

ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL

**MECHANICAL ACTIVATION-ASSISTED LEACHING WITH SALINE
WATER OR DILUTE ACID FOR LITHIUM RECOVERY FROM BORON
PROCESSING PLANT TAILINGS**



M.Sc. THESIS

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Department of Mineral Processing Engineering

Mineral Processing Engineering Programme

AUGUST 2025

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AUGUST 2025

İSTANBUL TEKNİK ÜNİVERSİTESİ ★ LİSANSÜSTÜ EĞİTİM ENSTİTÜSÜ

**BOR ÜRETİM TESİSİ ATIKLARINDAN LİTYUM GERİ KAZANIMI İÇİN
TUZLU SU VEYA SEYRELTİK ASİT İLE MEKANİK AKTİVASYON
DESTEKLİ LİÇ**

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To my family and my dear sister,



FOREWORD

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ABBREVIATIONS

Act	: Activation
AL	: Acid Leaching
BPR	: Ball to Powder Ratio
DMS	: Dense Media Separation
EDS / EDX	: Energy Dispersive X-ray Spectroscopy
EV	: Electrical Vehicles
FTIR	: Fourier Transform Infrared Spectroscopy
ICP-OES	: Inductively Coupled Plasma Optical Emission Spectroscopy
IEA	: International Energy Agency
LIB	: Lithium Ion Battery
LOI	: Loss on Ignition
MA	: Mechanical Activation
MTA	: General Directorate of Mineral Research and Exploration
PM	: Planetary Mill
ROM	: Run of Mine
rpm	: Revolutions Per Minute
SB	: Styrene-Butadiene Rubber (SBR)
SEM	: Scanning Electron Microscopy
SL	: Salt Leaching
SM	: Stirred Mill
STEPS	: Stated Policies Scenario
USA	: United States of America
VM	: Vibrating Mill
WL	: Water Leaching
XRD	: X-Ray Diffraction
2/3Ws	: Two/Three-Wheelers



SYMBOLS

Å	: Angstrom
°C	: Degrees Celsius
cm³	: Cubic Centimeters
ΔG	: Gibbs Free Energy Change
ΔH	: Enthalpy Change
ΔS	: Entropy Change
g	: Gram
K	: Kelvin
kg	: Kilogram
λ	: Wavelength
lt / L	: Liter
mL	: Milliliter
mg	: Milligram
min	: Minute
mm	: Millimeter
MPa	: Megapascal
μm	: Micron
pH	: Power of Hydrogen / Potential of Hydrogen
ppm	: Parts Per Million
T	: Temperature
V	: Volt
Σ US %	: Cumulative Undersize Curve



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MECHANICAL ACTIVATION-ASSISTED LEACHING WITH SALINE WATER OR DILUTE ACID FOR LITHIUM RECOVERY FROM BORON PROCESSING PLANT TAILINGS

SUMMARY

Lithium (Li) is a soft, silver-white alkali metal that has become an increasingly strategic resource, primarily due to its critical role in lithium-ion batteries used in electric vehicles and renewable energy storage systems. High electrochemical potential, low atomic weight, and high energy density make lithium indispensable for battery technologies. As one of the most electropositive elements on the periodic table, lithium enables the production of high-voltage cells, making it ideal for rechargeable batteries. Due to their light weight, long cycle life, and high energy efficiency, lithium-ion batteries have the potential to reduce dependence on fossil fuel-based systems and significantly lower carbon emissions. In this context, the use of lithium is not only a technological choice but also a strategic solution in terms of environmental sustainability. Due to its high reactivity, lithium is never found in its pure form in nature; instead, it occurs in various mineral and brine deposits. Major lithium-bearing minerals include spodumene, lepidolite, petalite, and zinnwaldite. Additionally, lithium can be recovered from alternative sources such as lithium-rich clay minerals, primarily composed of phyllosilicates with a 2:1-layer structure. These structures exhibit charge imbalances caused by isomorphic substitutions in the tetrahedral and octahedral sheets, making them suitable for cation exchange and chemical reactions.

Lithium resources are generally classified into hard rock deposits (pegmatites), lithium-rich brine reservoirs (salt flats), and volcano-sedimentary deposits. While South American countries dominate brine sources, countries like Australia possess significant spodumene reserves. In recent years, the increasing global demand for lithium has fueled interest in alternative sources such as clay minerals and industrial wastes. This growing demand necessitates the evaluation of lower-grade and more complex reserves. In this regard, clay minerals are considered sustainable, economically viable, and accessible alternative sources. In Türkiye, dolomitic clays associated with borate deposits, particularly in the Eskişehir-Kırka region, offer strategic potential for such applications. Lithium production methods vary depending on the source. Lithium recovery from ores typically involves roasting followed by hydrometallurgical processing, while brine-based extraction relies on solar evaporation, precipitation, solvent extraction, and ion exchange. Recently, mechanical activation has emerged as a promising pretreatment technique that enhances surface reactivity and disrupts crystal structures, thereby improving leaching efficiency.

In this study, lithium recovery was investigated through both direct acid leaching and mechanical activation-assisted methods. Dolomitic clay waste obtained from the Eskişehir-Kırka Boron Plant was used as the raw material. Mechanical activation was carried out using various high-energy mills, including planetary mills (PM), stirred mills (SM), and vibrating mills (VM). The activated samples were subjected to sulfuric acid leaching under varying acid concentrations, temperatures, and leaching durations.

Additionally, a two-stage leaching method combining saltwater leaching and acid leaching (SM Act.-WL+AL) was also evaluated. Experimental results revealed that mechanical activation significantly improved lithium solubility by increasing the surface area and disrupting the crystal structure of the clay minerals.

Lithium recovery without any mechanical pretreatment, in the temperature range of 25–80 °C was between 12.17% and 13.17%, with lithium concentrations in solution reaching 21.9–23.7 ppm. However, the addition of 10% NaCl slightly reduced the yield and concentration (22.5 ppm, 12.50%), indicating a minor inhibitory effect of salt on untreated samples. Conversely, mechanical activation effectively mitigated this issue and enhanced lithium dissolution. For example, samples activated with the planetary mill (PM) exhibited significant improvement: 80.5 ppm (44.72%) with no salt, 87.2 ppm (48.44%) with 10% NaCl, and 96.1 ppm (53.39%) with 25% NaCl. Stirred mill (SM) activation achieved lithium recoveries of 54.11%, 60.72%, and 63.67% for 0%, 10%, and 25% salt additions, respectively. Similarly, vibrating mill (VM)-activated samples showed recoveries of 36.72% (0% salt), 41.00% (10% salt), and 42.06% (25% salt). These findings demonstrate that mechanical activation not only enhances the leaching kinetics by increasing the surface accessibility but also reduces the negative effects of salt presence in the leaching medium.

In acid leaching experiments, lithium recovery also increased significantly with acid concentration. For raw (ROM) samples, lithium recovery gradually increased from 22.06% at 0.75 mol/L to 24.56% at 1.00 mol/L, 32.89% at 1.25 mol/L, 91.94% at 1.50 mol/L, and ultimately reached 100.00% at 1.75 mol/L. For mechanically activated samples, the improvements were even more striking. PM-activated materials achieved 70.06% recovery at 0.50 mol/L H₂SO₄, rising to 76.00% at 0.75 mol/L, 84.06% at 1.00 mol/L, and reaching 100.00% at 1.25 mol/L. Similarly, SM-activated samples recorded 72.08%, 80.69%, 88.61%, and 95.56% recoveries at corresponding acid concentrations. VM-activated samples exhibited 62.06% at 0.50 mol/L, 72.44% at 0.75 mol/L, and peaked at 91.67% at 1.00 mol/L, though a slight decline to 64.28% at 1.25 mol/L was observed, possibly due to reprecipitation phenomena or saturation effects.

Complementary surface analyses (EDS/EDX) demonstrated significant ion redistribution after activation. Na⁺ ions were enriched on PM-treated surfaces, whereas Ca²⁺ and Mg²⁺ ions became dominant in SM and VM-treated samples. Additionally, FTIR and XRD results confirmed major disruptions in crystal structures, confirming that mechanical activation is a viable pre-treatment to enhance lithium extraction performance from low-grade dolomitic clays.

In conclusion, mechanical activation is an effective and applicable method for lithium recovery from low-grade clay minerals and industrial wastes. This study demonstrates that high lithium yields can be achieved through mechanical activation alone, and by using low concentrations of sulfuric acid, recovery can be increased to 100%. This approach not only offers environmental advantages by minimizing chemical use but also represents a cost-effective solution. The type of mill and processing parameters play a decisive role in the degree of crystal structure disruption and leaching efficiency. Moreover, the evaluation of dolomitic clays in regions such as Kırka, which contain borate deposits, offers a strategic opportunity as alternative sources for Türkiye. These findings support the integration of mechanical activation into lithium recovery workflows, particularly from complex or low-grade resources, while also contributing to waste management and aligning with principles of sustainable production.

BOR İŞLEME TESİSİ ATIKLARINDAN LİTYUM KAZANIMI İÇİN MEKANİK AKTİVASYON DESTEKLİ TUZLU SU VEYA SEYRELTİK ASİT LİÇİ

ÖZET

Lityum, günümüzün en stratejik elementlerinden biri olarak kabul edilmekte ve özellikle yenilenebilir enerji teknolojileri ile elektrikli araçların gelişimiyle birlikte önemi giderek artmaktadır, özellikle lityum iyon bataryaların üretiminde yaygın olarak kullanılmaktadır Kimyasal sembolü Li ve atom numarası 3 olan bu alkali metal, periyodik cetvelin ilk periyodunda yer almakta ve oldukça düşük yoğunluğa sahip olması sayesinde bilinen en hafif metaldir. Bununla birlikte, lityumun batarya teknolojilerinde tercih edilmesinin asıl nedeni, periyodik cetvelde en elektropozitif elementlerden biri olması ve bu sayede yüksek elektro-kimyasal potansiyele sahip olmasıdır. Lityumun düşük atom ağırlığı ve yüksek enerji yoğunluğu, onu şarj edilebilir batarya sistemlerinde benzersiz kılar. Bu elektrokimyasal özellikleri, bataryaların daha hafif, daha verimli ve daha uzun ömürlü olmasını sağlar. Lityum iyon bataryalar, yüksek enerji yoğunlukları, uzun çevrim ömürleri ve hafif yapıları sayesinde taşınabilir elektronik cihazlardan elektrikli araçlara kadar geniş bir uygulama alanına sahiptir. Bu bataryalar, fosil yakıta dayalı enerji sistemlerinin yerini alabilecek potansiyele sahip olduğu için karbon emisyonlarının azaltılmasına da önemli katkı sunmaktadır. Bu yönüyle, lityum kullanımı çevresel sürdürülebilirlik açısından da stratejik bir öneme sahiptir. Mobil cihazlardan elektrikli araçlara, enerji depolama sistemlerinden savunma sanayine kadar geniş bir kullanım alanı bulunan lityum, aynı zamanda jeopolitik önemi giderek artan kritik mineraller arasında değerlendirilmektedir.

Lityum, doğada serbest halde bulunmamakta; bunun yerine çeşitli bileşikler şeklinde minerallerde veya tuzlu su kaynaklarında yer almaktadır. Genellikle iki ana kaynaktan yoğunlaşmaktadır: katı haldeki silikat mineralleri ve sıvı haldeki tuzlu su (brine) rezervuarları. Katı kaynaklara örnek olarak spodümen ($\text{LiAlSi}_2\text{O}_6$), lepidolit ($\text{K}(\text{Li},\text{Al})_3(\text{Al},\text{Si},\text{Rb})_4\text{O}_{10}(\text{F},\text{OH})_2$), petalit ($\text{LiAlSi}_4\text{O}_{10}$) ve zinvaldit verilebilir. Bu mineraller, pegmatit tipi jeolojik ortamlarda oluşur ve çoğunlukla Avustralya, Kanada, Çin ve Zimbabve gibi ülkelerde bulunur. Tuzlu su kaynakları ise, çoğunlukla kurak bölgelerde yer alan göl yataklarında ve tuz çöllerinde yoğunlaşır. Güney Amerika'daki "Lityum Üçgeni" (Arjantin, Şili ve Bolivya) bu anlamda dünyanın en büyük rezervlerine sahiptir. Bu kaynaklar, düşük işletme maliyetleri nedeniyle caziptir ancak litredeki lityum içeriği çok düşük (genellikle %0,02-0,15) olduğu için ön zenginleştirme ve buharlaştırma gibi süreçler gerektirir.

Bunun dışında, son yıllarda volkanik kökenli tortul kayalarda ve kil minerallerinde de lityum tespit edilmiş ve bu alanlarda araştırmalar artmıştır. Özellikle hektorit ve jadarit gibi killerin, sürdürülebilir ve ekonomik lityum üretimi açısından gelecekte önemli kaynaklar arasında yer alması beklenmektedir. Bu tür killeri, 2:1 tipi tabaka yapısına sahip fillosilikatlar grubunda yer almakta ve bu yapılar tetrahedral ve

oktahedral katmanlardan oluşmaktadır. Kristal yapılarında meydana gelen izomorfik yer değiştirmeler sonucu negatif yük oluşmakta ve bu da onları katyon değişimi ve çözünme reaksiyonları açısından uygun hale getirmektedir.

Lityum üretim süreçleri, cevherin ya da çözeltinin fiziksel ve kimyasal özelliklerine bağlı olarak farklılık göstermektedir. Sert kayalardan lityum kazanımı, genellikle öğütme, kavurma ve ardından asidik ya da alkali liç işlemleriyle gerçekleştirilir. Özellikle spodümen cevheri, önce α -fazdan β -faza dönüştürülür ve sonrasında sülfürik asit veya sodyum karbonat ile liç işlemine tabi tutulur. Öte yandan, tuzlu su kaynaklarından lityum üretimi, daha az enerji tüketen fakat zaman açısından daha uzun süren buharlaştırma tekniklerine dayanır. Bu yöntemlerde, tuzlu su yüzey havuzlarında aylar süren bir buharlaştırma sürecine bırakılır, ardından çöktürme ve solvent ekstraksiyonu gibi işlemlerle saflaştırılır. Ancak bu süreç, çevresel etkiler ve su kullanımı açısından eleştirilmektedir. Son yıllarda geliştirilen yeni teknolojiler, özellikle düşük tenörlü cevherler ve endüstriyel atıklardan lityum geri kazanımını mümkün kılmaktadır. Bu yöntemlerden biri olan mekanik aktivasyon, malzemenin öğütme yoluyla kristal yapısının bozulmasını ve yüzey enerjisinin artırılmasını sağlar. Bu işlem, lityum içeren malzemenin asidik çözeltilerle daha kolay reaksiyona girmesine neden olarak liç verimini artırır. Mekanik aktivasyon işlemi, gezegen değirmeni, karıştırmalı değirmen ve titreşimli değirmen gibi farklı cihazlarla gerçekleştirilebilmektedir. Öğütme süresi, frekans, bilya boyutu ve katı/sıvı oranı gibi parametreler, işlemin etkinliğinde belirleyici rol oynar.

Bu çalışmada, lityum geri kazanımı hem doğrudan asit liçi hem de mekanik aktivasyon destekli yöntemler aracılığıyla araştırılmıştır. Hammadde olarak Eskişehir-Kırka Bor Tesisinden temin edilen dolomitli kil atığı kullanılmıştır. Mekanik aktivasyon işlemleri; gezegen değirmeni (PM), karıştırmalı değirmen (SM) ve titreşimli değirmen (VM) gibi çeşitli yüksek enerjili öğütücülerle gerçekleştirilmiştir. Aktive edilen numunelere, değişen asit konsantrasyonları, sıcaklıklar ve liç süreleri altında sülfürik asit liçi uygulanmıştır. Ayrıca, tuzlu su liçi ve asit liçinin birleştirildiği iki kademeli bir liç yöntemi (SM Act. - WL+AL) de değerlendirilmiştir. Deneysel sonuçlar, mekanik aktivasyonun lityum çözünürlüğünü önemli ölçüde artırdığını göstermiştir; bunun nedeni, aktivasyonun yüzey alanını artırması ve kil minerallerinin kristal yapısını bozarak çözünürlüğü kolaylaştırmasıdır.

