

Effect of mechanical activation on lithium and alkali cation release from dolomitic clay wastes of boron processing plant

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Abstract: With the significant increase in lithium demand and production, alternative resources such as lithium-bearing clays have increasingly attracted attention and have been considered as a potential source. In addition to conventional Li recovery methods such as acid treatment and roasting, more economical and environmentally friendly techniques such as mechanical activation followed by water leaching are also being considered. In Türkiye, wastes from boron processing plants, containing approximately 900 ppm of lithium and mainly of dolomitic clays and unrecovered boron minerals (~10-13% of waste), are considered as a potential lithium source. However, due to high dolomite and boron mineral contents, the waste material may release significant amounts of alkaline earth ions such as Na⁺, K⁺, Mg²⁺, Ca²⁺, and B₂O₃ during leaching, which may interfere with lithium extraction from the solution. In this study, the leaching behavior of lithium, alkali ions, and other possible elements (e.g., B₂O₃, Fe³⁺, and Al³⁺) from both raw clay waste and mechanically activated forms of this waste material was investigated in detail. The results showed that water leaching without sodium salt of activated waste samples achieves about 44.7–57.7% lithium recovery, yielding high lithium concentrations (80–115 ppm), low levels of alkali ions (4430 ppm Na⁺, 114 ppm K⁺, 20 ppm Ca²⁺, and 7 ppm Mg²⁺), and almost no detectable Fe³⁺ (<0.2 ppm) or Al³⁺ (0.07 ppm) ions. On the other hand, a single problem was encountered where 0.95 % of B₂O₃ concentrations did not decrease in water leaching at even room temperature.

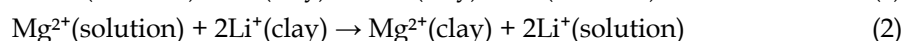
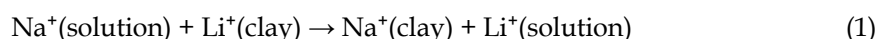
Keywords: lithium-bearing clays, mechanical activation, water leach, alkali, and metal ion release

1. Introduction

Due to its properties, lithium is widely used in various industries, such as battery production (71%), the ceramics and glass industry (14%), lubricating grease in oil production (4%), polymer production (2%), metallurgy (2%), air conditioning systems (1%), and other uses (6%) (Swain, 2017; Martin et al., 2017; USGS, 2021). Lithium is primarily extracted from ores containing minerals such as spodumene, lepidolite, amblygonite, and petalite. Among lithium sources, brines and various ores (e.g., spodumene, lepidolite) are considered valuable for lithium extraction due to their economically viable lithium content. More than 80% of the world's lithium production comes from spodumene operations in Australia and brine operations in Chile and Argentina (Li et al., 2019). The sharp increase in lithium salt prices since 2010, along with projections of continued price growth, has prompted the reconsideration of previously uneconomical lithium-bearing minerals as viable sources for lithium extraction (Büyükburç et al., 2006; Martin et al., 2017). Although both the known reserves and lithium contents of such sources are relatively low, lithium-bearing clay minerals have recently received significant attention as a potential lithium source and are considered a promising solution to meet increasing lithium demand (Seredin and Tomson, 2008). Efficient lithium recovery from certain lithium-bearing clay minerals requires specifically designed extraction methods; typically, through acid leaching and salt roasting, although alternative methods such as chlorination and alkalization have also been investigated in the literature (Meshram et al., 2014). For lithium recovery from lithium-bearing clays,

particularly in cases where lithium is embedded in the octahedral layers of the crystal lattice, it can only be released by breaking down the crystal structure through thermal treatment or chemical dissolution. With these processes, 80–90% recovery can be achieved. However, these conventional processes present several disadvantages: high operational costs (due to high temperatures and costly reagents), difficulties in managing acidic wastes from leaching, difficulties in water recovery after leaching, and non-selective dissolution (leaching of ions such as Al^{3+} , Mg^{2+} , Na^+ , K^+ , and Fe^{3+} together with lithium).

In response to these problems, a new patented method was introduced by Tesla researchers in 2021 (Tesla Inc., 2021). This method involves: (i) dissolving interlayer lithium using a cation exchange process with NaCl (up to 10% of the clay weight), (ii) disrupting lithium trapped in the cage structure by high-energy mechanical agitation (mechanochemistry), and subsequently leaching with water in the presence of table salt. This patented method offers a more selective and environmentally friendly approach, utilizing: (a) Interlayer cation exchange: Lithium ions located between clay layers are exchanged with Na^+ and/ or Mg^{2+} ions in solution due to lithium's higher affinity for water (Eqs. 1 and 2). However, studies have shown that NaCl is more cost-effective and provides more selective dissolution than MgCl_2 (Tesla Inc., 2021), (b) Mechanical breakdown of the crystal structure: High-energy milling (e.g., planetary mills, stirred or vibratory mills) for approximately two hours disrupts the cage structure, releasing lithium ions, (c) Mechanical activation instead of heat treatment: Instead of high-temperature roasting, the cage structure is mechanically broken down. The activated clay is then mixed with water at $\sim 65^\circ\text{C}$ for about two hours, allowing lithium to dissolve.



Owing to their high energy density, High energy mills are also well-suited for inducing mechanical activation processes (Gábor Mucsi, 2019). Smekal (1952) (from Musci, 2019- main source) was one of the first researchers to introduce the concept of "mechanical activation," which was defined as "processes induced by mechanical energy that enhance the chemical reactivity of a system without altering its chemical composition." According to Smekal (1952), mechanical activation can occur in several distinct states which were later classified and described in more detail as follow by Juhász and Opoczky (1990) (from Mucsi, 2019): a) Mechanical dispersion (size reduction) when the higher reactivity of the material is achieved by the increased specific surface area b) Surface activation when the mechanochemical reactions are taken place on the particle surface, and c) Mechano-chemical activation when the whole volume of the particle is transferred to other structure as well.

According to Tesla's patent data, this process minimizes the co-dissolution of other metal ions (Al^{3+} , Ca^{2+} , Mg^{2+} , Fe^{3+}), thus simplifying lithium purification and reducing recovery costs. These alkali and metal ions have been reported as a serious problem in the selective separation of lithium from the leach solution. That is, the presence of competing elements such as Na^+ , K^+ , Ca^{2+} , and Mg^{2+} makes it difficult to separate lithium from leach solutions, similar to salt-lake brines (Song et al., 2011; Ushak et al., 2016; Pramanik et al., 2019).

