermic low-temperature peaks observed at temperatures lower than 200°C (Fig. 7) could not be identified easily because of the presence of many identified and unidentified hydrated phases formed in-situ in the sulfuric acid+waste mixtures, the small intensity endothermic peak observed at 85°C , especially in the mixture prepared at acid/waste ratio of 260, probably belongs to the dehydration of $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ phase (van Essen et al., 2009; Li et al., 2018). Besides, the low-temperature endotherms at 116°C and 148°C in the DTA curve of acid+waste mixture prepared at optimum acid/waste ratio 180 may be related to $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, respectively (Christensen et al., 2008; El Hazzat et al., 2020).

3.4. Sulfuric acid roasting-water leaching of the waste sample

The extraction of lithium by the application of sulfuric acid roasting-water leaching process from the waste sample at different temperatures is presented in Fig. 8 for acid/waste ratios of 90, 180 and 260,

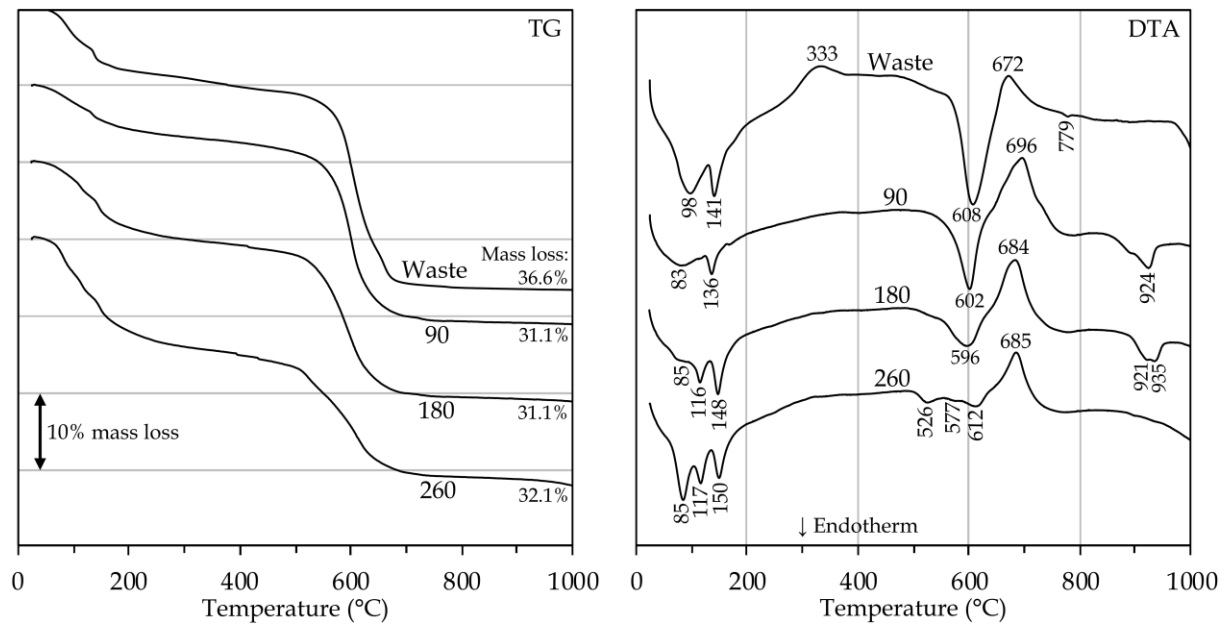


Fig. 7. TG/DTA curves of the waste sample and the dried waste samples (no high-temperature treatment) containing sulfuric acid at indicated acid/waste ratios

respectively. It can be seen that increasing the roasting temperature in the range of 650 to 750°C has a beneficial effect on the extraction of lithium. The highest extractions of lithium with 80.0%, 85.7% and 87.7% at acid/waste ratios of 90, 180 and 260, respectively, were consistently obtained at the roasting temperature of 750°C. A further increase in the roasting temperature to 800°C appeared to adversely affect the amount of lithium extracted from the waste sample, probably due to the reaction of lithium with newly formed water-insoluble silicate phases (Zhang et al., 2022) or the volatilization of lithium (May et al., 1980). Therefore, a roasting temperature of 750°C was selected as the optimum roasting temperature for lithium extraction.