Mekanik ön işlem uygulanmamış (ROM) örneklerde, 25–80 °C sıcaklık aralığında lityum geri kazanımı %12,17 ile %13,17 arasında değişmiş ve çözeltideki lityum konsantrasyonu 21,9–23,7 ppm seviyelerine ulaşmıştır. Bununla birlikte, %10 NaCl ilavesi, geri kazanım ve konsantrasyonda hafif bir düşüşe neden olarak (22,5 ppm, %12,50) tuzun işlem görmemiş matris üzerindeki hafif engelleyici etkisini ortaya koymuştur. Buna karşılık, mekanik aktivasyon bu etkiyi ortadan kaldırarak lityum çözünmesini önemli ölçüde artırmıştır. Örneğin, gezegen değirmeni (PM) ile aktive edilen numunelerde tuz ilavesine bağlı olarak geri kazanım değerleri sırasıyla tuzsuz ortamda 80,5 ppm (%44,72), %10 NaCl ile 87,2 ppm (%48,44) ve %25 NaCl ile 96,1 ppm (%53,39) olarak belirlenmiştir. Karıştırmalı değirmenle (SM) aktive edilen numunelerde geri kazanım oranları %0, %10 ve %25 tuz ilaveleri için sırasıyla %54,11, %60,72 ve %63,67 olarak gerçekleşmiştir. Titreşimli değirmenle (VM) aktive edilen örneklerde ise sırasıyla %36,72 (0% tuz), %41,00 (10% tuz) ve %42,06 (25% tuz) geri kazanım elde edilmiştir. Bu sonuçlar, mekanik aktivasyonun lityumun çözünme kinetiğini ve yüzey erişilebilirliğini artırarak tuzun olumsuz etkisini azaltabildiğini göstermektedir.

Asit liçi deneylerinde ise artan H_2SO_4 konsantrasyonu ile birlikte geri kazanımda belirgin bir artış gözlemlenmiştir. Ham (ROM) örneklerde lityum geri kazanımı, 0,75 mol/L'de %22,06'dan başlayarak sırasıyla 1,00 mol/L'de %24,56, 1,25 mol/L'de %32,89, 1,50 mol/L'de %91,94 ve 1,75 mol/L'de %100,00 düzeyine ulaşmıştır. Mekanik aktivasyon uygulanan örneklerde bu artış daha da çarpıcı olmuştur. Gezegen değirmeni (PM) ile aktive edilen örneklerde, 0,50 mol/L H_2SO_4 ile %70,06, 0,75 mol/L'de %76,00, 1,00 mol/L'de %84,06 ve 1,25 mol/L'de %100,00 geri kazanım sağlanmıştır. Karıştırmalı değirmen (SM) ile aktive edilen örneklerde ise sırasıyla %72,08 (0,50 mol/L), %80,69 (0,75 mol/L), %88,61 (1,00 mol/L) ve %95,56 (1,25 mol/L) geri kazanım elde edilmiştir. Titreşimli değirmenle (VM) aktive edilen numunelerde bu oranlar sırasıyla %62,06 (0,50 mol/L), %72,44 (0,75 mol/L) ve %91,67 (1,00 mol/L) olup, 1,25 mol/L'de ise geri kazanım %64,28'e gerilemiştir. Bu düşüş yeniden çökelme (reprecipitation) veya matris doygunluğu gibi nedenlere bağlanabilir.

Tamamlayıcı yüzey analizleri (EDS/EDX), aktivasyon sonrası iyon dağılımında önemli değişimler olduğunu ortaya koymuştur. PM ile işlenen yüzeylerde Na^+ iyonlarının baskın olduğu görülürken, SM ve VM ile aktive edilen örneklerde Ca^{2+} ve Mg^{2+} iyonlarının daha belirgin olduğu gözlemlenmiştir. Ayrıca FTIR ve XRD analizleri, kristal yapıların önemli ölçüde bozulduğunu doğrulamıştır. Bu bulgular, düşük tenörlü dolomitli killerden lityum geri kazanımının, mekanik aktivasyonla desteklenen tuzlu su ya da asit liçi yöntemleriyle önemli ölçüde iyileştirilebileceğini göstermektedir.

Elde edilen bu bulgular, sadece cevherlerden değil, aynı zamanda endüstriyel atıklardan ve düşük tenörlü kaynaklardan da yüksek verimli lityum kazanımının mümkün olduğunu göstermektedir. Lityuma olan küresel talep, özellikle elektrikli araçlar ve enerji depolama teknolojilerindeki hızlı gelişmeyle birlikte her geçen gün artmaktadır. Bu artış, geleneksel kaynakların ötesinde alternatif rezervlerin değerlendirilmesini zorunlu kılmaktadır. Kil mineralleri bu bağlamda öne çıkan stratejik alternatif kaynaklardır. Türkiye, özellikle Eskişehir-Kırka bölgesindeki bor yataklarına bağlı olarak oluşan dolomitik killere açısından bu potansiyele sahip önemli bir ülke konumundadır. Bu çalışmada kullanılan Kırka kaynaklı dolomitik kil atıklarında yalnızca mekanik aktivasyon uygulanarak dahi anlamlı düzeyde lityum kazanımı elde edilmiş, düşük konsantrasyonlardaki H_2SO_4 kullanımıyla bu verimin %100 seviyesine çıkarılabildiği gösterilmiştir. Bu yaklaşım, hem kimyasal kullanımını minimize ederek çevre dostu bir süreç sunmakta, hem de atıkların değerlendirilmesi sayesinde sürdürülebilir ve döngüsel ekonomi ilkeleriyle uyumlu bir çözüm sunmaktadır. Mekanik aktivasyonun çevre dostu yapısı, kimyasal tüketimi azaltması ve enerji maliyetlerini düşürmesi, bu yöntemin sanayi ölçeğine taşınması açısından da büyük bir potansiyel sunduğunu göstermektedir. Bu bağlamda, gelecekte sürdürülebilir lityum üretimi için mekanik aktivasyon destekli hidrometalurjik yöntemlerin yaygınlaşması beklenmektedir.



1. INTRODUCTION

With an atomic number of 3 and an atomic weight of 6.941, lithium is the lightest metallic element and the 25th most abundant element in the Earth's crust, although its use in metallic form is limited. Its primary utilization is in compound form (Akgök and Şahiner, 2017; Obut et al., 2022). Lithium has approximately twenty industrial applications. Today, lithium and its derivatives are used in various sectors, particularly ceramics, glass, electronics, grease lubricants, metallurgy, silicon-based materials, optical systems, air filtration technologies, and the defense industry. The chemical industry in China, in particular, consumes a significant portion of the lithium concentrate produced worldwide (Akgök and Şahiner, 2017). Lithium compounds are also widely used in the pharmaceutical, ceramic, rocket propellant, aluminum, and nuclear energy sectors (Arslan, 2022). Industrial lithium production primarily takes the form of lithium carbonate and lithium hydroxide and is derived from two main sources: brines and pegmatites. Lithium-bearing clays, especially smectites, constitute another potential source (Obut et al., 2022). With the development of electric vehicles and energy storage technologies, the demand for lithium has increased, leading many countries to classify it as a critical raw material. Lithium production is predominantly sourced from brine reservoirs and ores such as spodumene and lepidolite; in recent years, it has also been recovered from secondary sources such as lithium-ion batteries. In hard rock-based production, the roasting process with sulfuric acid is generally used (Celep et al., 2022).

For a long time, the applications of lithium were limited to specialized areas such as high-temperature lubricants, certain types of ceramics and glass, and antidepressant medications. In recent years, the increasing demand for batteries has significantly boosted lithium consumption; demand is expected to increase sixfold from 2020 levels by 2030. This has led to a global search for new lithium sources and a reassessment of existing reserves (Dini et al., 2022). Reducing the carbon footprint is critically important for a sustainable world. Since the Industrial Revolution, the increase in

carbon emissions due to fossil fuel consumption has necessitated the use of renewable energy sources. However, energy storage systems are required to manage the energy produced by these sources. Commercialized in 1991, lithium-ion batteries have become fundamental components of portable devices and the decarbonized energy movement due to their long cycle life, high capacity, and efficiency. However, the production of raw materials such as cobalt, lithium, and graphite being concentrated in specific countries creates bottlenecks in the supply chain. The COVID-19 pandemic and the Russia-Ukraine War have exacerbated this vulnerability. Türkiye stands out with its geopolitical position, labor force, and raw material resources; however, its non-ferrous metal exports are characterized by low added value. The production of high-tech products will enhance the country's export volume and potential. Energy storage systems and lithium-ion batteries have strategic importance in today's world, where resource management is increasingly crucial (Gülcan et al., 2023).

Electric vehicles play a key role in the decarbonization of transportation. Although their production phase results in higher carbon emissions, their carbon footprint during use is significantly lower than that of gasoline and diesel vehicles. This difference is more evident in countries using clean energy, and their advantages increase as electricity grids become decarbonized. Figure 1.1 reflects the number of electric vehicles on roads worldwide, showing the cumulative total of vehicles sold over the years (excluding retired vehicles). This number, which was around 26 million in 2022, has rapidly increased in a short time and has now reached 60 million (Ritchie, Roser, and Rosado, 2024). The major challenges for electric vehicles have been the inability to develop batteries with low power and long range. Significant investments have been made for this purpose; however, the desired power and energy density have not yet been achieved. The primary goal is to produce economically and strategically sustainable, long-lasting, and high-performance batteries (Şen et al., 2024).

Lithium-ion battery chemistry is a technology preferred for efficient energy storage, and Türkiye has made investments in this field; Aspilsan Energy, which started mass production of 18650 Li-ion batteries in 2022, has been a pioneer in this transformation. While diesel vehicle production and the use of internal combustion engines have been restricted in many countries, Türkiye has also taken steps to reduce carbon emissions, and as seen in Figure 1.2, the areas of use for renewable energy and energy storage

systems have expanded beyond power plants to include homes, UPS systems, defense, medicine, transportation, and communication (Özdemir, 2023).

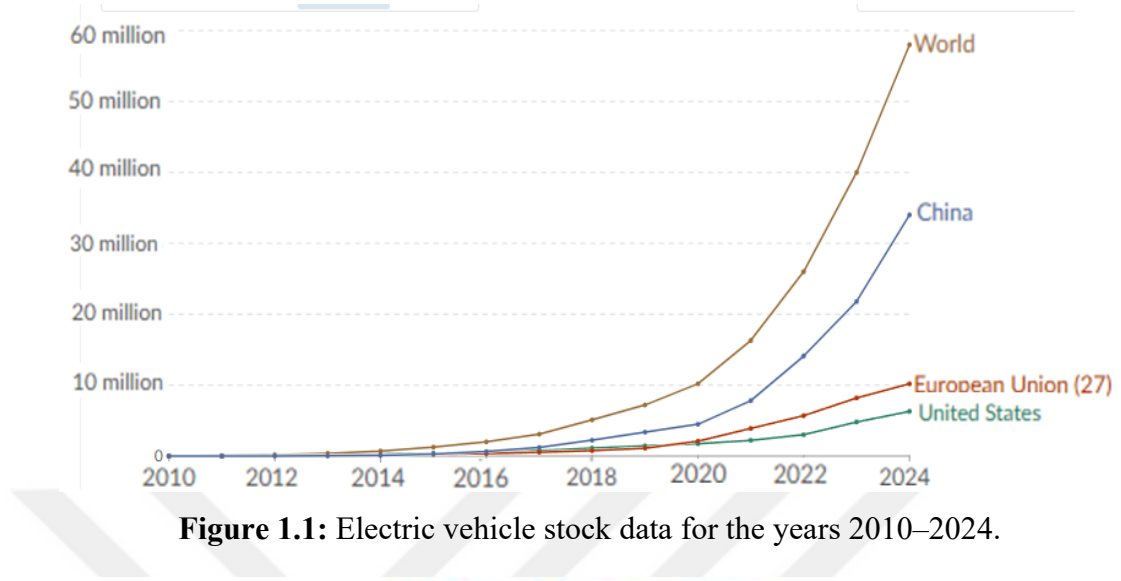


Figure 1.2: The use area of batteries.

Lithium, although it is considered a critical material in many industries, especially electric vehicles, due to its superior properties such as being an electrochemically active metal with low redox potential and high specific capacity, its low concentrations in natural reserves and the difficulties in extraction from hard rocks make continuous supply challenging and this situation affects global prices. Approximately 66% of the world's lithium is obtained from brine sources, and 34% from hard rocks. In alternative sources such as seawater, geothermal fluids, and oil field brines, the lithium content is quite low (<0.25 mg/L). Recovery of lithium from brines is less costly and more energy-efficient compared to hard rocks. Therefore, it is important to develop innovative and economic processes for alternative sources in order to meet increasing

demands (Arslan, 2022). There is no lithium source with economic value in our country. However, although the presence of lepidolite within pegmatites in the Yozgat Sorgun region is known, significant results have not been obtained from studies conducted. In studies carried out in some lakes in our country, it has been observed that the lithium content does not exceed 40 ppm, while 325 ppm lithium has been detected in Lake Tuz. However, Mg^{2+} content of Lake Tuz is 38,000 ppm. Again, various studies have shown that the lithium content in clays in boron fields approaches 2000 ppm. As a result of studies conducted in the Kestelek, Emet, Kırka, and Bigadiç fields where boron is mined, it has been determined that the lithium content in the Bigadiç and Kırka regions is higher than in the Kestelek and Emet regions. In these fields, it has been observed that there is an inverse relationship between boron content and lithium content, and it has been determined that as the particle size decreases, the lithium content increases. Table 1.1 presents the main lithium-bearing pegmatite minerals, their approximate chemical compositions, and commercial $LiO_2\%$ contents (Akgök ve Şahiner, 2017).

Table 1.1: Basic pegmatites bearing lithiums.

Mineral	Chemical Formula	LiO_2 Commercially(%)
Spodumene	$LiAlSi_2O_6$	4-7
Lepidolite	$K_2Li_3Al_4Si_7O_{21}(OH,F)_3$	3-4
Amblygonite	$LiAl(F,OH)PO_4$	8-9
Petalite	$LiAlSi_4O_{10}$	2-4

Recovery of lithium from brines is more economical and feasible compared to traditional mining methods, and production is possible even with lower lithium content. However, the determining factor in this process is the Mg/Li ratio, and the ideal value is considered to be at most 6:1. As seen in Table 1.2, due to the high ratio in lakes in Türkiye, economic production does not appear to be feasible. For example, although the Mg/Li ratio is high in the Great Salt Lake in the USA, production is still possible due to the size of the reserves. In boron deposits such as Kırka and Bigadiç in Türkiye, lithium content up to 0.30% has been detected. In studies conducted by MTA and ETİ Maden, lithium recovery of 0.12–0.15% has been achieved from clay wastes, and no mining cost occurred in this process. In the recovery of lithium from clays, processes such as roasting, leaching, and precipitation with sodium carbonate are applied; in preliminary trials, a yield of 82% has been achieved (Arslan, 2022).

Table 1.2: The presence of lithium and other major ions in Turkish brine lakes.