A wide range of techniques for the extraction of lithium and its selective separation from Mg^{2+} have been extensively studied due to the chemical similarity and co-existence of these elements in various natural brines and mineral sources or leach solutions. These methods include chemical precipitation using selective reagents, adsorption onto functionalized materials with high lithium affinity, solvent extraction with tailored organic ligands, and concentration–evaporation processes optimized for differential solubility. Additionally, electrochemical separation techniques such as electro-dialysis and lithium-ion selective electrodes have shown promising results in terms of their precision and scalability. Membrane separation technologies, including nanofiltration and ion-selective membranes, offer energy-efficient alternatives for lithium–magnesium separation. Moreover, reaction-coupled separation processes that integrate chemical reaction steps with physical separation methods have emerged as a novel and potentially more efficient approach to increase lithium selectivity in complex matrices (Sun et al, 2021; Ni et al., 2023).

Within this context, this study aimed to investigate the effect of mechanical activation on the Boron Processing Plant wastes (Türkiye) as lithium bearing source and to understand the dissolution of lithium ions from the tailings based on other accompanying competing alkali and metal ions such as K^+ , Na^+ , Ca^{2+} , Mg^{2+} , B_2O_3 , Al^{3+} , and Fe^{3+} that affect the selective lithium recovery from leach solution.

2. Materials and methods

2.1. Materials

The sample used as a lithium source in this study was supplied from ~~Kırka~~ Boron Plant Tailings (Eskisehir, Türkiye) and was in mud form when taken. In the plant, ROM boron mineral is concentrated through a dissolution process in hot water ($96\pm 2^\circ\text{C}$), sedimentation, decanting for solid-liquid separation, and a crystallization process, as shown in Fig. 1. Dissolved boron minerals are separated from dolomitic clay gangue minerals in two stages employing dissolution sluice and decanter centrifuge. The sediments from the dissolution sluices and decanter centrifuges are combined and dumped into a waste storage area. The representative samples in the form of mud from this waste storage area were dried in an open atmosphere and crushed to -2 mm prior to several analyses, mechanical activation, and leaching tests.

The results of chemical analysis on Boron Plant waste material were performed on ICP-OES, and XRD analysis are given in Table 1 and Fig. 1. As seen from Table 1, the tested waste sample mainly contains dolomite and small amounts of other accompanying minerals such as Tincalconite, Illite, Clinocllore, Zeolite, Muscovite, and Halite. It is worth noting that the waste sample has a rather complex structure containing mostly dolomite, different clay, and boron mineral occurrences (Fig. 2). The chemical analysis of the sample illustrates the high amount of both Mg (10.16%) and Ca (11.16%) and loss on ignition (LOI) value (34.08%) which proves the presence of dolomite. The Na (2.15%) and K (0.62%) contents are related to the presence of Halite, Zeolite, Muscovite, and Illite minerals in small amounts (Fig. 2).

Table 1. The chemical analysis of the Boron Plant waste material

Element	Value	Element	Value	Element	Value	Element	Value
Al (%)	0.69	Co (ppm)	1.26	La (ppm)	< 5	SiO ₂ (%)	16.34
Be (ppm)	1.63	Na (%)	2.15	Mg (%)	10.16	Sr (ppm)	9770
Ca (%)	11.16	Fe (%)	0.25	V (ppm)	4.43	Li (ppm)	900
Ce (ppm)	15.9	K (%)	0.62	Zr (ppm)	6.25	LOI (%)	34.08

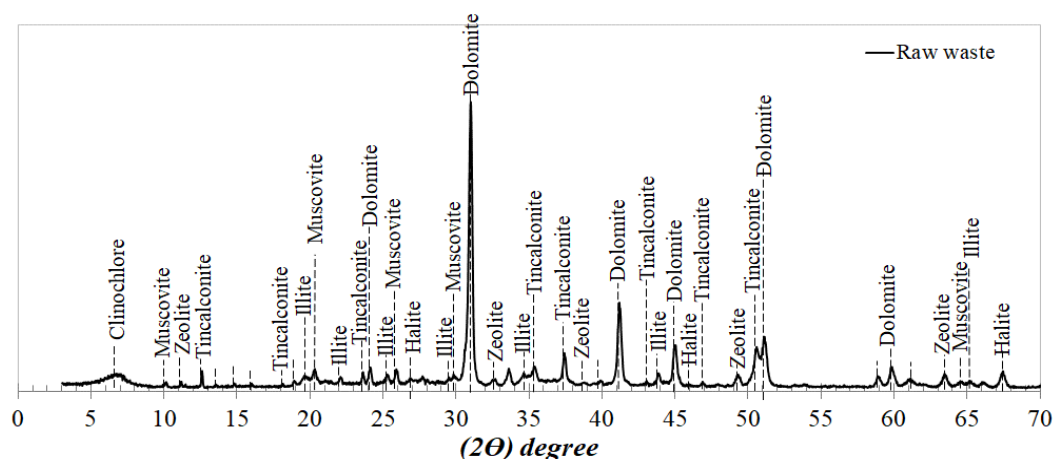


Fig. 1. XRD Pattern of the Boron Processing Plant wastes

In water leaching, commercial/technical grade pickle salt was used instead of table salt proposed by Tesla Group (2021) for isomorphous substitution between Na from salt and Li from wastes. The ion release properties of pickle salt used in general water leach tests are given in Table 2.

Table 2. The ion release of pickle salt in water (at 80°C leaching temperature and L/S: 5:0.1)

Element	Value (ppm)	Element	Value (ppm)	Element	Value (ppm)
K ⁺	10.19	Ca ²⁺	19.01	Fe ³⁺	0.0
Na ⁺	9628	Mg ²⁺	7.04	Al ³⁺	0.0

2.2. Methods

Fig. 2 shows the flowsheet of the experimental procedure for this study. As seen in Fig. 2, the sample was first dried in an oven overnight, then the dried sample was crushed down to -2 mm using a lab-scale jaw crusher prior to mechanical activation and leaching tests. Next, the crushed sample was mechanically activated using a Planetary Mill followed by water leaching without Pickle salt. The mechanical activation tests were performed at optimum operational conditions: -2 mm material feed size, 5 mm monosize zirconium ball loading, grinding media/material weight ratio of 15.6, and mechanical activation at 500-2000 rpm shaft speed for 150 min. To better understand the effect of mechanical activation on ion release during water leaching, only the intensity of the mechanical activation dependent on the shaft speed was included in the study.