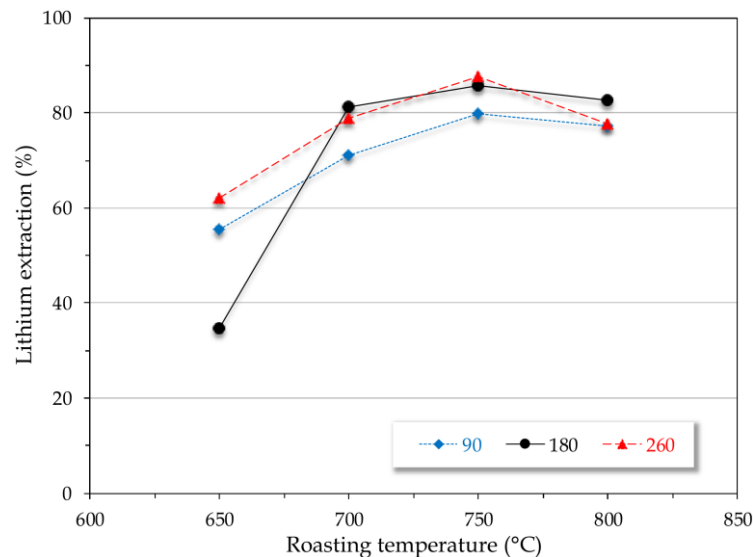


Fig. 8. Extraction of lithium from the waste sample by sulfuric acid roasting-water leaching process at different acid/waste ratios and temperatures (color online)

The XRD patterns of the waste samples heated at the optimum roasting temperature of 750°C in the absence and the presence of sulfuric acid (at an acid/waste ratio of 180, the optimum condition) were also determined (Fig. 9). Fig. 9 shows that in addition to the CaMgSiO_4 phase that formed at 750°C in the absence of sulfuric acid, the silicate phase of $\text{CaMgSi}_2\text{O}_6$ was also identified in the sulfuric acid-

added and then heat-treated sample at 750°C. The formation of the $\text{CaMgSi}_2\text{O}_6$ phase, in addition to the CaMgSiO_4 phase, might also indicate the reduced interaction between free silicon dioxide and lithium in the roasted mixture, resulting in higher lithium extraction percentages. In Fig. 9, the high-intensity XRD peaks of the CaSO_4 phase, which transformed from in-situ formed $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (see Fig. 6) by high-temperature heating, were easily seen in the pattern of acidified and heated waste sample. On the other hand, the separate peaks belonging to the water-soluble Li_2SO_4 phase could not be detected in the XRD pattern of the sulfuric acid added and heated sample, probably due to the low lithium (0.17% Li) content of the waste sample. The low-intensity peaks in the complex XRD pattern of the acidified and heated sample obtained at an optimum acid/waste ratio of 180 may well belong to the unidentified phases of sodium/calcium and/or magnesium sulfate phases formed.

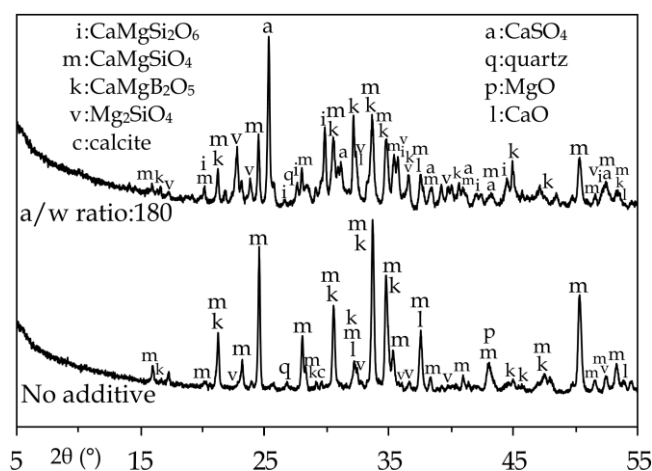


Fig. 9. XRD pattern of the waste sample heated at 750°C (bottom) and XRD pattern of the waste sample heated at 750°C in the presence of sulfuric acid at an acid/waste (a/w) ratio of 180 (top)

In the literature, a few studies, i.e., Ulusoy and Gulmez (2012) and Karakas et al. (2019), seemed to focus mainly on the extraction of lithium from the waste of the Kirka boron plant by roasting-water leaching process using gypsum as the sulfation additive. Karakas et al. (2019) reported an optimum lithium extraction of 89.4% by roasting the Kirka waste:limestone:gypsum (1000 kg:300 kg:300 kg) mixture for 1 hour at 950°C followed by room temperature water leaching for 30 minutes at solid:liquid ratio of 1:6. In a similar study, Ulusoy and Gulmez (2012) roasted the Kirka waste with the addition of limestone and gypsum (Kirka waste:limestone:gypsum ratio of 1000 kg:600 kg:600 kg) for 0.5 hour at 800-900°C prior to water leaching for 30 minutes at 60°C. They obtained relatively low extractions of 66, 62 and 64% for lithium from the Kirka waste at roasting temperatures of 800, 850 and 900°C, respectively. In the same study, they also tested the addition of NaCl into the roasting feed at Kirka waste:limestone:gypsum:NaCl ratio of 1000 kg:400 kg:400 kg:400 kg, and found that the lithium extraction improved to 81, 83 and 82% after roasting at 800, 850 and 900°C, respectively. In comparison, a lithium extraction of 85.7% was achieved by roasting the Kirka waste with sulfuric acid (180 kg acid per 1000 kg waste on a dry basis) for 1 hour at 750°C followed by water leaching for 30 minutes at ambient temperature in the current study. Therefore, the applied sulfuric acid roasting-water leaching process offers the benefits of achieving high lithium extractions (i.e. >80%), treating quantitatively more waste than those processes that require additives such as $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and CaCO_3 , and lower roasting temperatures.