Lakes	Li ⁺ (mg/L)	K ⁺ (mg/L)	Mg ⁺ (mg/L)
Lake Tuz	318-325	12.000-12.100	37.500-38.000
Lake Boluk	25-27	2.000-2.050	8.700-8.800
Lake Tersakan	31	2.000-2.050	6.000
Lake Acıgöl	30-33	1.000	4.100

Mechanical activation, unlike conventional grinding, is a process with higher energy intensity and improves both the kinetics and efficiency in extractive metallurgy. While reducing particle size and increasing specific surface area, it creates defects and amorphization in the crystal structure; thus, reaction temperature and duration decrease, dissolution/reaction rates and metal recovery increase. Therefore, downstream processes such as leaching can be carried out with lower energy, higher efficiency, and in a shorter time (Apaydın, 2010).



2. GENERAL INFORMATION

2.1 Lithium

2.1.1 Historical development of lithium

The element lithium was nucleosynthesized within the first few minutes of the Big Bang approximately 13.7 billion years ago (Figure 2.1). It was one of the three primordial elements of our universe, but due to a reason still unknown today (the so-called "lithium problem"), its abundance is much lower not only than the other two primordial elements (hydrogen and helium), but also than that of heaviest elements whose synthesis requires extremely harsh conditions such as star formation or supernovae (Xu, 2019).

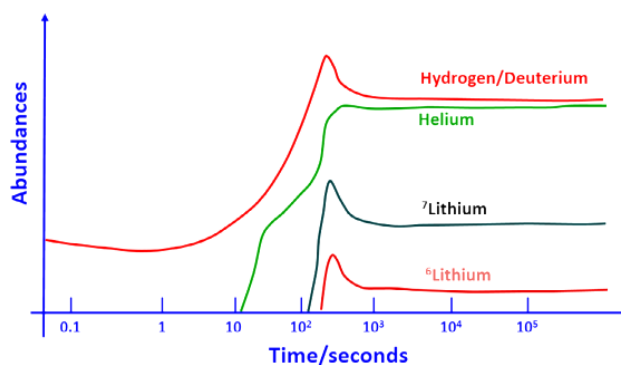


Figure 2.1: The nucleosynthesis of lithium along with other primordial elements at the beginning of the universe.

On our planet, the abundance of lithium is not only rare, but its distribution is also extremely irregular. Most of the lithium reserve in the Earth's crust, more than 70%, is located in a chain of salt lakes on the South American continent, in a narrow region intersecting Chile, Bolivia, and Argentina, known as the “Lithium Triangle” (Figure 2.2) (Xu, 2019; Kaya, 2022).

In 1817, the young Swedish chemist Johan August Arfwedson discovered a new alkali in the mineral Petalite ($\text{LiAlSi}_4\text{O}_{10}$), which consumed more acid than all known alkalies. Berzelius proposed the name “lithion,” derived from the Greek word “lithos” (stone), because this alkali was discovered for the first time as specific to a mineral,

and he stated that the corresponding element should be named “lithium.” This name was first mentioned in writing in a letter by Berzelius in January 1818. The high reactivity of lithium made it difficult to isolate and closely associated it with electrochemistry. Even today, it can only be obtained in pure form through the electrolysis of molten salts. In the periods following its discovery, lithium was used in the treatment of diseases such as gout, asthma, and depression, and even as a food and beverage additive; for example, the name of the soda 7Up originates from this, where "7" represents the atomic weight of lithium (6.95) and "Up" refers to lithium’s mood-enhancing effect. In 1908, Edison claimed that lithium hydroxide increased battery capacity, although he could not explain the reason. Lewis and Keyes were the first to scientifically and accurately measure the electrochemical potential of lithium, revealing that it had “the highest electrode potential ever measured” at 3.30 V; this property laid the foundation for today’s lithium-based battery technologies (Xu, 2019). Lithium metal has been preferred as an anode material since the 1970s due to its high capacity and low weight (Şen et al., 2024).

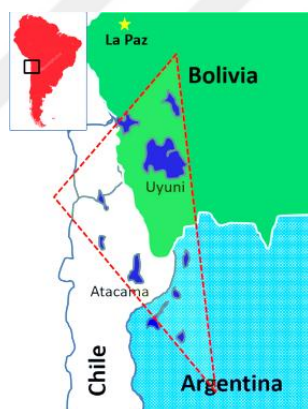


Figure 2.2: The lithium triangle, south america (Xu, 2019).

2.1.2 General properties of lithium

Lithium, with the symbol Li, an atomic weight of 6.941, and atomic number 3, is the lightest solid alkali element with a density of 0.543 g/cm³. Lithium is a soft and silvery-white element and exists in solid form at 25°C (room temperature) (Akgök and Şahiner, 2017; Kaya, 2022; National Center for Biotechnology Information, 2025). As seen in Figure 2.3, lithium, which is included in the alkali metals group of the periodic table, shares chemical properties similar to those of alkaline earth metals. Lithium has 5 isotopes and its mass number varies between 5 and 9. Lithium boils at 181°C and melts at 179 °C. In particular, lithium is electrochemically active with a high electrode

potential of -3.05 V and has the highest specific heat capacity among all solid elements. Since it has a single electron in its outermost orbit, it is a highly electropositive metal with high thermal and electrical conductivity (Arslan, 2022). Li is an electropositive metal with the highest reactivity and high thermal and electrical conductivity. Li is highly reactive and flammable in its pure form. Li cannot be found in nature as a free element; it can be found in the forms of $\text{Li}^+(\text{aq})$, $\text{LiOH}(\text{s})$, $\text{Li}(\text{s})$, $\text{LiH}(\text{s})$, $\text{LiSO}_4^-(\text{s})$, $\text{Li}_2\text{O}(\text{s})$, and $\text{Li}_2\text{O}_2(\text{s})$ (Kaya, 2022). It reacts with nitrogen, oxygen, and water vapor in the air and has never been found in its pure form in nature. Therefore, Li is stored in an inert atmosphere such as pure kerosene or mineral oil, or under vacuum (Balaram et al., 2024).

The figure shows a periodic table with Lithium (Li) highlighted in a large teal box. To the right of the box, a table lists its properties:

Atomic Mass	7.0 u
Electron Configuration	$[\text{He}]2s^1$
Oxidation States	+1
Year Discovered	1817

Below this table is a button labeled "View All Properties". The periodic table itself shows elements from Hydrogen (H) to Oganesson (Og), with Lanthanide and Actinide series at the bottom.

Figure 2.3: Lithium in the periodic table (National Center for Biotechnology Information, 2025).

2.1.3 Utilization area of lithium

In the fight against global climate change, the use of renewable energy sources instead of fossil fuels in sectors such as transportation and energy production, which cause high greenhouse gas emissions, is of great importance. In this context, electric vehicles powered by long-lasting and highly efficient lithium-ion batteries play a key role in reducing carbon emissions (Balaram et al., 2024). The lower air and noise pollution created by electric vehicles, their energy savings, and the support of sustainability-focused policies in many countries accelerate this transformation process and constitute an important step toward reducing environmental impacts (Bediroğlu and Gençer, 2024).

With the widespread use of portable electronic devices and electric vehicles, the importance of lithium-ion batteries, which are the main energy source of these systems, has rapidly increased in recent years. Especially the electric vehicle-focused developments in the automotive sector have popularized the use of these batteries and increased lithium demand. Lithium-ion batteries, which have been used in portable devices since the 1990s, are today also the main power source for electric vehicles (Celep et al., 2022). The continuously increasing demand for lithium-ion batteries (LIBs) has caused the percentage of lithium consumption used in the battery sector to rise from 29% in 2013 to 87% in 2023. Figures 2.4a and 2.4b show the change in end-uses of lithium between 2013 (Figure 2.4a) and 2023 (Figure 2.4b) (Petrakis et al., 2025).

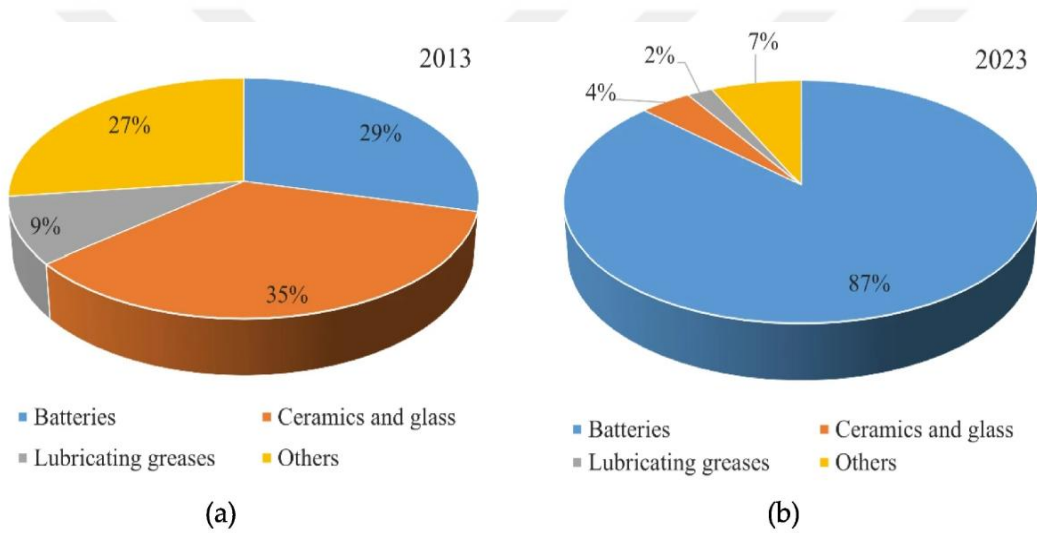


Figure 2.4: Utilization areas of lithium in (a) 2013 and (b) 2023.

Lithium can be used directly in the glass and ceramic industry. Lepidolite lowers the melting point of glass, increases its viscosity, improves its workability, and reduces its brittleness. Spodumene and petalite can be directly added to ceramic mixtures. It is widely used in industry. Its two most important compounds are in the form of carbonate and hydroxide. Lithium carbonate is used in glass and ceramic armor processing. It provides high brightness and durability and increases chemical strength. Lithium hydroxide monohydrate can be reacted with animal fats to produce lithium-based grease (Akgök and Şahiner, 2017).

In 2030, under the Stated Policies Scenario (STEPS), excluding 2/3Ws, the number of EVs will reach 250 million, increasing fourfold compared to 2024. More than 90% of these vehicles will be electric cars. Although the 2/3Ws stock, which exceeds all EVs

in 2024, will rise to 170 million in 2030, it will remain behind the electric car stock. In this scenario, EVs will constitute 15% of all vehicles, while China's share in the global EV stock will decrease from 70% to 55% (International Energy Agency [IEA], 2025).

Lithium metal is used as a component of aluminum and manganese alloys, which are known for their high mechanical strength despite being lightweight. Therefore, Li is used in the production of lightweight alloys with elements such as aluminum, cadmium, copper, and manganese for aircraft and space applications, as well as in the production of high-strength, corrosion-resistant components for military applications. Metallic Li and its hydrides are used as super energy additives in rocket propulsion. Magnesium-lithium (Mg-Li) alloys developed in the early 20th century have exceptional properties such as corrosion and wear resistance and are therefore used in lightweight fields such as aerospace, automotive, and electronics.

Li is used to produce tritium through neutron bombardment for nuclear fusion via low-energy nuclear fission and can fuel fusion reactors that power spacecraft. Lithium was used in earlier hydrogen bombs and is currently used in the construction of modern nuclear weapons. Additionally, lithium isotopes are used for various purposes in the nuclear industry. For example, Li is used as a nuclear coolant and also as a pH regulator in the coolant material of the primary circuits of pressurized water nuclear reactors. The most important use of Li and Be in weaponry involves the construction of thermonuclear weapons. These two metals are placed inside the warhead as main components to activate nuclear bombs.

Lithium compounds are used in the plastic industry to produce wear-resistant synthetic rubbers, thermoplastic rubbers, and polyethylene, and to produce thermoplastics and polymers for special applications. Alkyl lithium compounds initiate polymerization by materials such as alkyl lithium compounds and styrene-butadiene rubber (SBR), which is widely used in rubber production (Balaram et al., 2024). Table 2.1 presents the areas of use of lithium and the changing rates over the years (Celep et al., 2022; USGS, 2023).

Although the medical and psychiatric use of lithium dates back approximately 150 years, its place in modern psychiatry began with John Cade's demonstration of its therapeutic effects in mania in 1949. Today, lithium is preferred as a mood stabilizer

in the maintenance treatment of bipolar disorder and also constitutes an important option for enhancing the effects of antidepressants in treatment-resistant depression. In addition, it exhibits anti-suicidal, immunomodulatory, and neuroprotective properties; it offers protective effects against dementia and promising outcomes in neurodegenerative disorders. However, despite these strong clinical and biological effects, lithium is still not sufficiently used in mood disorders (Rybakowski, 2020).

Table 2.1: Utilization areas of lithium and their share by (%) by years (Celep et al., 2022; USGS, 2023).

Use of area	2010	2015	2019	2020	2023
Battery	23	31	65	71	80
Glass and ceramics	31	35	18	14	7
Grease	10	8	5	4	4
Metallurgy	4	6	3	2	2
Air conditioning	5	5	1	1	1
Polymer		5	3	2	
Aluminum production	3	1			
Other	24	9	5	6	5
Total	100	100	100	100	100

2.1.4 Economic perspective on lithium

Global lithium trade is generally conducted based on private contracts between producer and consumer companies. As seen in Figure 2.5, the market is driven by four major firms that hold the majority of production (Akgök and Şahiner, 2017).

- Sichuan Tianqi Lithium Industries, based in China, controls approximately 40% of the market with its state-supported structure.
- Sociedad Química y Minera de Chile (SQM), operating in Chile, holds a 26% share through its production based on the Atacama salt flat.
- Albemarle Corporation, based in the United States, originally rooted in the paper industry, now operates in the lithium and chemical sector and holds 20% of the market.
- Another major U.S.-based producer, FMC Corporation, holds a 12% share in the industry (Arslan, 2022).

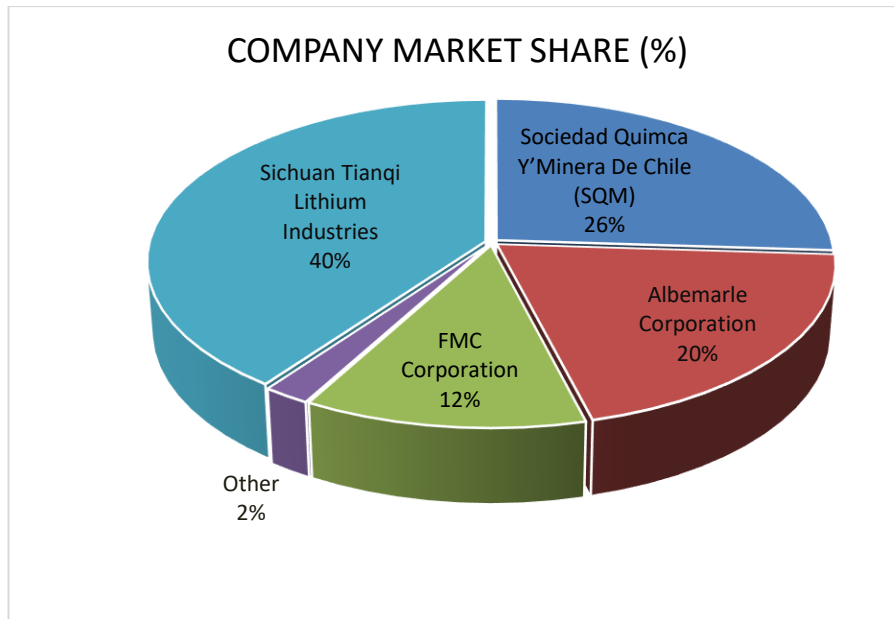


Figure 2.5: Market share of the main supplier companies worldwide.