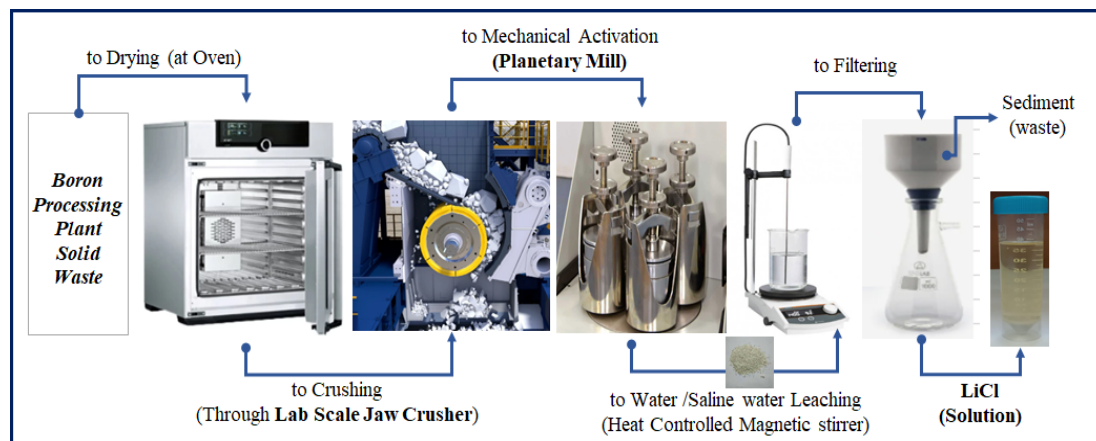


Fig. 2. Experimental flowsheet for mechanical activation and Saline water/water leaching

The activated samples were then subjected to water leaching tests using a temperature-controlled magnetic stirrer. In the leaching experiments, the salt concentration (technical grade pickle salt) was kept at 20% (w/w waste sample), and the leaching time, temperature, and liquid to solid ratio were kept constant at 60 min, 80°C, and 5:1, respectively. After the leaching, the leach pulps were filtered for solid/liquid separation, and the Li concentration and recoveries were analyzed/calculated according to the presence of the lithium in the leach solution.

For the determination of the surface morphology and elements of the raw material, active powder and post-leaching materials (leach residues) were examined in detail using a scanning electron microscope (SEM, HITACHI SU3500) and subjected to elemental surface analysis with an electron dispersive spectroscopy (EDS, Oxford AZtech). Additionally, all samples were characterised by an X-ray diffraction analyser (XRD, RIGAKU Miniflex 600) using a $K\alpha$ tube. XRD analyses were done between 3 and 90° using a wavelength of 1.5406 (Å) and a scan step size of 0.02°.

3. Results and discussion

3.1. Physical properties of activated products

As part of the experimental procedure, the samples were first subjected to mechanical activation (dry process) using a Planetary Mill. The operational parameters and milling conditions used for sample activation are summarized in Table 3. The degree of crystallinity (DoCr, %) of the raw and mechanically activated samples was determined from the XRD patterns based on the ratio of crystalline peak area to total diffraction area, and the results are presented in Table 4. As seen from Table 4, the milling experiments conducted at varying shaft speeds produced notable changes in both particle-size distribution and mineral crystallinity, revealing the complex interplay between mechanical stress intensity and the structural response of the clay-dolomite mixture. The raw sample exhibited a broad size distribution ($d_{90} \approx 102 \mu\text{m}$; $d_{50} \approx 14.6 \mu\text{m}$), which progressively narrowed under mechanical activation. At moderate shaft speeds (500–1000 rpm), substantial size reduction was observed, particularly at 750 rpm, where d_{90} decreased to $\sim 60 \mu\text{m}$ and d_{50} to $\sim 3.9 \mu\text{m}$, indicating efficient breakage and dispersion of clay aggregates. However, at higher speeds (1250–2000 rpm), particle sizes again

shifted toward coarser distributions, suggesting re-agglomeration or insufficient energy transfer due to dynamic instability within the milling chamber.

Table 3. Mechanical activation operational parameters and cell/ball properties

Variables	Operating Ranges
Sample Mass (g)	15
Ball Mass (g)	280
Ball to Powder ratio (BPR)	20:1
Ball size (mm)	8 mm (monosize)- Zirconia
Cell Volume (cm ³)	300
Mixing speed (rpm)	0-2000
Mixing time (min)	150

Crystallinity data further demonstrate the differential response of individual minerals to mechanical activation. Dolomite exhibited a slight but consistent increase in relative crystallinity at elevated speeds (e.g., 36.39% at 1500 rpm), likely reflecting the preferential breakage of more reactive or less ordered phases within the matrix, thereby enriching the relative proportion of intact dolomite crystallites. In contrast, clay minerals such as muscovite, chlorite, and illite displayed a marked decrease in crystallinity with increasing shaft speed. For instance, muscovite crystallinity declined from 5.80% in the raw sample to 2.92% at 1500 rpm, while chlorite dropped from 1.74% to 0.72%. These reductions indicate progressive lattice disorder, layer distortion, and partial amorphization—well-known consequences of high-energy milling. Zeolite and tinalconite also showed minor decreases, although the magnitude of structural deformation was less pronounced than in phyllosilicates, consistent with their comparatively more rigid framework structures.

Table 4. Particle size parameters, degree of crystallinity, and semi-quantitative mineralogical indicators of raw and mechanically activated samples

	Shaft Speed (rpm)	Particle Sizes (μm)			Degree of Crystallinity (%)					
		d ₉₀	d ₅₀	d ₁₀	Dol.	Musc.	C'Chlore	Zeo.	Tinc.	Illite
<i>Raw</i>	0	102.53	14.62	0.9	31.49	5.80	1.74	4.43	10.39	7.17
<i>Active samples</i>	500	106.36	6.24	0.73	32.41	4.15	1.35	4.22	10.25	6.22
	750	59.77	3.86	0.67	NA	NA	NA	NA	NA	NA
	1000	65.37	7.58	0.89	32.2	3.29	1.11	3.69	10.16	5.52
	1250	62.03	14.03	1.24	NA	NA	NA	NA	NA	NA
	1500	80.99	11.68	0.98	36.39	2.92	0.72	3.85	10.64	5.88
	2000	103.86	11.6	0.94	34.54	4.35	0.70	4.72	10.40	6.00

Overall, the results demonstrate that shaft speed exerts a non-linear but highly significant influence on both particle breakage and mineral structural modification. Moderate speeds promote effective comminution and disordering of clay minerals—conditions favorable for enhanced reactivity—whereas excessively high speeds may lead to particle aggregation and reduced activation efficiency. These observations are consistent with the mechanistic understanding of mechanical activation, where optimal energy input must balance impact intensity, milling dynamics, and heat generation to maximize structural alteration without inducing counterproductive effects such as agglomeration.

3.2. Structural and surface characterization

3.2.1. XRD analysis

Fig. 3 shows the XRD patterns of raw and activated samples at various shaft speeds. As seen in Fig. 3, the mechanical activation process caused the collapse of the peaks of some minerals, such as clinocllore,

muscovite, illite, tinalconite, and halite, and a decrease in the intensity of Dolomite's reflection. As indicated by Manosa et al. (2023), through mechanical activation, particle morphology undergoes significant alterations, with a shift from crystalline to amorphous structures. Hydroxyl groups are dissociated from the structure, leading to weakened bonding.