3.5. Thermodynamic evaluation of the sulfation process

The waste sample contained many different interacting components (CaO , MgO , SiO_2 , B_2O_3 and Al_2O_3) in various amounts (see Table 1). Besides, the in-situ formed calcium sulfate phase is also present in the high-temperature reaction medium. Therefore, only a preliminary thermodynamic evaluation could be carried out using HSC Chemistry 9 (Outotec) at temperatures between 25°C and 1000°C for explaining the sulfation process based on the simultaneously occurring reactions given in Equations (3) to (8). For a more comprehensive thermodynamic analysis, the information on the conditions of formation of

different lithium silicates (i.e., Li_2SiO_3 , $\text{Li}_2\text{Si}_2\text{O}_5$, Li_4SiO_4 , LiAlSiO_4 and $\text{Li}_2\text{MgSiO}_4$) and lithium sulfates (i.e., Li_2SO_4 , LiNaSO_4) at high-temperatures must be known for this multi-component system. Furthermore, the interactions between the other main components present, i.e. B_2O_3 and Na_2O , in the waste sample should be also taken into consideration.

The lithium, which is released from the smectite phase after its decomposition, may be found as Li_2SiO_3 and/or $\text{Li}_2\text{Si}_2\text{O}_5$ phases (Green et al., 1970) in the reaction medium. As seen in Fig. 10, the conversion of these lithium-containing phases to the water-soluble Li_2SO_4 phase according to Equations (3) and (4) at the roasting temperatures with the help of CaSO_4 was thermodynamically favourable. In these reactions, the reactant CaSO_4 is presumed to be transformed from the in-situ formed $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ phase (El Hazzat et al., 2020). In addition, the silica released from the smectite may react with dolomite in the waste sample to form CaMgSiO_4 according to Equation (5). Dolomite may also interact with lithium silicates according to Equations (6) and (7) to form the Li_2O phase, from which the formation of lithium sulfate (Equation (8)) was also thermodynamically feasible (negative free energy) (Fig. 10).

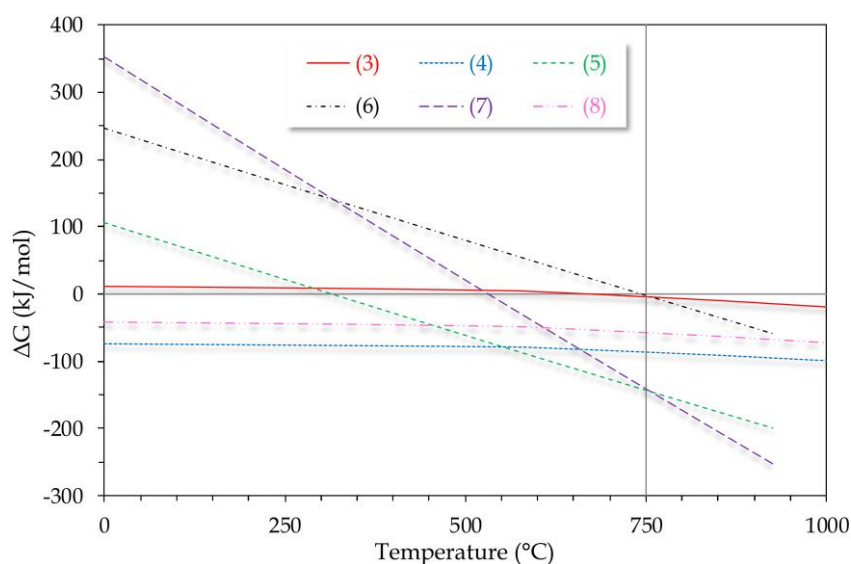
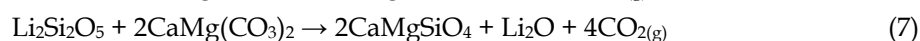
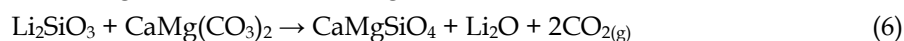
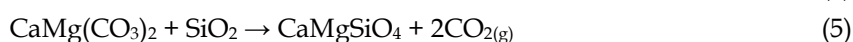
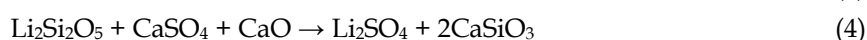
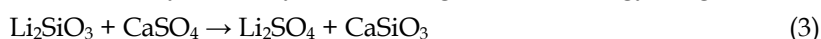