2.2 Lithium-Containing Ores

Before the 1980s, lithium was mostly extracted from pegmatite ores, and with the discovery of brine deposits, the focus shifted to lithium extraction from brines. This change enabled the development of new techniques, significantly reduced costs, and made salt lake brines the main source of lithium carbonate, metallic lithium, and other lithium compounds (Yang et al., 2025).

Although more than 150 types of lithium-containing ores have been identified worldwide, only a few types are significant in terms of extraction. Among these, spodumene, lepidolite, clay-type lithium ores (such as hectorite), petalite, amblygonite, and eucryptite stand out. The main properties of these ores are detailed in Table 2.2. In the mining industry, the most commonly used mineral is spodumene due to its high lithium content (around 6% Li_2O) and large reserves. Spodumene ($\text{LiAlSi}_2\text{O}_6$) is converted from α -spodumene to reactive β -spodumene by roasting, allowing lithium extraction with acidic or basic solutions. Lepidolite ($\text{K}(\text{Li},\text{Al})_3(\text{Si},\text{Al})_4\text{O}_{10}(\text{F},\text{OH})_2$) has a lower lithium content (around 3% Li_2O) compared to spodumene, and although it presents processing difficulties due to its fluoride content, it is economically valuable because it contains rare metals such as rubidium and cesium. Clay-type ores (e.g., hectorite) have large deposits in countries such as China and the USA and contribute to the development of advanced recovery

technologies. Minerals such as petalite, amblygonite, and eucryptite are less abundant, scattered, and have low usage rates and remain underdeveloped (Yang et al., 2025).

Table 2.2: Information about common lithium-containing minerals (Yang et al., 2025).

Mineral	Theoretic Li ₂ O content (%)	Density (g/cm ³)	Hardness (Mohs)	Color
Spodumene LiAlSi ₂ O ₆	8.03	3.1–3.2	6–7	White, grey, green, purple, colorless
Lepidolite K(Li,Al) ₃ (Si,Al) ₄ O ₁₀ (F,OH) ₂	7.7	2.8–3.3	2.5–4.0	White, grey, purple, yellow, colorless
Hectorite Na _{0.3} (Mg,Li) ₃ Si ₄ O ₁₀ (OH) ₂	1.17	2–3	1–3	Earthy, white
Petalite LiAlSi ₄ O ₁₀	4.5	2.4	6–6.5	Grey, yellow, white
Amblygonite (Li,Na)Al(PO ₄)(F,OH)	7.4	2.98– 3.11	5.5–6	White, grey, yellow, colorless
Eucryptite	11.86	2.67	6.5	Brown, white

2.3 Lithium Deposits and Reserve Areas

Lithium deposits are divided into three main types based on historical and current production and the mineral systems approach: pegmatites, closed-basin brines, and volcano-sedimentary deposits. Pegmatite deposits are the most common type on a global scale (Figure 2.6) and are found on all seven continents. The formation ages of these deposits span a wide time range from the Mesoarchean to the Cenozoic. Closed-basin lithium brine deposits are primarily located in the high-altitude, extremely arid basins of the modern Andean and Himalayan mountain belts. However, lower-grade brine deposits can also be found at lower altitudes around the world.

Volcano-sedimentary lithium deposits are also widespread globally, with the largest and highest-grade examples generally restricted to Cenozoic closed basins in extensional continental settings where coeval rhyolitic volcanism is observed. An example of such formations is the Basin and Range region in the United States and

Mexico. In addition to these, there are also other types of lithium deposits such as continental brines, geothermal brines, and rare-metal granites. However, lithium production from these deposits has not yet become commercially viable at the present time (Benson et al., 2025).

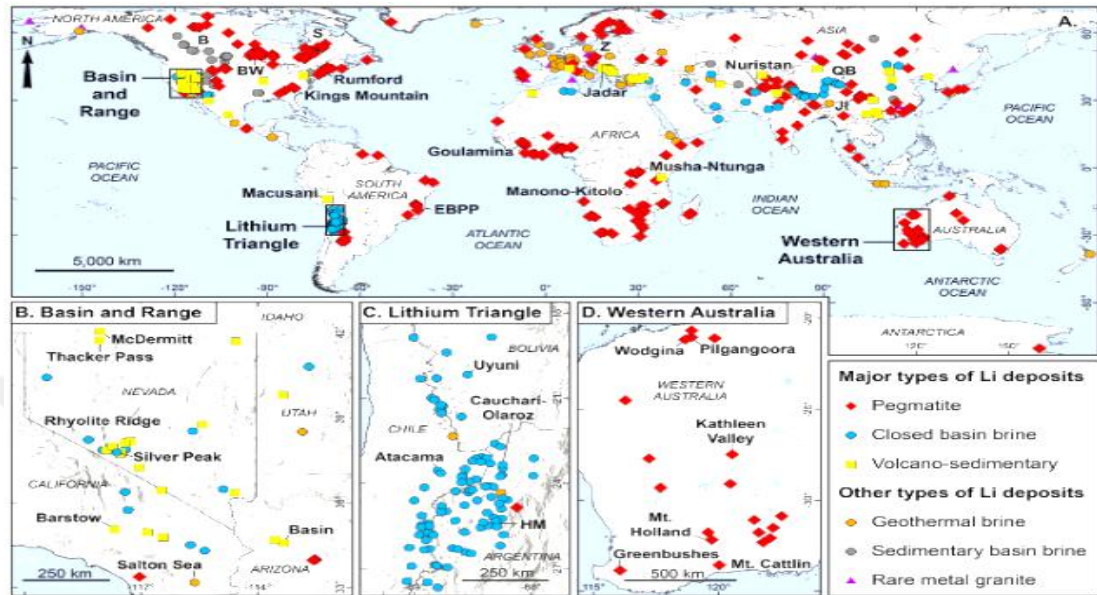


Figure 2.6: (A) Global distribution of lithium deposits classified by deposit type, with inset maps providing detailed views of the three largest lithium provinces worldwide: (B) Basin and Range, (C) Lithium Triangle, and (D) Western Australia. (Abbreviations: B = Bashaw district, BW = Big Whopper, EBPP = Eastern Brazilian pegmatite province, HM = Salar del Hombre Muerto, JI = Jiajika, QB = Qaidam basin, S = Shaakichiuwaanaan, Z = Zinnwald.).

2.3.1 Pegmatite-type lithium deposits

Granitic pegmatites are an important source of rare metals such as lithium, tin, tantalum, niobium, beryllium, cesium, rubidium, scandium, thorium, uranium, and rare earth elements. However, the total content of rare metals in these deposits is generally low, and lithium-rich pegmatites constitute only a small portion of these deposits. For economic production, the lithium oxide content must be approximately 0.6%. Pegmatite deposits generally exhibit a zoned structure; the outer parts are rich in feldspar, the middle zones contain rare element minerals, and the core is enriched in quartz (Üçerler, 2022). Approximately one-quarter of global lithium reserves are found in pegmatite deposits, where both open-pit and underground mining methods are applied. Although the extraction process is more costly compared to brine-based sources, the lithium grade in pegmatites is generally higher, and the recovery of valuable by-products such as tin or tantalum reduces operating costs (Akgöz and

Şahiner, 2017). Pegmatite-type deposits are the most important solid lithium deposits and generally develop in association with granite intrusions. They are rich in lithium minerals such as spodumene, lepidolite, petalite, and amblygonite. Lithium-Cesium-Tantalum pegmatites have high grades and are often economically exploitable (Yin et al., 2024). Prominent pegmatite deposits worldwide include Kings Mountain and Quebec in North America; Greenbushes and Mt. Cattlin in Australia; Bikita in Zimbabwe, Africa; Fregenedo-Almendro in Portugal, Europe; Vishnyokovskoe and Goltzovoe in Russia; and Jiajiaka, Dahongliutan, and Ke'eryin in China (Üçerler, 2022). Among these deposits, Greenbushes stands out as one of the highest-grade areas with approximately 1.6% lithium content and a reserve capacity of 560,000 tons (Akgöz and Şahiner, 2017). In general, granitic pegmatites offer high-grade but limited-volume lithium reserves, with the most productive deposits concentrated in Australia, Africa, and North America (Akgöz and Şahiner, 2017; Üçerler, 2022).

2.3.2 Lithium deposits in brine reservoirs

A large portion of lithium-rich brine deposits develop in lacustrine evaporites in geologically young and closed basins where precipitation is low and evaporation is high. While the most notable examples of these deposits are found in the Central Andes and China, smaller-scale formations are located in the western United States and North Africa. Brines associated with lacustrine evaporites exhibit a broader chemical diversity compared to marine-origin evaporites and possess local lithium enrichment potential. Although the exact mechanism of lithium concentration in these brines is not well known, possible sources include the weathering of felsic volcanic rocks, geothermal fluids associated with volcanic systems, and the influence of underlying magma chambers. Additionally, rock–water interactions are thought to alter brine compositions through processes such as the removal of magnesium from brine via chlorite precipitation (Kesler et al., 2012).

Approximately 66% of global lithium reserves are found in brine deposits, and the majority of production is sourced from these deposits. Brines are categorized into three main groups: geothermal, continental, and petroleum-related. Among these sources, the "Lithium Triangle" region formed by Chile, Argentina, and Bolivia stands out. The Salar de Atacama field in Chile, covering an area of 3,000 km², is one of the most significant examples, with a lithium content of 1,400 ppm and approximately 6.3

million tons of reserves. Although Bolivia's Salar de Uyuni hosts approximately 50% of the world's lithium reserves, its high Mg/Li ratio makes it more difficult to process. This condition slows the evaporation process and increases production costs (Akgöz and Şahiner, 2017).

2.3.3 Volcano-sedimentary deposits

Volcano-sedimentary deposits have emerged in recent years as potential sources of lithium with rapidly developing projects. Typical examples of these deposits include current mining sites such as the Thacker Pass project located in the state of Nevada, USA. In previous classifications, these deposits were often referred to as “clay-type” or “hectorite-type,” but today the term volcano-sedimentary classification is preferred because not all lithium-bearing minerals in these systems are of clay nature. In these deposits, minerals such as smectite, illite, and jadarite are the main lithium-bearing phases. Two significant volcano-sedimentary lithium regions stand out globally: The Tethyan belt covering Eastern Europe and Western Türkiye, and the Basin and Range region in North America. These deposits have mostly formed in structurally controlled extensional basins or areas associated with volcanic complexes. The Thacker Pass deposit in Nevada is notable for its smectite- and illite-rich minerals, while the Jadar deposit in Serbia is a globally important lithium source due to its hosting of the jadarite mineral. In addition to these, some volcano-sedimentary systems do not contain typical clay mineral assemblages but still have lithium potential. For example, coal seams and associated aluminum-rich underclays, karstic bauxite deposits containing kostekite, and young or altered volcanic rocks observed in the Macusani volcanic area of Peru are included in this group. These deposits have so far been limitedly explored and hold potential for future exploration efforts (Benson et al., 2025).

Approximately 8% of the world's lithium reserves are found in clays, especially in the minerals smectite and hectorite. In the Kings Valley of Nevada, USA, 48 million tons of reserves containing 0.27% lithium have been identified, while in the Sonora region of Mexico, 43.3 million tons of reserves with 0.3% lithium have been identified. These reserves are expected to increase with global exploration efforts (Akgöz and Şahiner, 2017).

2.4 Global Lithium Reserves

Currently, there are six types of lithium deposits: salt lake lithium brines, lithium pegmatites, lithium clays, lithium zeolites, petroleum-gas field lithium brines or geothermal lithium brines, and ion-adsorbed lithium. Pegmatite lithium deposits are of episodic ages and are mainly distributed in Precambrian orogenic belts such as the Western Australia Craton, the Congo Craton, the West African Craton, and the Canadian Shield. All other lithium deposit types except for pegmatite lithium deposits are mainly distributed in Cenozoic orogenic belts such as the Andes Lithium Triangle area, the Sichuan-Tibet region of China, and the North American Cordillera, and constitute approximately 75% of global lithium resources. Currently, salt lake lithium brines and lithium pegmatites have great exploration potential and are the main lithium deposit types being investigated and developed (Wanwan et al., 2023). Figure 2.7 shows the types and relative sizes of global lithium resources (Yin et al., 2024).

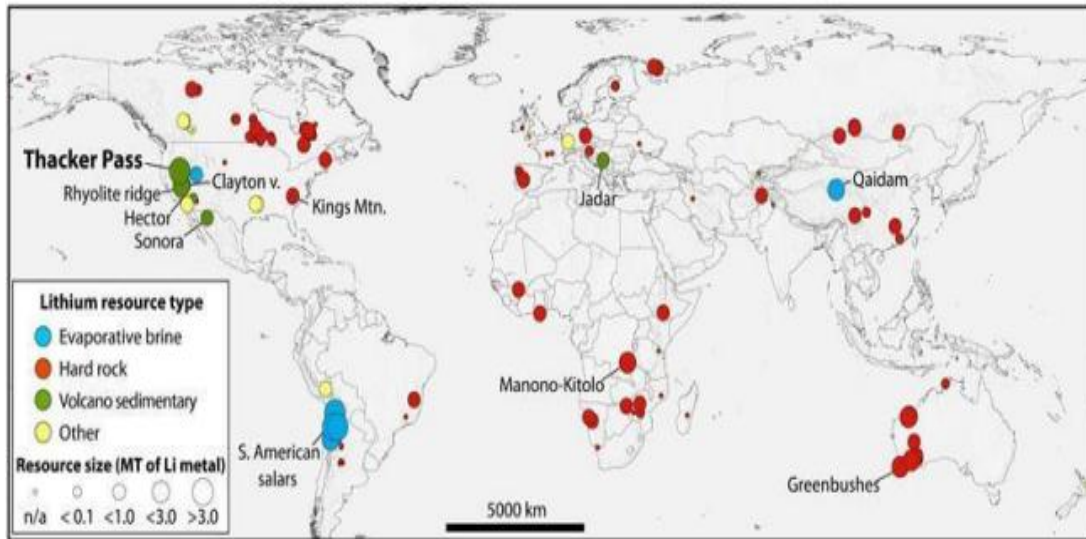


Figure 2.7: Map showing the types and relative sizes of global lithium resources (Current production is mainly derived from spodumene extracted from pegmatites in Australia (47%) and from brines beneath salt flats in Chile (30%), China (12%), and Argentina (5%)).

2.5 Lithium Reserves in Türkiye

No economically exploitable independent lithium source has yet been identified in Türkiye. Although the presence of lepidolite within pegmatites in the Yozgat-Sorgun region is known, studies conducted in this area have not yielded meaningful results. In research carried out in lakes, lithium content was generally found to be low, with

values not exceeding 40 ppm; only in Lake Tuz was 325 ppm lithium measured, but due to its high magnesium content (38,000 ppm), it was deemed limiting in terms of economic evaluation. On the other hand, studies conducted in boron deposits have identified lithium contents approaching 2000 ppm within clays. It has been observed that the Kırka and Bigadiç fields have higher lithium contents compared to Emet and Kestelek; additionally, it has been determined that as boron content increases, lithium decreases, and as particle size decreases, lithium content increases (Akgök and Şahiner, 2017).