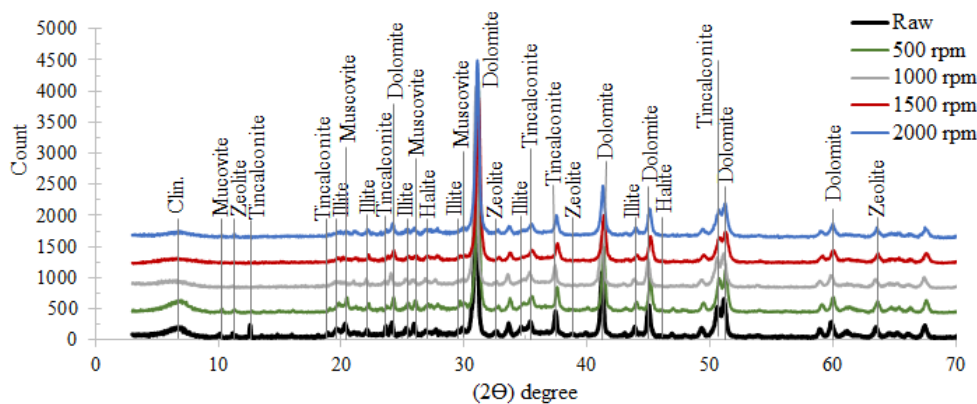


Fig. 3. XRD Pattern of activated products at various shaft speeds

3.2.2. FTIR analysis

Grinding and/or mechanical activation can significantly alter the FTIR peaks of minerals, particularly in clays, carbonates, and phyllosilicates. These changes can be attributed to structural disorder, particle size reduction, and changes in hydrogen bonds. Literature studies show that grinding and mechanical activation significantly affect the structural and chemical properties of clay minerals, as evidenced by changes in FTIR spectra. Increasing mechanical activation intensity leads to a decrease in the intensity of characteristic bands (O-H, B-O-H, CO₃, Al-O-H, Al-O-Si, Si-O-Si), which is attributed to partial amorphization, loss of crystallinity, and conversion of structural OH groups into adsorbed water (Yao et al., 2019; Manosa et al., 2023). Henmi and Yoshinaga (1996) found that dry grinding disrupted the tubular structure of imogolite, broke Si-O-Al bonds, and eliminated structural OH groups. Similarly, Christidis et al. (2004) observed that grinding reduced crystallite size, altered Si-O-Mg and Mg-O bonds, and increased cation exchange capacity in talc and smectite. Aglietti et al. (1996) reported that crystallinity decreased in kaolinite due to grinding and pressure, as well as earlier dehydroxylation and structural defects. Johnston et al. (2008) further confirmed that grinding induces structural disorder in kaolin-group minerals, which is evident by shifts in FTIR OH-stretching and Al-OH bending regions.

To determine the mechanical activation effect on FTIR characteristics depending on the intensity of mechanical activation, several FTIR analyses were performed on waste samples based on the mechanical activation intensity (Fig. 4). As seen in Fig. 4, the O-H stretching peaks related to the crystal and adsorbed water and B-O-H, B-O/C-O, and CO₃ peaks are diminished or disappeared through mechanical activation which can be attributed to partial amorphization, crystallinity loss, and transformation of structural OH groups into adsorbed water as mentioned by Yao et al. (2019) and Manosa et al. (2023).

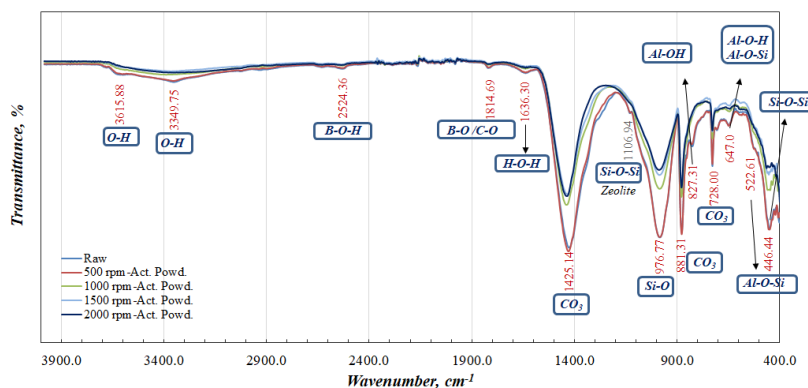


Fig. 4. FTIR analysis of the boron processing plant wastes and activated products at various shaft speeds

3.2.3. EDS/EDX analysis

Energy Dispersive X-ray Spectroscopy (EDS or EDX) is a valuable tool for examining the elemental composition and structural changes in clayey minerals subjected to mechanical activation. EDS provides insights into elemental distributions, phase transformations, and contamination effects during the activation process. Mechanical activation can generate surface defects, reactive sites, or free radicals (Manosa et al, 2023). These changes influence properties such as surface charge, cation exchange capacity, and adsorption behavior, particularly in minerals like illite and tincalconite. With the mechanical activation of the tested material, the distribution of alkali and other ions on the material surface was rearranged and the dominant alkali ion of Mg^{2+} was replaced by Na^+ ion due to the increase in the intensity of mechanical activation (Fig. 5). It was also observed that when the optimum mechanical activation shaft speed (1500 rpm) was reached (with respect to the lithium recovery), the dominant alkali ions of Mg^{2+} on the surfaces (in green) were replaced by Na^+ ions (in pinkish/purple color), which led to the increased lithium recoveries.

The water leach residues of the active powders were nearly identical, indicating that the surfaces remained dominated by Mg^{2+} ions, as observed in the raw material prior to leaching. These results suggest that Na ions, originating from potential minerals such as halite, tincalconite, and zeolite, become activated and migrate to the particle surfaces, where they are poised for isomorphic substitution with lithium. After leaching, the disappearance of Na^+ ions from the surfaces confirms their dissolution into the aqueous phase and subsequent removal through solid-liquid separation. To validate the proposed mechanism, ion analyses of the leachate were also conducted and are presented in the subsequent section of this study.