Fig. 10. Variation of free energy values of Equations (3)-(8) with temperature (color online)

To confirm the above-mentioned high-temperature sulfation process, the reaction given in Equation (3), which has the least thermodynamic tendency to occur, was chosen and simulated in the laboratory. In this test, an equimolar amount of lithium metasilicate (Fig. 11a) was reacted with calcium sulfate dihydrate (Fig. 11b) for one hour at 750°C. As expected (Fig. 10), the water-soluble Li_2SO_4 phase was formed as the main reaction product together with the insoluble CaSiO_3 phase (Fig. 11c).

The decomposition of calcium sulfate is known to give off sulfur dioxide at high temperatures (>1200°C). Although the presence of different additives (SiO_2 , Fe_2O_3 and/or Al_2O_3) may reduce the decomposition temperature to lower values (about 1000°C) (West and Sutton, 1954; Swift et al., 1976), these lower temperatures are still considerably higher than the selected temperature of 750°C. This suggests that the gas-phase sulfation process by calcium sulfate decomposition is unlikely to occur at 750°C. A further experiment was also carried out by reacting the equimolar mixture of reagent grade silicon dioxide and calcium sulfate dihydrate and it was found that neither calcium oxide nor calcium silicate(s) did not form after heating this mixture for one hour at 750°C, indicating that the calcium sulfate remained unreacted with silicon dioxide.

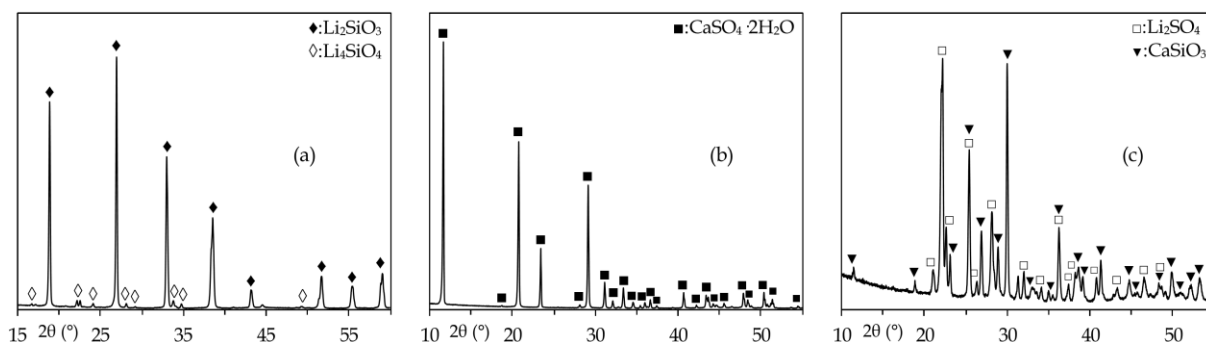


Fig. 11. XRD patterns of (a)lithium metasilicate, (b)calcium sulfate dihydrate and (c)the product of the reaction between (a) and (b) for one hour at 750°C

4. Conclusions

In this work, a sulfuric acid roasting-water leaching process was demonstrated for the treatment of Kırka boron plant waste for the contained lithium value. Following detailed characterization of the waste sample, the effects of roasting temperature and the amount of sulfuric acid on the extraction of lithium from the waste having 0.37% Li_2O were studied. Dolomite, smectite and borax were identified as the main mineral phases within the waste. In the absence of sulfuric acid, the CaMgSiO_4 phase was formed as the dominant phase by the decomposition of dolomite, smectite and calcite in the temperature range of 650°C and 800°C. The addition of sulfuric acid to the waste sample led to the in-situ formation of calcium sulfate dihydrate, which is extensively used as the external sulfation agent in the literature, under ambient conditions. The optimum conditions were determined to be a roasting temperature of 750°C and an acid/waste ratio of 180 under which a lithium extraction of 85.7% was achieved. In the study, possible mechanisms for the sulfation of lithium in the waste sample were explained. In conclusion, the findings of this study indicated that the proposed sulfuric acid roasting-water leaching process may be used for the processing of the large amount of lithium-containing clayey waste that has already been accumulated over the years in the Kırka plant.

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