Although no economically exploitable independent lithium source has yet been identified in Türkiye, research shows that certain amounts of lithium are present in boron deposits. It has been determined that lithium content increases as particle size decreases and is inversely proportional to boron content. In Türkiye, which possesses 73% of the world's boron reserves, these deposits are located in the regions of Eskişehir-Kırka, Kütahya-Emet, Balıkesir-Bigadiç, and Bursa-Kestelek. Due to the clay and carbonate minerals contained in boron ores, they can be enriched through washing and classification processes; however, approximately 50% waste is generated during the boron ore enrichment process. Some of this waste is stored on-site, while the rest is stored in dams, and it has been shown through research that they contain valuable elements such as lithium, rubidium, and cesium. It has been indicated that these elements are found particularly associated with clay minerals in Türkiye (Şensöz et al., 2021).

2.6 Lithium Production Processes

Lithium can be produced from primary sources such as ores (spodumene, lepidolite, petalite, and zinnwaldite) or brine sources (lake and seawater), as well as from secondary sources such as lithium-ion batteries. Lithium is recovered from ore concentrates obtained after physical beneficiation through hydrometallurgical and pyrometallurgical methods. From brine sources, lithium is recovered using methods such as extraction, precipitation, adsorption, and ion exchange (Celep et al., 2022).

The increasing demand for lithium has made production from both ores and alternative sources such as brine inevitable. The production process from ores, especially from lithium-bearing minerals like spodumene, includes roasting followed by leaching. In contrast, lithium recovery from brines involves steps such as evaporation,

precipitation, adsorption, and ion exchange. Lithium from recycled sources is recovered through leaching of lithium-ion batteries followed by precipitation, ion exchange, solvent extraction, or electrolysis. According to data in the literature, approximately 250 tons of spodumene ore or 750 tons of brine need to be processed to produce 1 ton of lithium. Alternatively, to obtain the same amount of lithium, approximately 28 tons of lithium-ion batteries from mobile phones and laptops or 256 electric vehicle batteries need to be recycled. Lithium can be obtained by leaching the concentrate obtained from the flotation of pegmatites with hot acid, followed by precipitation as lithium carbonate. Although this method is costly due to high temperature and energy consumption, the high lithium content of pegmatites partially offsets this cost. On the other hand, while brine sources offer lower production costs, some spodumene deposits have not yet been exploited due to this economic advantage. Seawater also contains lithium; however, its concentration is insufficient for economic production. Lithium metal can be obtained either by carbothermic or metallothermic reduction of lithium oxide or hydroxide, or by electrolysis of lithium chloride. In this context, comparatively evaluating the advantages and disadvantages of existing and emerging technologies is critically important for the efficient use of resources (Meshram et al., 2014).

2.6.1 Lithium production process from ores

The main techniques used in the beneficiation of lithium minerals are shown in the generalized flow diagram in Figure 2.8 and include gravity separation (DMS), magnetic separation, and froth flotation. In recent years, sorting has also been considered a potential method. Dense media separation is generally used to discard coarse ore waste, but it can also be used to produce lithium concentrates from high-grade ores. Flotation is used to process fine particle-sized feed and when high-grade concentrates are required. Magnetic separation is used to remove ore minerals with high iron content in order to make the concentrate suitable for use in ceramic and glass production (Tadesse et al., 2019).

It is a multi-stage process involving physical and chemical treatments of the ore. The spodumene mineral must be beneficiated due to the iron and other impurities it contains; however, minerals such as petalite, lepidolite, and amblygonite can be used directly. In this process, a high lithium content is economically important. In addition,

valuable elements such as tantalum, beryllium, and cesium can also be obtained as by-products from the ore; however, an excess of impurities may increase refining costs and render production inefficient (Akgök and Şahiner, 2017).

The simplified scheme of lithium extraction from hard rock pegmatites is presented in Figure 2.9. The production process can be summarized as follows:

1. The ore is reduced in size by crushing and grinding.
2. Lithium minerals are concentrated by the flotation method.
3. The enriched product is subjected to calcination and subsequently to hydrometallurgical processes (leaching) to extract lithium into solution.
4. The obtained solution is converted into lithium carbonate or lithium hydroxide as the final product, depending on the application (Akgök and Şahiner, 2017).

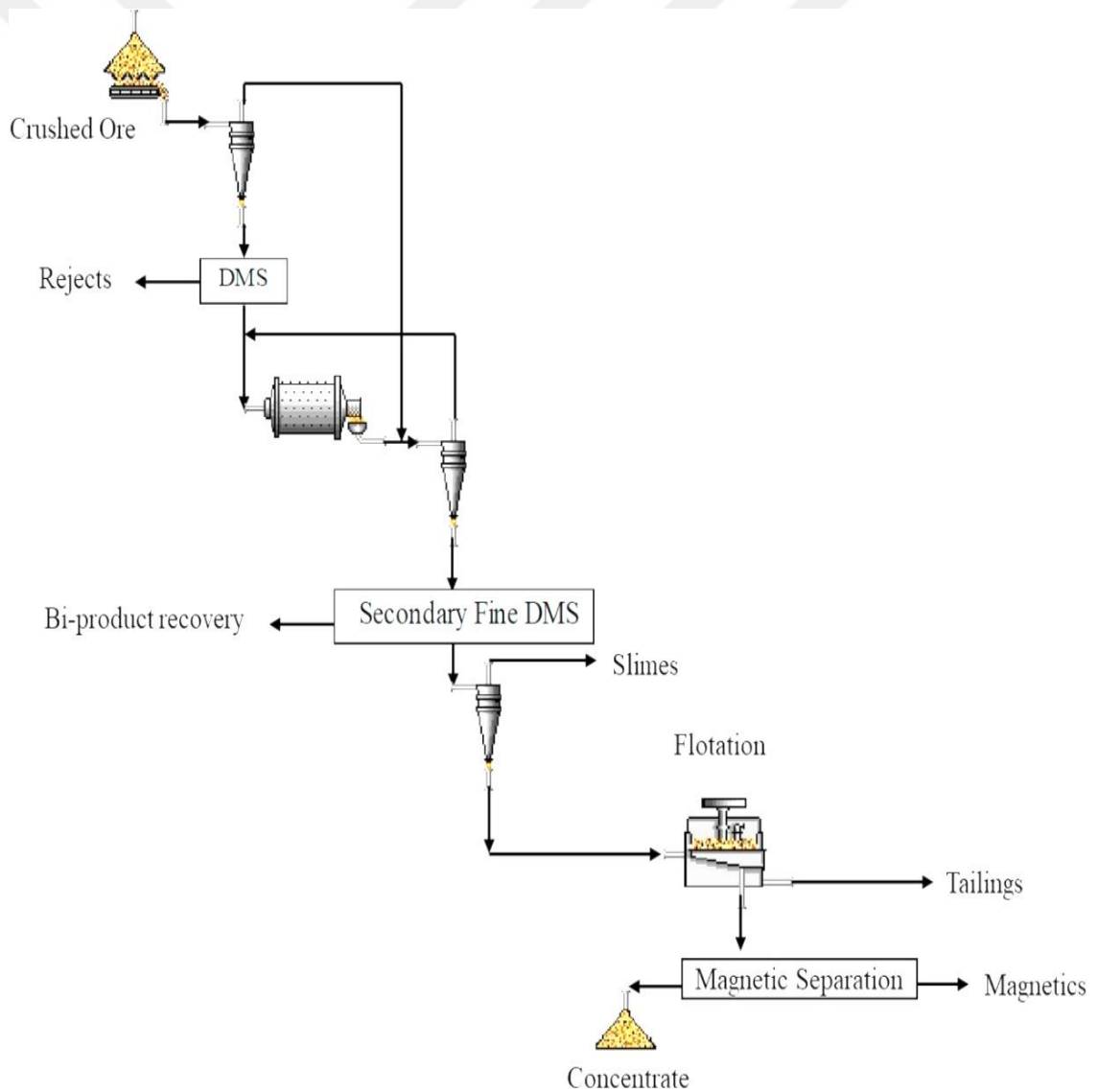


Figure 2.8: Generalized flow sheet for obtaining concentrate from lithium minerals in ores.

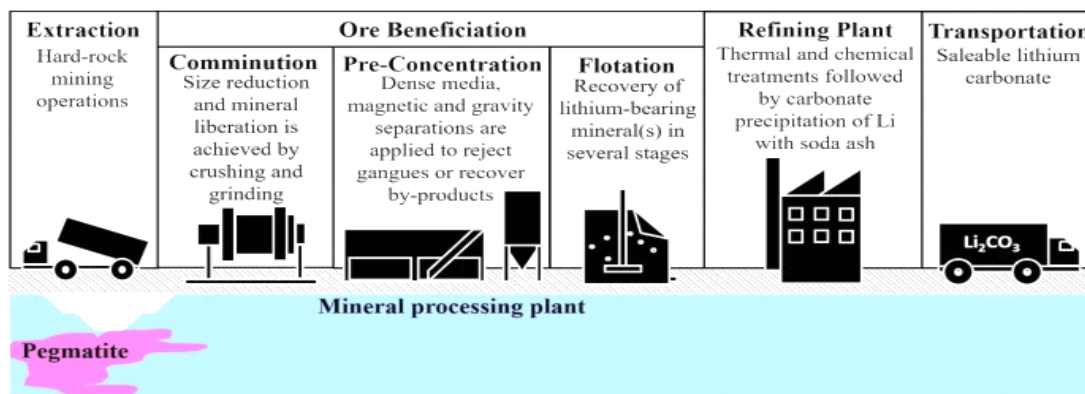


Figure 2.9: Simplified scheme of lithium extraction from hard rock pegmatites (Petrakis et al., 2025).

Although numerous lithium minerals are found in pegmatites, only a few of them possess commercial value and can be economically extracted. Among these are spodumene, which is the most concerning and important lithium-bearing mineral due to its high lithium content, as well as lepidolite and petalite. Other minerals with lower economic significance include amblygonite/montebrazite, zinnwaldite, and eucryptite (Petrakis et al., 2025). Lithium recovery from ores is carried out using various physical and physicochemical methods depending on the mineralogical characteristics. Methods such as optical sorting, gravity concentration (shaking table, spiral, and dense medium), magnetic separation, and flotation are applied for the separation of lithium-bearing minerals like spodumene from gangue minerals. In particular, the dense medium method is preferred for the separation of spodumene from minerals such as quartz and albite, while magnetic separation is used to remove iron-bearing gangue minerals. The concentrates obtained after beneficiation are generally subjected to calcination or roasting in a sulfuric acid medium to convert them into soluble lithium compounds. Minerals such as spodumene and petalite are converted into the β -form at 1000–1100 °C to prepare them for the leaching process. Some minerals, such as amblygonite, can be directly treated with appropriate reagents at lower temperatures. The resulting solution is neutralized with soda and lime to remove impurities and is then subjected to filtration. Finally, lithium carbonate is precipitated by adding sodium carbonate to the purified leach solution, or other lithium compounds such as LiCl or LiOH are obtained through electrodialysis (Celep et al., 2022). The sulfate process flow sheet for the recovery of Li from spodumene is presented in Figure 2.10(a), and the alkali process flow sheet for the recovery of Li from spodumene is presented in Figure 2.10(b) (Choubey, 2016).

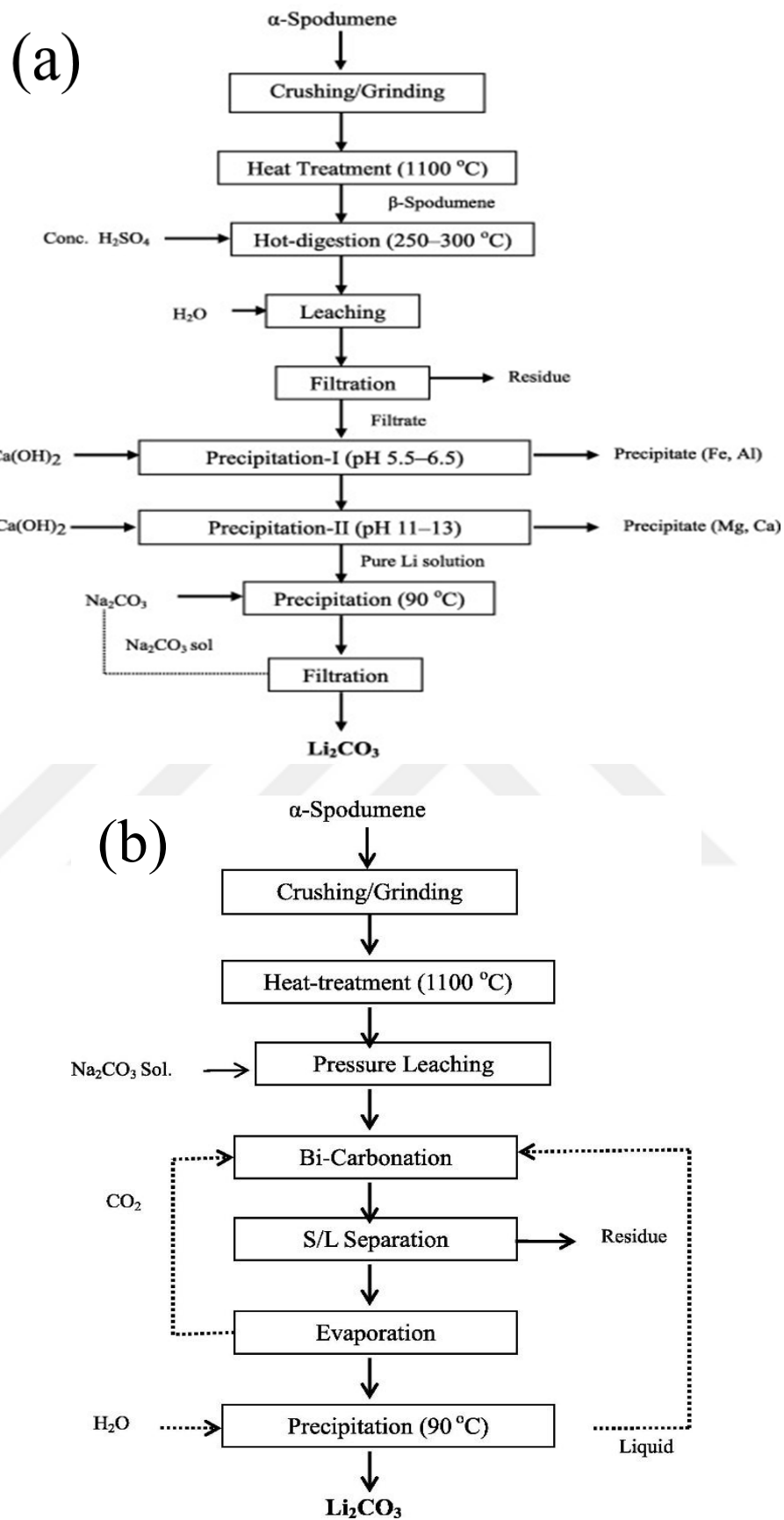


Figure 2.10: (a) Sulfate process flow sheet for lithium recovery from spodumene (b) Alkali process flow sheet for lithium recovery from spodumene.

2.6.2 Lithium production process from brines

Before the 1980s, lithium was mostly extracted from pegmatite ores; however, with the discovery of brine deposits, the focus shifted to lithium extraction from brines. This change enabled the development of new techniques, significantly reducing costs and making salt lake brines the main source of lithium carbonate, metallic lithium, and other lithium compounds (Yang et al., 2025). Efficient production requires hot, dry, and sunny climate conditions with low humidity and sufficient evaporation time. The economic viability of the reserve depends on lithium grade, magnesium/lithium and sulfate/lithium ratios, and the separability of impurities. Today, most of the production using this method takes place in Chile, Argentina, and China (Akgök and Şahiner, 2017). Lithium is extracted from brines using solar evaporation consisting of several stages in Figure 2.11 (Petrakis et al., 2025). Brines are pumped into large evaporation ponds for 18 to 24 months to achieve lithium concentration. Then, lithium is extracted using chemical solvents and reagents. Typically, a lithium production route from brines involves techniques such as precipitation, adsorption, and/or solvent extraction (Petrakis et al., 2025).