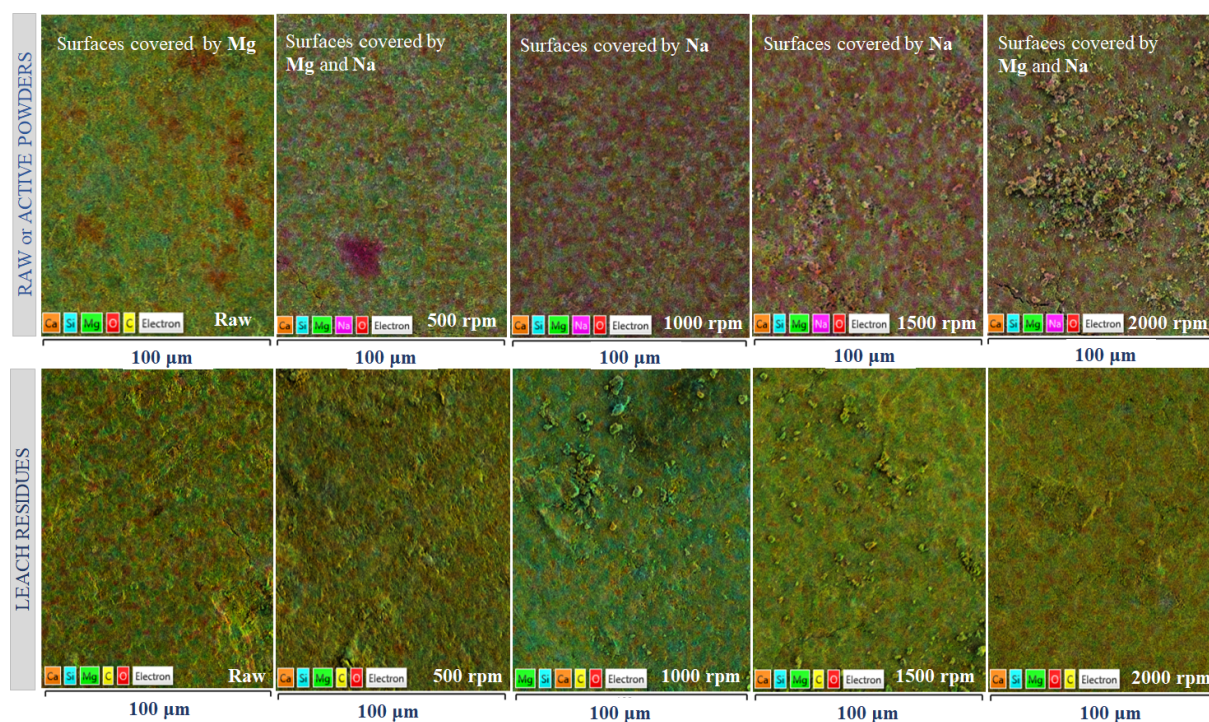


Fig. 5. EDS images of raw and mechanically activated samples at 500 rpm, 1000 rpm, 1500 rpm, and 2000 rpm (images at the top) and their leach residues (images at the bottom)

3.3. Leaching characteristics of ROM and activated samples

3.3.1. Lithium leach recoveries

Fig. 6 presents the lithium leaching recoveries, dissolved ion concentrations, and residual lithium contents in the leach residues of mechanically activated powders treated at different shaft speeds, compared with those of the raw, untreated material. As seen in Fig. 6, when the raw tailing sample is leached in water—regardless of whether salt is added—approximately 12–13.5% of the lithium present in the solid readily dissolves. Water-leaching tests conducted on the untreated sample at room

temperature and with short leaching durations yielded similar results. This behavior is most likely attributable to the lithium already present in the recycled process water of the boron enrichment plant (approximately 300 ppm Li in plant effluent), which remains associated with the tailings due to entrained process water.

With mechanical activation, and particularly with increasing activation intensity (i.e., higher shaft speed), lithium release from the crystal lattice becomes progressively easier. This enhancement continues up to a shaft speed of 1500 rpm. At higher speeds, however, the increasing centrifugal force reduces the effective gravitational load on the grinding media, limiting their ability to exert sufficient impact or shearing forces on the settled powder. Additionally, the intensified mechanical action may promote particle agglomeration or induce recrystallization of previously amorphized structures, both of which could hinder further lithium liberation. Experimental results indicate that the optimum shaft speed for mechanical activation is 1500 rpm, under which 57.71% of the lithium is dissolved into the leach solution.

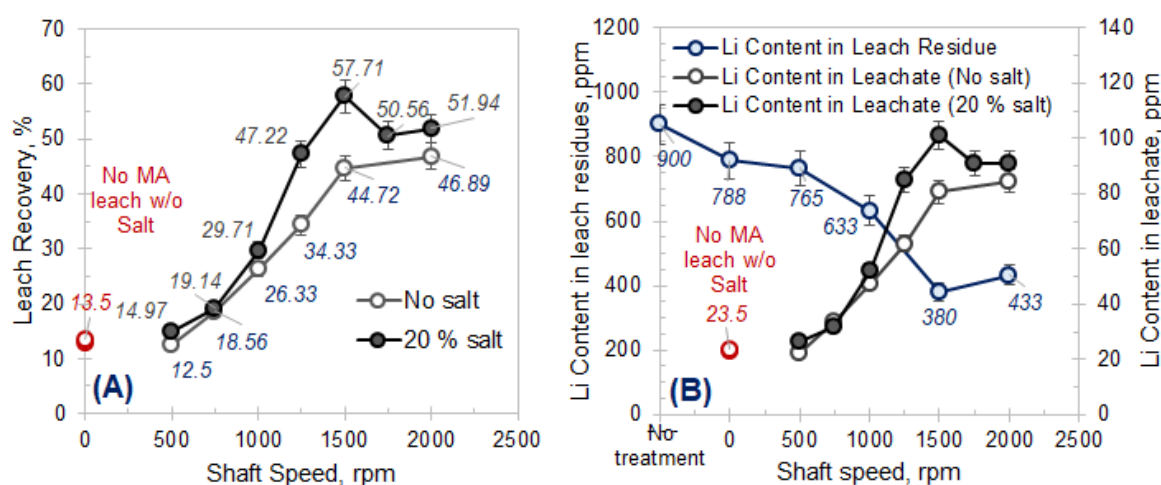


Fig. 6. The effect of both mechanical activation and salt addition on Lithium recovery (A) and Lithium contents (B)- (Solution pH: in the range of 8.7-9.1 varied based on the mechanical activation level and salt addition)

3.3.2. Ion release in ROM leaching with/without salt addition

The raw clayey tailings were introduced to water leaching experiments without salt to characterize the lithium, monovalent (K^+ and Na^+), divalent (Ca^{2+} and Mg^{2+}) alkali, and other accompanying ions such as B_2O_3 , Fe^{3+} , and Al^{3+} , which can cause problems in the recovery of dissolved lithium from leach solutions. Water leaching in the tested raw waste sample yielded only 10-13% of lithium recovery without salt addition (Fig. 6). It is seen that 19-24 ppm Li (L/S ratio is 5) at even room temperature is released together with other alkali and accompanying ions. Since the tested waste sample was in the mud/slurry form obtained from the boron concentration plant and recycled plant water contained 300-350 ppm lithium (information from the plant operators), it is thought that this naturally dissolved lithium in the recycled plant water was considered to be attributed to lithium, which remains as solid waste with a small amount of plant water.

Fig. 7 shows the dissolution of other accompanying ions. The water leach of the tested raw waste sample allows the release of small amounts of alkali cations except Na^+ and non-detectable levels of Fe^{3+} and Al^{3+} ions. Na^+ ion concentration was determined at the levels of 8400-10680 ppm. Surprisingly, the B_2O_3 release was observed at high levels (14000-15000 ppm) in water leaching for the leaching temperature of 80°C, and similar dissolution rates were also observed even at room temperature. B_2O_3 dissolution rates are attributed to inefficient boron plant processing (both leaching and solid-water separation).