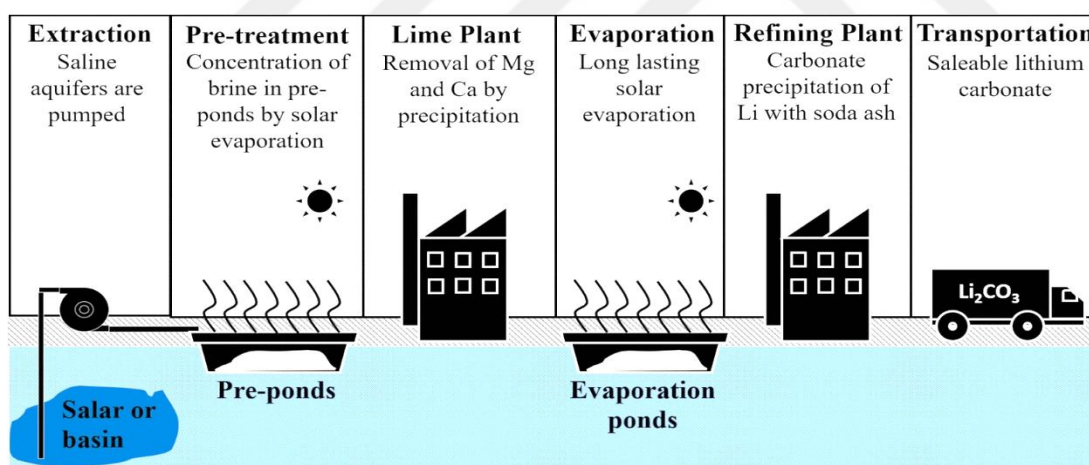


Figure 2.11: Simplified scheme of lithium extraction from brines.

Lithium-bearing brines are formed by the gradual dissolution of lithium-containing rocks and their accumulation in groundwater systems over time. The production process can be summarized as follows:

1. Drilling and Pumping: Subsurface lithium-bearing brine is extracted to the surface.
2. Evaporation Ponds: The brine is transferred to large evaporation ponds.

3. Natural Evaporation: Through solar radiation and climatic conditions, water evaporates and lithium in the solution becomes concentrated.
4. Concentrate Formation: Lithium is typically concentrated up to 1–2%.
5. Chemical Purification: The concentrated solution undergoes chemical treatment to be converted into lithium carbonate or lithium hydroxide (Akgök and Şahiner, 2017).

The presence of elements such as sodium, potassium, and especially magnesium in brine sources complicates the lithium recovery process. These elements negatively affect evaporation rate and lithium chloride formation, thereby reducing lithium yield, purity, and separation efficiency. Particularly, it is recommended that the magnesium/lithium ratio be below 6. Therefore, efficient separation of lithium from such complex solutions requires high precision and suitable process conditions (Arslan, 2022).

Lithium production from brine sources is widely preferred due to its low cost. Since the lithium concentration in these sources is generally very low (0.15–50 ppm), pre-concentration processes are required before production. This process typically begins with a series of evaporation steps, during which other salts such as NaCl and KCl are precipitated, resulting in a solution containing approximately 6–7% lithium. However, lithium carnallite ($\text{LiCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$), which forms during this process, may adversely affect product purity. To obtain high-purity products, impurities such as Mg, Ca, Fe, Al, and B in the solution must be removed. For this purpose, methods such as precipitation, solvent extraction, ion exchange, and adsorption are used. In particular, magnesium is removed by converting it to $\text{Mg}(\text{OH})_2$ using $\text{Ca}(\text{OH})_2$ or dolomite; however, the precipitate formed has a fine and non-crystalline structure, making filtration difficult. Furthermore, the presence of boron (100–700 ppm) may cause problems especially during the electrodialysis stage, and is therefore removed using solvent mixtures of iso-octyl alcohol and kerosene. In the final stage, lithium carbonate (Li_2CO_3) and lithium chloride (LiCl) with a purity of 99.5–99.99% are obtained. For products with higher purity, Li_2CO_3 is redissolved and purified by ion exchange. Similarly, LiCl can be dissolved in isopropanol and recovered with 99.9% purity through distillation and ion exchange processes. Through these processes, high-purity lithium products can be obtained from brine sources (Celep et al., 2022). A generalized process flow sheet for lithium recovery from brine is presented in Figure 2.12 (Choubey et al., 2016).

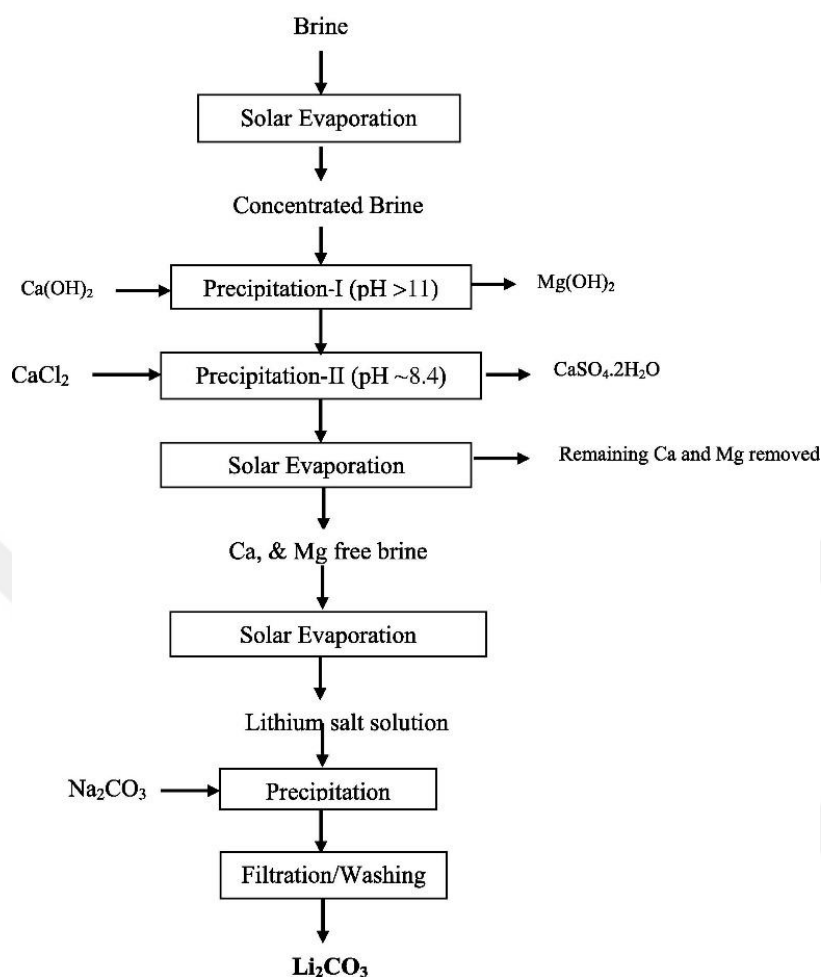


Figure 2.12: Generalized process flow sheet for Li recovery from brine.

2.6.3 Lithium recovery from secondary sources

The methods used for lithium recovery from lithium-ion batteries include pyrometallurgy, hydrometallurgy, biometallurgy, mechanochemical processes, chemical extraction, and membrane technologies. Pyrometallurgical methods are advantageous due to the lack of need for pretreatment and the simplicity of the process; however, they carry environmental and economic disadvantages such as high temperature requirements, lithium loss, and hazardous gas emissions. Hydrometallurgical processes stand out due to their high metal recovery rates and applicability with environmentally friendly reagents; however, the acids used may pose environmental risks. Biometallurgy is prominent for its low cost and eco-friendliness, but the long duration of the process and the difficulty of managing microorganisms are limiting factors. Mechanochemical methods offer high recovery

efficiency with lower energy consumption, yet data regarding their industrial-scale applicability are limited. Chemical extraction techniques, particularly those using halogenated oxidants, can enable fast and high-purity lithium recovery; however, these methods require complex reaction conditions and the use of hazardous chemicals. Finally, membrane technologies are highlighted for their eco-friendly features such as low energy consumption, high selectivity, and zero waste production; nevertheless, technical challenges such as membrane stability, fouling, and industrial scalability remain. Despite their different advantages and limitations, all of these methods offer valuable approaches that can be used in various scenarios for sustainable and efficient lithium recovery (Butt et al., 2022).

2.7 Lithium-Bearing Clay Minerals, Their Structures and Properties

Today, lithium is mostly obtained from hard rocks and brine sources. However, lithium can also be found in clay and mica minerals such as smectite, kaolinite, mica, illite, and chlorite. Lithium extraction from clay is a relatively recent method and constitutes approximately 8% of existing lithium sources. Figure 2.17 presents a general overview of current lithium extraction sources by country (Graveland, 2024).

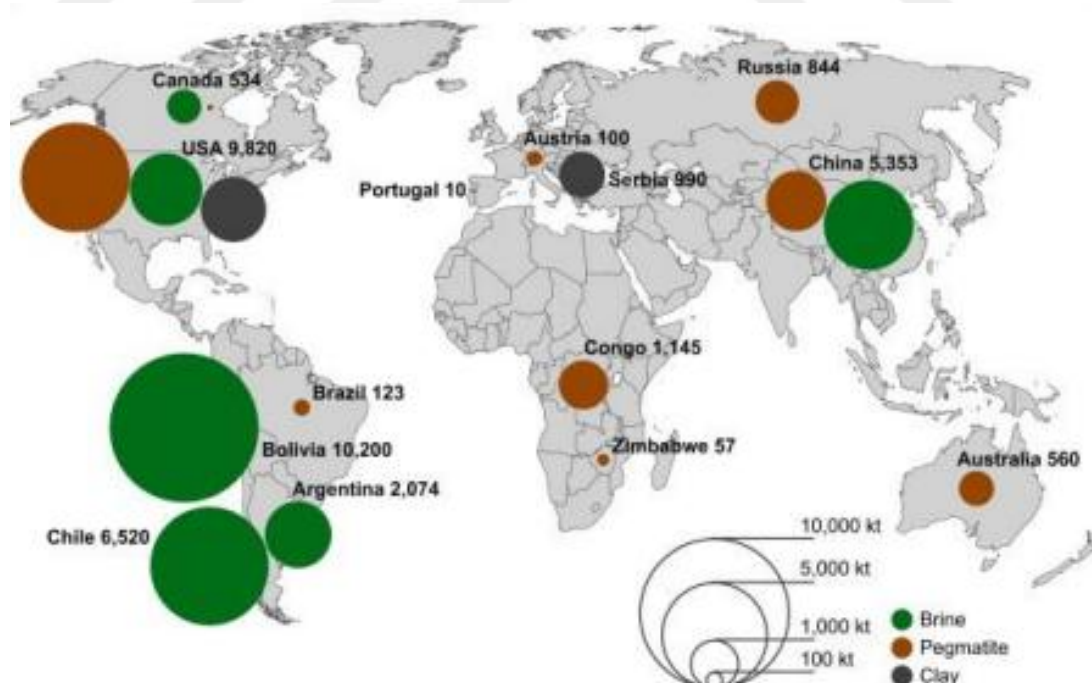


Figure 2.13: The distribution of lithium resources by country and deposit type (in thousand tons).

Naturally occurring lithium-bearing clay minerals primarily include lepidolite (polyolithionite, trilithionite), zinnwaldite, masutomilite, swinefordite, hectorite, cookeite, and jadarite. The Li_2O content of lepidolite ranges from 1.2% to 5.9%, while that of zinnwaldite is around 2–3%; these values are lower compared to spodumene, which contains approximately 5.8–8.1% Li_2O . Despite their low grades and complex mineralogical compositions, studies in the literature have demonstrated that these minerals present significant potential as alternative lithium sources. Currently, the identified reserves of lithium-bearing clay minerals constitute approximately 7% of global lithium resources. In particular, various lithium-containing clay deposits have been identified in specific regions of China and Europe. In this context, the recovery of lithium from these minerals may contribute to global lithium supply security and enable the geographical diversification of the market. Comprehensive investigation of these minerals and their integration into industrial processes is regarded as a key resource development strategy to meet the growing global demand (Zhao et al., 2023).

Lithium-bearing clay minerals have been identified as belonging to the phyllosilicate group, and their crystal structures are primarily of the 2:1 layer type, consisting of two tetrahedral sheets and one octahedral sheet (Figure 2.18a). These structures are classified as either dioctahedral or trioctahedral depending on the cation occupancy in the octahedral sheets. The combination of tetrahedral and octahedral sheets may, under certain conditions, result in a negatively charged structure. This negative charge arises due to (i) the substitution of Si^{4+} ions with Al^{3+} and Fe^{3+} ions in the tetrahedral regions, (ii) the substitution of Al^{3+} , Fe^{3+} , and Mg^{2+} ions with Li^{+} and similar cations in the octahedral regions, and (iii) the presence of structural vacancies. Such charge variability is one of the most characteristic features of 2:1 type phyllosilicates and enables the interlayer spaces of these structures to be filled with exchangeable cations. These negatively charged 2:1 layers are balanced by interlayer cations such as K^{+} , Na^{+} , Ca^{2+} , and Li^{+} , which facilitate interlayer bonding. These cations may also be replaced by Rb^{+} , Cs^{+} , and H_2O , thereby affecting the ion exchange capacity (Zhao et al., 2023).

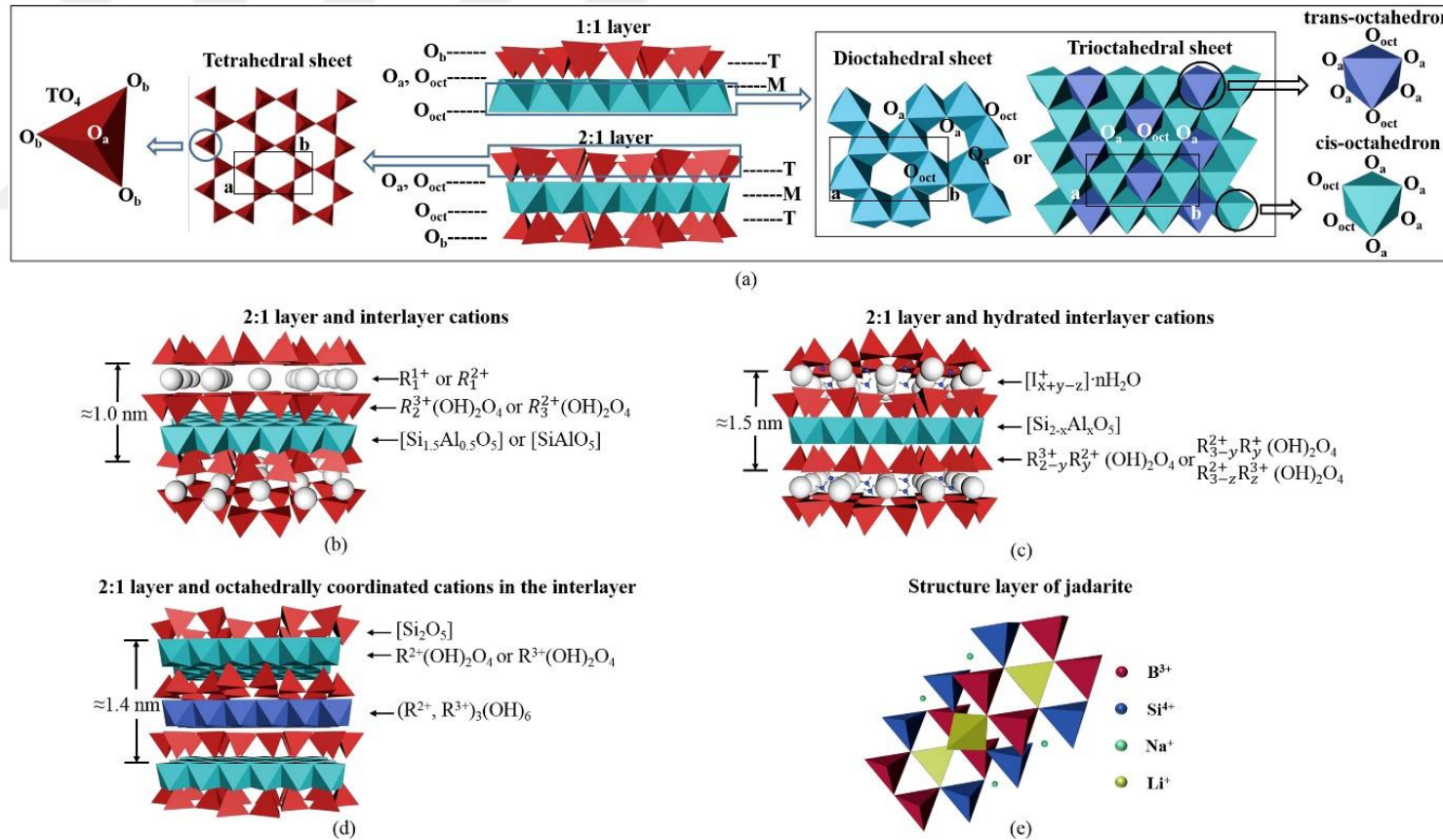


Figure 2.14: Schematic description of sheet layer in clays (a) Tetrahedron [TO₄]: This structure comprises tetrahedral, dioctahedral, and trioctahedral layers, as well as models of 1:1 and 2:1 layer structures. The orientations of cis- and trans-octahedra are indicated, where O_a and O_b refer to the apical and basal oxygen atoms, respectively. The parameters "a" and "b" denote the unit-cell dimensions, while M and T represent the octahedral and tetrahedral cations, respectively. Additionally, O_{oct} refers to the anions (OH, F, Cl) located in the octahedral sites. (b) structure layer of lepidolite, zinnwaldite, and masutomilite, (c) structure layer of swinefordite and hectorite, (d) structure layer of cookeite, (e) structure layer of jadarite.

Lepidolite, zinnwaldite, and masutomilite are trioctahedral mica minerals with a 2:1 structure. This structure consists of an octahedral cation sheet located between two tetrahedral sheets (Figure 2.18b). In mica minerals, cations such as K^+ , Na^+ , Al^{3+} , Fe^{3+} , Mg^{2+} , and Si^{4+} are situated in specific layers. Lepidolite belongs to the polyolithionite–trilithionite series, while zinnwaldite is classified among micas with high Fe content. Micas generally contain high levels of Li, Rb, and F, and moderate levels of Cs. Li-muscovite represents a dioctahedral mica solid solution series between trilithionite and muscovite with low lithium content (Figure 2.19).

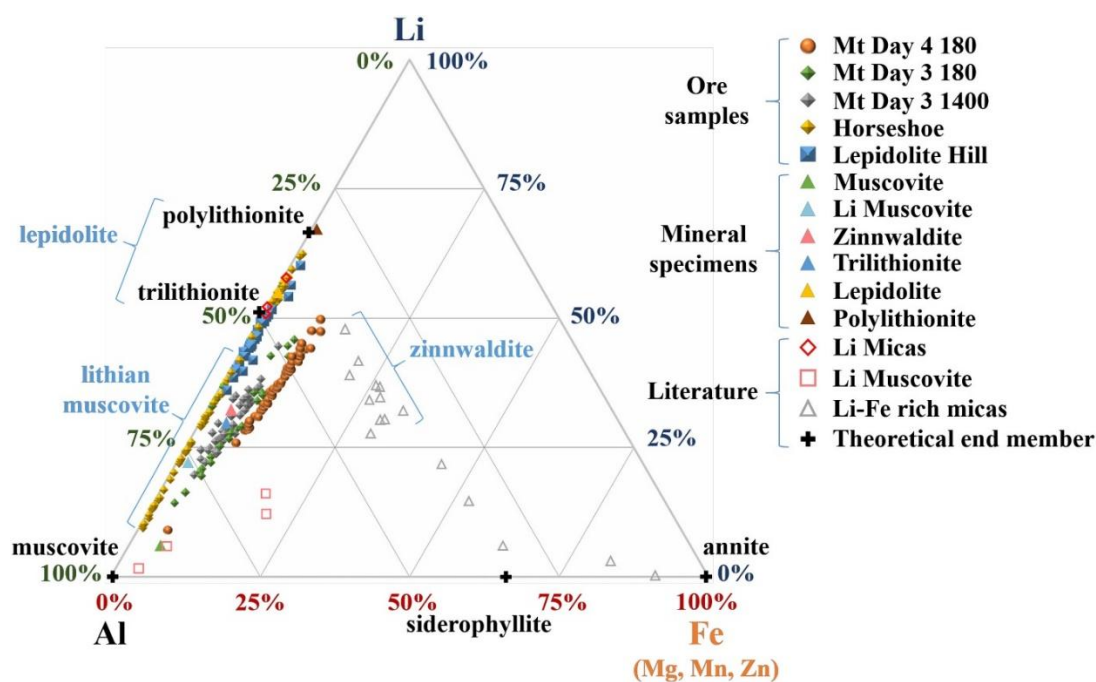


Figure 2.15: A comparison of reported lithium-bearing micas is presented in the Li-Al-Fe ternary diagram. The diagram displays data on mica minerals, ore samples, and some specific compositions reported in the literature. Theoretical end-member compositions are indicated in the diagram with cross marks.

Figure 2.18b illustrates the structure of mica group minerals such as lepidolite, zinnwaldite, and masutomilite, which possess a 2:1 layered silicate structure composed of an octahedral cation sheet located between two identical tetrahedral sheets. Figure 2.18c represents the structure of clay minerals belonging to the smectite–vermiculite (sv) group, such as swinefordite and hectorite; this structure is also 2:1 layered and contains water molecules and exchangeable cations between the layers, with lithium typically occupying octahedral positions. Figure 2.18d shows the structure of cookeite, a chlorite mineral with di-trioctahedral character; its structure consists of two

tetrahedral sheets with different compositions and charges, separated by a Li^+ -rich octahedral layer. Figure 2.18e illustrates the structure of the jadarite mineral, which is composed of a single planar layer formed by tetrahedrally coordinated Li, Si, and B atoms; Na^+ ions are located in octahedral positions between these layers (Zhao, Wang, and Cheng, 2023).

2.7.1 Clay-type lithium deposits

In the early 1970s, the United States succeeded in recovering approximately 75% of its lithium from ancient weathering crust clay rocks. Nowadays, clay deposits containing hectorite in the western United States represent a significant source of lithium. Among the globally recognized clay-type lithium deposits are the McDermitt and Thacker Pass deposits in Nevada, USA, the Sonora Basin in Mexico, and the Jadar lithium deposit in Serbia (Yin et al., 2024).

The primary minerals of the lithium-rich clays found in these deposits include hectorite, saponite, and steatite. In particular, the jadarite mineral discovered in Serbia's Jadar deposit stands out with its rare borosilicate structure containing both boron and lithium. Jadarite is considered one of the few unique minerals in the world that can simultaneously support the production of both boron and lithium. In this deposit, the Li_2O content can reach up to 7.3%, with an average grade of around 1.8%. According to current reserve estimates, there is a Li_2O resource of 2.06 million tonnes within approximately 114.6 million tonnes of ore. The discovery of this new mineral and the detailed investigation of the Jadar deposit have provided significant momentum for the exploration of sedimentary lithium deposits in Eastern Europe and on a global scale (Yin et al., 2024).

Jadarite is one of the new-generation lithium minerals belonging to the zeolite group and was discovered in 2007 exclusively in Serbia's Jadar Basin. It occurs in nodules within a carbonate-rich, fine-grained matrix in layers exceeding 7 m in thickness. The deposit is reported to contain over 125 million tonnes of inferred reserves with a Li_2O content of 1.8%. The mining rights to this site belong to Rio Tinto, and commercial production is planned to commence in 2025 (Szlugaj and Radwanek-Bak, 2022).

Hectorite, discovered in the town of Hector in California, USA, is also mined on a small scale in the Kings Valley deposit of the McDermitt caldera located on the Nevada-Oregon border. In this region, there are 7 million tonnes of measured reserves

containing 0.457% Li, 8 million tonnes of indicated reserves containing 0.435% Li, and 7 million tonnes of inferred reserves containing 0.416% Li. While hectorite and bentonite have traditionally been used primarily in the production of drilling muds for the petroleum industry, in recent years they have gained significance as lithium sources. Additionally, the Sonoran Desert in northern Mexico and the Bigadiç borate deposit in Türkiye also contain noteworthy hectorite reserves (Yin et al., 2024).

Clay-type lithium deposits have been identified particularly in the United States since the 1970s and have been studied in various regions, notably the McDermitt Caldera. In the international literature, different terms have been used to classify these deposits; however, due to terminological ambiguities, some researchers have referred to all clay-bearing deposits as "sedimentary type." The authors of this study emphasize that clay-type deposits should be subdivided into three subtypes (Zheng et al., 2023).

One classification method divides clay-type lithium resources into three types: volcanic type, carbonate type, and jadarite type.

- Volcanic clay-type lithium resources are primarily concentrated in regions such as Kings Valley, Sonora, and Hector, and are generally formed through the alteration of tuffs resulting from volcanic eruptions. In this process, lithium contained in the ash released after volcanic eruptions is leached by brine and hydrothermal solutions and gradually becomes enriched within clay minerals present in crater lake sediments. In this way, volcanic-origin clay-type lithium deposits are formed. The main lithium-bearing minerals in these types of resources are illite and smectite, in which lithium is directly bound to the crystal lattice structure. Volcanic clay-type lithium resources are also characterized by their high SiO₂ (>50%) and Mg (>10%) content.
- Carbonate-type lithium resources, on the other hand, are formed through the weathering and sedimentation of carbonate rocks. During this process, carbonate rocks undergo alteration into clay minerals, within which lithium becomes enriched, forming clay-type lithium deposits. The main lithium-bearing minerals in these types of deposits are clay minerals such as montmorillonite, diasporite, and kaolinite. Lithium is found adsorbed between the layers of these mineral structures. Unlike volcanic-origin sources, the main

components of carbonate-type lithium deposits are SiO_2 and Al_2O_3 , and they contain significantly lower levels of Mg.

- Jadarite-type lithium resources are primarily composed of the mineral jadarite. Jadarite is a rare mineral that contains both lithium and boron, with the chemical formula $\text{LiNaSiB}_5\text{O}_7(\text{OH})$. This mineral contains 7.3% Li_2O and 47.2% B_2O_3 . Similar to volcanic and carbonate-type lithium deposits, jadarite also has a high SiO_2 content and contains a significant amount of Na. However, the Mg content in jadarite is negligible, which provides a significant advantage during the lithium separation process (Xie et al., 2024)

2.7.2 Leaching of lithium-bearing clays

The main methods used for extracting lithium from clay-based lithium resources include direct leaching, additive roasting–water leaching, and roasting–ion exchange leaching. All reported studies have been conducted at the laboratory scale.

2.7.2.1 Direct leaching method

The direct leaching method aims to dissolve lithium directly from the ore using leaching reagents such as water or acid, without any prior roasting or mechanical activation treatment. The schematic flow of this method is presented in Figure 2.20. However, in applications using only water, even under high temperature (200 °C) and high pressure (1.55 MPa) conditions, the lithium dissolution rate remains below 1%, indicating that water is an ineffective solvent. In contrast, direct leaching using acidic solutions significantly increases lithium extraction efficiency. For example, in clay-type ores containing approximately 0.36% Li_2O , lithium dissolution efficiencies up to 89% can be achieved using sulfuric acid. In bentonite-type clay samples with higher lithium content (1.2% Li_2O), lithium dissolution efficiency can reach 90% when the particle size is reduced to 40 μm , the liquid-to-solid ratio is adjusted to 5 mL/g, sulfuric acid concentration is set at 7 mol/L, leaching temperature is increased to 250 °C, and the process is carried out for 90 min. In addition, in complex bauxite ore wastes containing minerals such as kaolinite, boehmite, diaspore, illite, and anatase, lithium dissolution efficiency can reach up to 96.35% under conditions of mixed acid use with 60% acid concentration, a 4 mL/g liquid-to-solid ratio, a leaching temperature of 100 °C, and a duration of 3 hours (Xie et al., 2024).

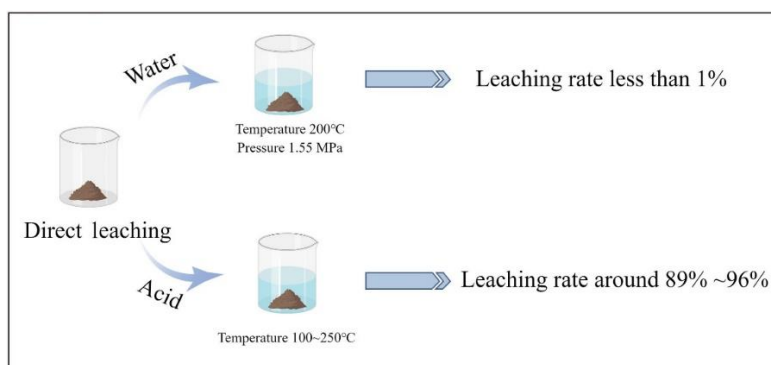


Figure 2.16: Schematic diagram of the direct leaching method.

2.7.2.2 Leaching method after additive roasting

The additive roasting–water leaching method is based on the high-temperature roasting of the ore sample with the addition of specific additives (carbonates, sulfates, chlorides, limestone, gypsum, etc.), followed by the dissolution of lithium using water (Figure 2.21). The additives used in this method may be naturally occurring minerals or industrial by-products. In the studies conducted, roasting was generally carried out at temperatures between 900–1000 °C, followed by water leaching with specific solid-to-liquid ratios. As a result of these studies, lithium dissolution efficiency was observed to exceed 80%. In particular, for montmorillonite-type clays, carbonate-, sulfate-, and chloride-based additives were found to be effective; combinations of limestone and gypsum, as well as selective chlorination processes, were identified as among the most efficient methods for lithium extraction. Additionally, mixed additive systems were observed to provide higher leaching efficiency compared to single-additive systems. However, the requirement for multiple additives in this method leads to an increase in post-process impurities, thereby increasing the complexity and cost of separation and purification processes (Xie et al., 2024).

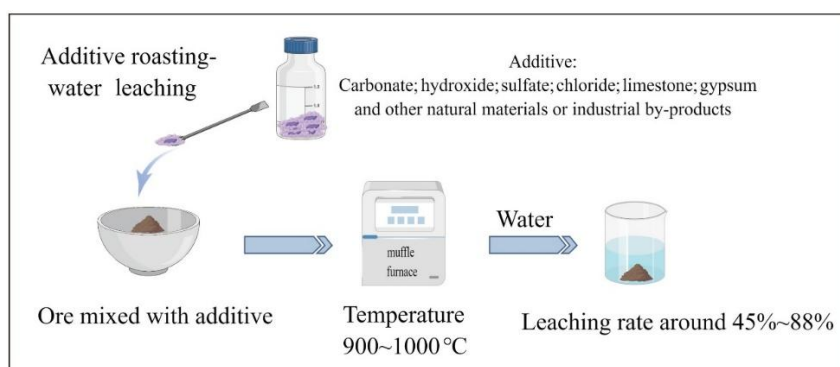


Figure 2.17: Schematic diagram of the additive roasting–water leaching method.