3.3.3. Ion release in mechanically activated material leaching with/without salt addition

Since the lithium recovery in water (in the absence and presence of salt) was very low for the raw waste material, a mechanical activation process was applied to the raw waste material by means of a planetary

mill. After the detailed study for optimization of the mechanical activation procedure, the optimum operating conditions of mechanical activation were determined as previously mentioned. Therefore, the activated powders were produced to be used in detailed leaching experiments to determine the optimum ranges of leaching parameters. Fig. 8 shows the water leaching (with/without salt) properties of mechanically activated raw waste material at different shaft speeds for 150 min. The optimization tests showed that water leaching at 80°C leaching temperature and 60 min leaching time with L/S ratio of 5 (Boylu et al, 2026) provided 41-44% Li recovery, and this recovery could be increased up to 53-54% with the addition of 20% salt (w/w) (Fig. 8).

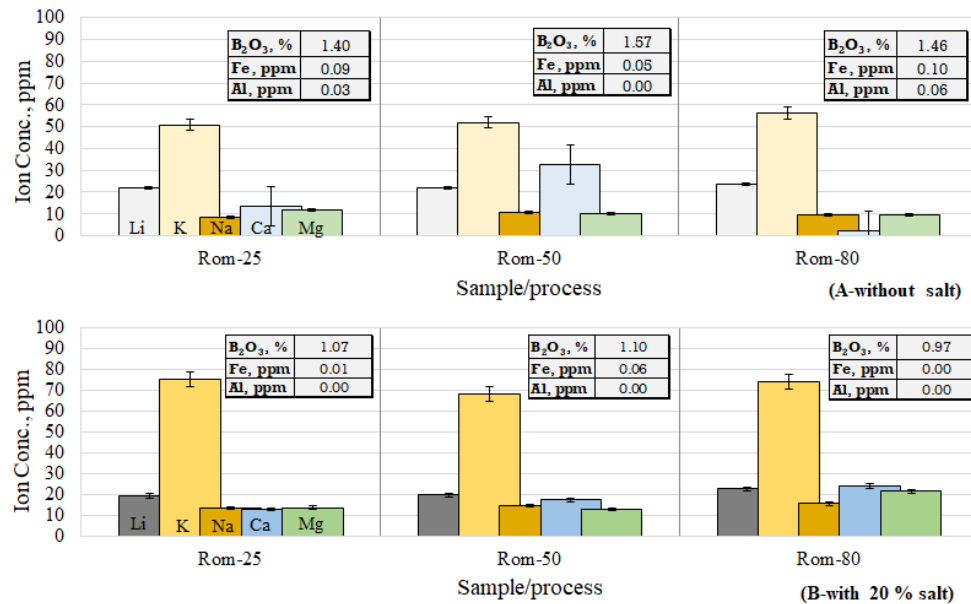


Fig. 7. Dissolution of Li⁺, alkali, and other accompanying ions in water (a) without salt (b) in the presence of salt (ROM-25, ROM-50, and ROM-75 stand for water leach at 25, 50, and 80 °C) (Na ion concentrations should be considered as *1000) (Solution pH: in the range of 8.7-9.1 varied based on the salt addition)

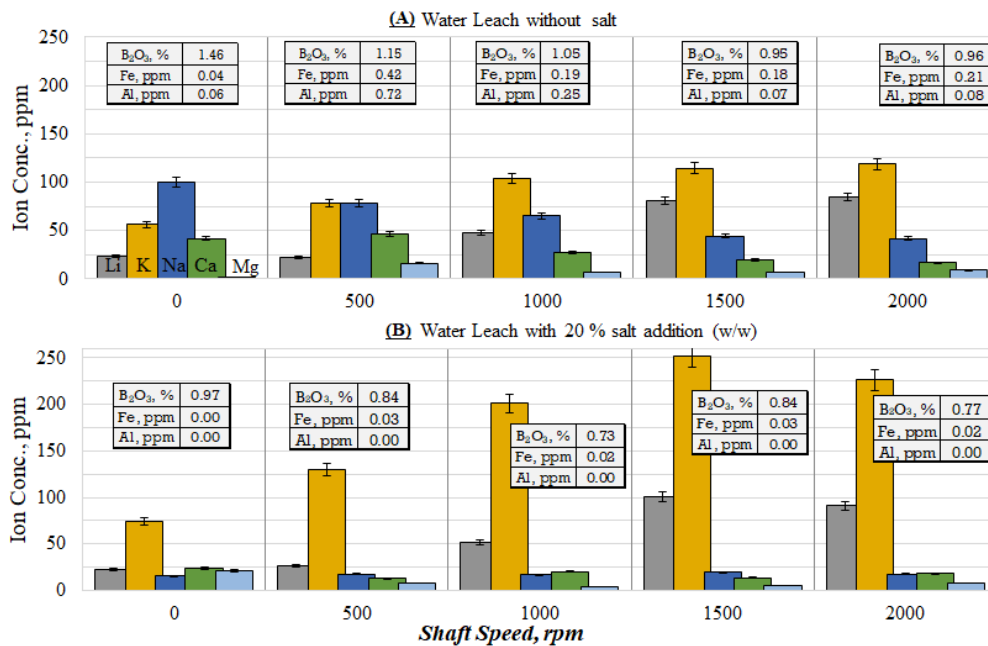


Fig. 8 9. Li⁺ and monovalent, divalent alkali ion and B₂O₃, Fe³⁺, and Al³⁺ ion release on water leaching of samples activated as a function of shaft speed (a-water leaching without salt addition, b-with salt addition). (Na ion concentrations should be considered as *1000) (Solution pH: in the range of 8.7-9.1 varied based on the mechanical activation level and salt addition)

Although these recoveries were relatively low compared to the conventional acid leaching and roasting + water leaching process, the alkali ions and other metal ions released were at very low levels (Fig. 8).

As seen in Figs. 8, by water leaching of mechanically activated wastes, 80-85 ppm Li^+ , 114-118 ppm K^+ , 4200-4400 ppm Na^+ , 17-20 ppm Ca^{2+} , 7-9 ppm Mg^{2+} , <0.21 ppm Fe^{3+} , >0.08 Al^{3+} , and 0.95-0.96% B_2O_3 ion concentrations were obtained in the leach solution.

To better understand lithium release behavior, correlations were performed for ion release into water in the absence of additional salt. The concentration of lithium released into the water was correlated with alkaline and B_2O_3 ion concentrations, as shown in Fig. 9. It was observed that the concentration of lithium ions in solution increased with the presence of potassium (K^+) ions. This trend is attributed to the presence of K-bearing minerals, specifically muscovite and illite, within the waste structure. Muscovite is the primary K-containing mineral, as indicated by FTIR peak changes. However, illite also contains potassium and may release K^+ ions upon structural deformation.

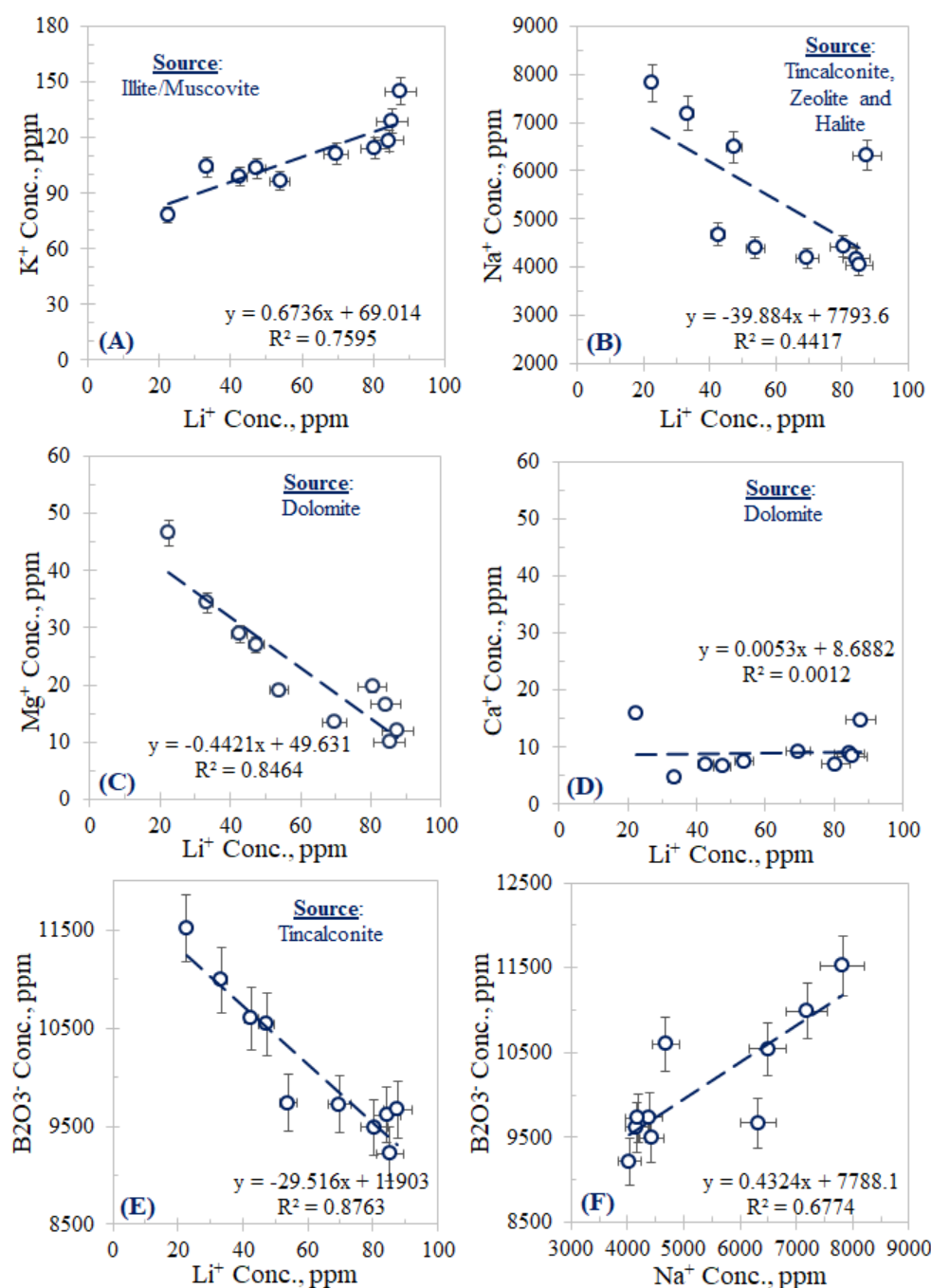


Fig. 9. Lithium release versus other ion releases

Therefore, it can be inferred that muscovite and/or illite are the main lithium-bearing minerals. Mechanical activation likely induces structural deformation in these minerals, thereby facilitating the simultaneous release of lithium and potassium ions, making them more readily dissolvable in water.

In contrast, the concentrations of Ca^{2+} , Na^+ , and B_2O_3 in the leach solution decreased as the lithium concentration increased. The dissolution rates of Ca^{2+} and Mg^{2+} ions are influenced by their mineralogical forms. The collapse of the carbonate (CO_3^{2-}) band, as observed in the FTIR spectra (Fig. 4 5), suggests a phase transformation from carbonate to oxide. This transformation may reduce the solubility of Ca^{2+} and Mg^{2+} in water.

The decrease in Na^+ concentration with increasing lithium dissolution is likely due to ion competition between Na^+ and Li^+ during the dissolution process. Additionally, the structure of boron minerals, upon losing their crystal water through mechanical activation, may undergo changes that hinder dissolution. As revealed by FTIR results, the resulting structural rigidity may make the crystal lattice more difficult to break, thus slowing the release of boron-related species into the solution.

Fig. 8 illustrates that the ion concentration for water leaching with 20% salt addition was also detected because these additional ion dissolutions could lead to serious problems in lithium extraction from the leaching solution as described above.

In the presence of salt (20% wt%), Li^+ dissolution can be increased up to 101 ppm. Salt addition increased K^+ and Na^+ ion concentrations up to 252 and 1942 ppm, respectively, while other alkalis, metals, and B_2O_3 ions decreased to lower levels compared to the water leaching results without salt addition.

The process of mechanical activation followed by water leaching without salt addition allows quite low alkali and metal ion (Fe^{3+} and Al^{3+}) release and dissolution rates when compared to conventional acid treatment in our preliminary studies (Table 5 and Table 6). This makes the application of the mechanical activation + water leaching process more attractive since increased amounts of alkali ions will cause some serious problems in further processing of lithium carbonate production.

Table 5. Comparison of ion release in water leaching without salt addition for both ROM and activated samples under optimum mechanical activation conditions

Shaft Speed (rpm)	Salt add. (%) / (mol/dm ³)**	Li ⁺ Conc. (ppm)	Rec. (%)	K ⁺ (ppm)	Na ⁺ (ppm)	Ca ²⁺ ppm	Mg ²⁺ (ppm)	Fe ³⁺ (ppm)	Al ³⁺ (ppm)	B ₂ O ₃ (%)
0	0.00	23.6	13.11	56.0	1001	41.5	0.25	0.04	0.06	1.46
0	20.00	22.5	12.50	74.0	15506	23.8	21.33	0.00	0.00	0.97
1500	0.00	80.5	44.72	114.1	4431	19.7	7.03	0.18	0.07	0.95
1500	20.00	101.0	57.71	252.1	1942	13.2	5.52	0.03	0.00	0.84
AL*	1.25**	59.2	32.89	72.9	4984	541.0	13018	1.82	0.00	1.17
AL*	1.75**	180.0	100.00	192.4	5700	548.3	21060	117.6	341.7	0.79

* AL: Acid leaching of the ROM waste material (from our previous works)

** Acid Conc.

That is, the presence of alkaline earth ions, particularly Na^+ and K^+ , generally shows a negative effect on lithium recovery due to their chemical similarity to Li^+ and their competitive interactions during separation processes. This adverse influence can be evaluated under several key mechanisms. Alkaline earth ions such as Na^+ and K^+ have similar physicochemical properties to Li^+ , including monovalence and comparable ionic radii. These similarities make selective separation of lithium difficult, especially in ion exchange and precipitation-based recovery processes (Raiguel et al., 2024). Competition with Li^+ ions for binding or exchange sites reduces process efficiency and selectivity. Sodium carbonate (Na_2CO_3) is commonly used to precipitate lithium as lithium carbonate (Li_2CO_3). However, the presence of Na^+ and K^+ ions increases the ionic strength of the solution, thus increasing the solubility of Li_2CO_3 , negatively affecting the morphology and growth of Li_2CO_3 crystals (King et al, 2019), and reducing precipitation efficiency. Furthermore, these ions can compete with Li^+ ions for carbonate ions (CO_3^{2-}), preventing the formation of the desired lithium salt (Battaglia et al., 2022). During the

crystallization of lithium carbonate, Na^+ and K^+ ions can be incorporated into the Li_2CO_3 crystal lattice or adsorbed onto its surface. This contamination adversely affects the purity of the final product, which is particularly critical for high-purity, battery-grade lithium carbonate applications. In processes such as ion exchange and membrane filtration, Na^+ and K^+ ions compete with Li^+ ions for active binding sites due to their similar size and charge. This reduces the selectivity and efficiency of these separation methods, ultimately decreasing lithium recovery.

Table 6. Ion dissolution rates in water leaching without salt addition for both ROM and activated samples under optimum mechanical activation conditions

Shaft Speed (rpm)	Salt add. (%) / (mol/dm^3)**	K^+ (%)	Na^+ (%)	Ca^{2+} (%)	Mg^{2+} (%)	Fe^{3+} (%)	Al^{3+} (%)	B_2O_3 (%)
0	0.00	4.52	23.28	0.186	0.001	0.008	0.004	81.1
0	20.00	5.97	NA	0.107	0.105	0.000	0.000	53.9
1500	0.00	9.20	100.00	0.088	0.035	0.036	0.005	52.8
1500	20.00	20.33	NA	0.059	0.027	0.006	0.000	46.7
AL*	1.25**	5.88	100.00	2.424	64.065	0.364	0.000	65.0
AL*	1.75**	15.52	100.00	2.457	100.0	23.520	24.761	43.9

* AL: Acid leaching of the ROM waste material (from our previous works)

** Acid Conc.

Similarly, divalent alkaline earth ions such as Ca^{2+} and Mg^{2+} also negatively affect the selective lithium recovery from leach solution. The presence of Mg^{2+} ions affect the rate of evaporation as well as the formation of lithium chloride (LiCl), a necessary step for the production of lithium carbonate. As a result, the lithium yield, purity, and separation efficiency can be significantly reduced. For lithium recovery, a $\text{Mg}^{2+}/\text{Li}^+$ ratio of less than 6 is generally recommended (Peiro et al., 2013; Vikström et al., 2013; Sun et al., 2015; Pramanik et al., 2019). Therefore, an efficient process would be one that takes into account the effective separation of lithium from brines and/or leach solutions containing several competing elements.

Boron is also one of the main contaminants in leach solutions and may alter the chemical balance of the leaching solution by changing the pH or interacting with other minerals, which can reduce the lithium extraction efficiency. When boron is present in the same solution or ore as lithium, it can compete for extraction reagents or selective adsorption, reducing the efficiency of lithium extraction. Boron and lithium can co-precipitate under certain conditions. This means that boron can also form precipitates as lithium is separated from the brine or ore, potentially reducing the purity and efficiency of lithium extracted, which in turn will affect the performance of lithium-ion batteries. Impurities in lithium salts can reduce the efficiency of lithium in battery reactions, resulting in reduced battery capacity and lifespan. To overcome the challenges posed by boron, specialized boron removal techniques are often used in lithium extraction processes, particularly in brine or clay-based operations. These methods may include Selective ion exchange (Bonin et al, 2021), solvent extraction (Guo et al, 2020), and membrane filtration/advanced filtration methods, such as reverse osmosis or nanofiltration. So, although the lithium leaching recoveries are not as high as in conventional acid leaching, providing the dissolution of those competing ions will make the further extraction process easier and more feasible in an environmentally friendly way since the use of acid will be eliminated and acid contamination at waste dumping areas will be avoided.

Based on the combined XRD, FTIR, and SEM-EDS results, lithium leaching from the mechanically activated waste is governed by partial structural collapse of Li-bearing muscovite/illite phases. Mechanical activation induces lattice disorder and partial amorphization, thereby facilitating lithium release into solution. However, a fraction of lithium remains un-extracted due to its association with structurally resilient silicate frameworks and dolomitic phases that are less susceptible to mechanochemical breakdown. This mechanistic interpretation explains the incomplete lithium recovery observed even under optimized activation and leaching conditions.

4. Conclusions

Lithium recovery from clayey minerals generally requires the decomposition of the crystal lattice to release lithium from the mineral framework. In addition to conventional acid leaching and roasting processes, mechanical activation using high-energy milling has been proposed as an alternative approach to induce structural breakdown without the application of acids or elevated temperatures. Mechanical activation may also offer advantages in terms of limiting the dissolution of competing ions, which commonly complicates downstream lithium extraction.

In this study, mechanical activation was applied to boron processing plant waste using a planetary mill. High-energy milling induced significant structural deformation, promoting the selective dissolution of certain ions while suppressing the release of others. The distinct dissolution behaviors of lithium and alkali ions indicate that lithium is primarily associated with muscovite/illite phases in the waste material.

Optimization of mechanical activation and subsequent water leaching resulted in lithium recoveries of 44% without salt addition and 57.71% with 20% salt addition. Although these recoveries are lower than those typically achieved by acid leaching or roasting–water leaching routes, mechanical activation followed by water leaching produced leach solutions with substantially lower concentrations of co-dissolved impurities. In particular, Mg^{2+} , Ca^{2+} , Al^{3+} , and Fe^{3+} levels were significantly reduced compared to acid leaching, which is advantageous for the selective recovery of lithium, especially in the form of lithium carbonate.

A major remaining limitation of this approach is the high solubility of B_2O_3 in aqueous media. At ambient temperature, B_2O_3 concentrations in the leach solution reached 10,000–14,000 ppm, posing a serious challenge to selective lithium recovery. Additional hot-water washing steps could reduce boron levels but would lead to considerable lithium losses due to its increased solubility at elevated temperatures. Owing to the mineralogical characteristics of the waste and the close association between lithium and boron-bearing phases, wet pre-concentration strategies targeting B_2O_3 are therefore unlikely to be effective and may result in substantial lithium losses.

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