2.7.2.3 Roasting–ion exchange leaching method

The roasting–ion exchange leaching method is based on the roasting of the ore sample followed by the dissolution of lithium through the exchange of Li^+ ions with other metal ions in a salt solution or with H^+ ions in an acid solution (Figure 2.22). This method is more suitable for carbonate-type lithium resources, where lithium is adsorbed between the layers of mineral structures, as it facilitates the easier displacement of lithium (Xie et al., 2024).

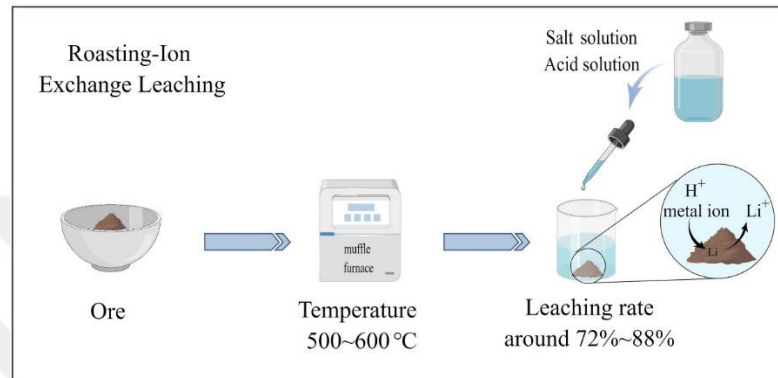
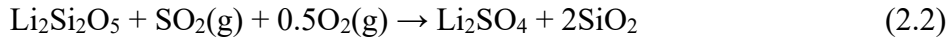


Figure 2.18: Schematic diagram of the roasting–ion exchange leaching method.

Most studies focus on the extraction of lithium from pegmatites containing spodumene, lepidolite, petalite, amblygonite, or zinnwaldite through acidic and alkaline chemical processes. However, the extraction of lithium from lithium-bearing smectites has received comparatively less attention. For montmorillonite-type clays (0.6% Li), a process involving roasting above 900°C with the addition of limestone and gypsum has been applied, converting the lithium in the clay into water-soluble lithium sulfate (solubility: 34.2 g/100 g H_2O at 25°C) (Eqs. 2.1 and 2.2), followed by leaching of the calcined residue with water. To increase lithium concentration, the leach solution was evaporated, and lithium was recovered as Li_2CO_3 (99% purity) by the addition of Na_2CO_3 , achieving a recovery efficiency of 80%. In addition, the effects of various parameters, including the dosages of gypsum and limestone, roasting duration, and temperature, have been demonstrated. In this context, the addition of gypsum and limestone was shown to enhance lithium extraction, with the optimum clay:limestone:gypsum ratio being 5:3:3. Increasing the temperature from 750°C to 1000°C improved lithium extraction; however, temperatures above 1000°C had an adverse effect. In a similar study, various process alternatives such as direct acid and water leaching, pressure leaching, acid curing prior to water leaching, and roasting with carbonates and chlorides were tested. These studies found that high lithium

recoveries could be achieved in acid-based tests, albeit at the expense of high acid consumption and extensive dissolution of impurities such as aluminum and iron. These researchers identified selective chlorination and especially sulfation roasting in the presence of gypsum and limestone as the most promising approaches for the effective extraction of lithium from montmorillonite-type clays.



In boron ore processing plants in Türkiye, significant quantities of smectite-type clay wastes containing lithium have accumulated over the years. These wastes offer noteworthy resource potential for lithium recovery. In this context, various leaching methods have been evaluated on a clay sample obtained from the Kırka region, containing 0.56% Li₂O (main phases: dolomite, montmorillonite, hectorite). Lithium extraction by water leaching remained quite limited (2.4%); however, in acid leaching conducted under conditions of 80 °C temperature, 10% solid content, -500 µm particle size, and 160 g/L H₂SO₄ concentration, lithium was dissolved at a rate of 99%. Nevertheless, the selectivity of this method was low, with iron, magnesium, and calcium also dissolving at rates of 43.0%, 58.1%, and 35.0%, respectively. Water leaching applied after roasting with gypsum (approximately 17%) at 900 °C for 2 hours achieved a lithium extraction efficiency of 77%. In studies conducted on clay samples obtained from the Bigadiç region, parameters such as the gypsum/waste ratio, limestone/waste ratio, roasting temperature, and duration were optimized, and under the most favorable conditions, a lithium dissolution efficiency of 88% was obtained. These studies generally indicate that for lithium recovery from clay wastes generated by boron processing plants in Türkiye, the gypsum-assisted roasting–water leaching method, employing gypsum as a sulfation agent, represents a viable approach (Obut et al., 2022).

2.8 Tesla Process

Tesla’s U.S. patent application is titled “Selective Extraction of Lithium from Clay Minerals.” This patent, developed by Tesla, Inc. and published under US 2021/0207243 A1, presents an innovative method for the selective extraction of lithium from clay minerals. The patent describes a new process developed to obtain

lithium efficiently and selectively from clay minerals. Unlike conventional acid leaching methods, this process is based on ion exchange carried out by high-energy milling (e.g., using a ball mill, planetary ball mill, or vibratory mill) and the use of appropriate cation sources (e.g., NaCl, MgCl₂, CaCl₂). The process involves the preparation of a mixture of the clay mineral and the cation source, subjecting this mixture to high-energy milling, and subsequently applying liquid leaching to obtain a lithium-rich leach solution. This method reduces high acid consumption, limits the dissolution of impurities (especially Al, Fe, Ca, and Mg) into the solution, and can increase lithium extraction efficiency to over 50%. Moreover, the process can operate within a temperature range of 20–100 °C and a pH range of 5–10, facilitating the selective separation of other elements in addition to lithium. This innovative technology aims to reduce both the production cost and environmental impact of lithium-ion battery manufacturing. The process described in the patent consists of three main stages: first, a lithium-containing clay mineral and an appropriate cation source are provided. In the second stage, the clay mineral and the cation source are co-ground in a high-energy mill. This mechanical activation stage disrupts the crystal structure of the clay mineral, making it easier to release lithium ions. In the final stage, a liquid leaching process is applied to obtain a lithium-rich leach solution. This method enables more efficient lithium separation and reduces the environmental impact compared to conventional acid leaching methods. The patent carries significant potential, especially for the processing of hectorite and similar clay minerals. Furthermore, the high-energy grinding and liquid leaching conditions used in the process (high grinding energy, suitable pH and temperature ranges) aim to maximize lithium recovery efficiency (Sun et al., 2021).

1. A method for extracting lithium from a lithium-containing clay mineral involves;
 - Providing a lithium-containing clay mineral,
 - Grinding the clay in a high-energy mill,
 - Forming a mixture by combining the clay mineral with a cation source either before or after grinding; wherein the cation source comprises a cation and an anion,

- Contacting the mixture of ground clay material and cation source with a solvent to extract lithium from the clay material and to produce a lithium-rich leach solution.
2. The cation source is mixed with the clay mineral prior to the high-energy milling process.
 3. The cation source is mixed with the clay mineral simultaneously during the high-energy milling process.
 4. The cation source is mixed with the clay mineral after the high-energy milling process.
 5. The clay mineral contains approximately 0.1–5 g Li/kg of clay.
 6. The clay material further comprises one or more of spodumene, lepidolite, zinnwaldite, smectite, hectorite, muscovite, or combinations thereof.
 7. The clay mineral also contains one or more of the elements sodium, potassium, iron, aluminum, calcium, magnesium, silicon, chromium, or combinations thereof.
 8. The cation in the cation source is selected from alkali metals, alkaline earth metals, or combinations thereof.
 9. The anion in the cation source is selected from halogens, SO_4 , NO_3^- , or combinations thereof.
 10. The cation source is selected from NaCl , KCl , Na_2SO_4 , K_2SO_4 , MgSO_4 , CaSO_4 , NaNO_3 , KNO_3 , CaCl_2 , MgCl_2 , $\text{Ca}(\text{NO}_3)_2$, $\text{Mg}(\text{NO}_3)_2$, or combinations thereof.
 11. The weight ratio of the cation source to the clay mineral is approximately between 1:3 and 1:50.
 12. The molar ratio of the cation to lithium in the cation source is approximately between 1:1 and 10:1.
 13. The high-energy milling process is performed using one or a combination of a planetary ball mill, Spex mill, attritor mill, high shear energy mill, vibratory mill.
 14. The clay mineral may also be pulverized prior to the high-energy milling process.
 15. The liquid leaching process is performed at approximately 20–100 °C.
 16. The weight ratio of the mixture to the solvent is approximately between 1:10 and 3:10.
 17. The lithium-rich leach solution contains at least 100 ppm lithium.

18. The lithium extraction efficiency of the lithium-rich leach solution is at least 50% relative to the clay mineral.
19. The pH of the lithium-rich leach solution is approximately between 5 and 10.
20. A mixing solvent may be provided to the clay mineral, cation source, and/or high-energy mill.
21. A lithium-rich leach composition;
22. A spent clay mineral containing no more than 5 g Li/kg clay,
23. And a lithium-rich leach solution comprising:
 - Water,
 - At least 100 ppm lithium,
 - No more than 10 ppm aluminum,
 - No more than 10 ppm iron,
 - No more than 8000 ppm potassium,
 - No more than 3000 ppm calcium,
 - No more than 3000 ppm magnesium,
 - And a pH of approximately 5–10 (Sun et al., 2021)

2.9 Mechanical Activation

Historically, mechanical activation dates back to the Stone Age, when it was first applied using simple tools such as mortars and pestles. With the Industrial Revolution, particularly after 1850, the development of steam-powered machines marked a significant turning point in mechanical activation processes. During this period, energy efficiency increased, and ball mills and cylindrical mills became widely used. Between 1900 and 1920, vertical roller mills were developed, and by the mid-20th century, autogenous and semi-autogenous mills were introduced into industrial applications. Around 1930, the invention of the first attrition mill, described as a vertical stirred media mill, represented a major technological advancement. Another critical development in the field of mechanical activation occurred in the 1990s with the introduction of high-speed stirred media mills. Today, mechanical activation and mechanical alloying are among the prominent technologies for producing high-value-added particulate products; particularly due to the absence of solvent use, these techniques have gained importance as environmentally sustainable synthesis methods within the scope of green chemistry (Mucsi, 2019).

Ostwald was the first scientist to use the term "mechanochemistry" by examining the relationship between chemical and mechanical energy, and he considered this field as a branch of physical chemistry alongside thermochemistry and electrochemistry. Since the 1920s, developments have been made in mechanochemistry, emphasizing that mechanical disintegration is based on physicochemical principles. The idea that mechanical effects can lead to chemical reactions dates back to prehistoric times, illustrated by examples such as generating fire through friction. Mechanical activation is a method that reveals defects in the crystal structures of materials by reducing their particle size, thereby decreasing the temperature and duration required for chemical reactions. High-energy milling increases the reactivity of materials, lowers activation energy, and accelerates the dissolution of valuable metals. When used as a pretreatment before leaching, it reduces energy consumption and waste emissions. Due to its ability to lower reaction temperature, increase dissolution rate, facilitate water solubility, and allow the use of lower-cost reactors, it is considered a significant method in metallurgical processes (Yılmaz and Yıldız, 2023).

Mechanical activation is a process that enhances the reactivity of a solid without altering its chemical composition; if the composition or structure changes during the process, it is referred to as a mechanochemical reaction. In this context, mechanical activation increases the reaction rate but does not alter the reaction mechanism (i.e., the reaction pathway or sequence). The behavior of a solid subjected to mechanical energy results from three simultaneous effects: structural disorder (increase in defects and dislocations), structural relaxation (relief of internal stresses), and structural variability (gradual changes in stability and properties over time). As a result, mechanical activation enhances reactivity through these permanent changes in the solid structure (Apaydın, 2010).

Current lithium recovery methods, namely ore mining and brine extraction, pose serious environmental and social problems. Ore mining leads to ecosystem destruction, water pollution, and high costs, whereas brine extraction, although less expensive, causes water scarcity in arid regions, contaminates groundwater, and creates tension between local communities and companies. Both methods are far from sustainable and can harm both nature and society. Therefore, in a time when lithium demand is rapidly increasing, it is of great importance to develop more

environmentally friendly, efficient, and socially just recovery methods (Jose et al., 2024).

The mechanical activation process is considered an environmentally friendly alternative compared to conventional technologies. Its main advantages include the simplicity of the method, its compatibility with environmentally safe solvents, and its applicability under metastable conditions. The grinding process reduces particle size and increases specific surface area. However, prolonged grinding can lead to agglomeration between particles. As a result of excessive grinding, structural degradation, partial dehydroxylation, and complete amorphization of the kaolinite phase may occur (Göktaş, 2023).

The main parameters affecting the grinding process in mechanical activation are as follows:

- The type of mill used,
- The type of grinding medium (e.g., rods, balls, etc.),
- The material of the grinding elements (steel, tungsten, alumina, etc.),
- The grinding atmosphere (air, inert gases, or reducing environment),
- The grinding method (dry or wet grinding),
- The size ratio between the balls and the material,
- The weight ratio between the balls and the material,
- The grinding temperature,
- The rotational speed of the mill,
- The total grinding duration (Korkut, 2022).

Mechanical activation is a widely applied process developed to control or reduce the particle size of materials and involves high-energy density grinding methods; thus, the selection of the grinding device is critically important depending on the properties of the material and the targeted application. Planetary mills, although superior in terms of energy efficiency and bulk energy density, generally operate in batch mode due to the absence of continuous feeding systems. The occurrence of chemical reactions during grinding is defined as mechanochemistry, and in this process, the mill is considered as a reactor. Mechanical activation increases the free energy by inducing structural changes such as increased surface area, amorphization, phase transitions, and reduction of crystallite size; this increase in free energy enables energy release

through amorphization, defect formation, agglomeration, and polymorphic transformations. Thus, it becomes possible to reduce both the reaction temperature and duration (Yılmaz, 2022).

2.9.1 Theories and models in mechanochemistry

Mechanochemistry was first introduced by Ostwald in 1887 and defined as a sub-branch of physical chemistry. After this definition, studies in the field increased, particularly after the 1920s, and in 1928, Pierce defined mechanochemistry as the science of mechanical disintegration. Various theories have been developed in the field of mechanochemistry:

- Hot-Spot Theory
- Magma-Plasma Model
- Spherical Model
- Dislocation and Phonon Theory
- Theory of Short-Live Active Centers
- Kinetic Model
- Impulse Model
- Theory of the Energy Balance
- Analogy Model

The most widely accepted model in mechanochemistry, the Magma–Plasma Model, was proposed by Thiessen and his colleagues in 1967 (Figure 2.23).

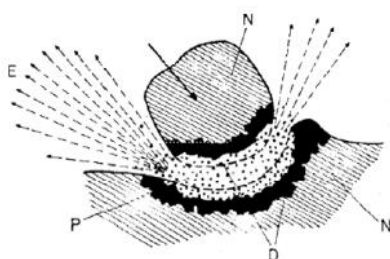


Figure 2.19: Magma–Plasma model (E – exo-electrons, N – undeformed solid, P – plasma, D – highly deformed surface layer).

This model suggests that a significant amount of energy is released at the contact points of colliding particles. The energy released leads to the formation of a special plasma state in the solid material. This plasma state is characterized by the emission of highly excited particles (electrons and photons) within very short time intervals. Due to

irregularities on the contact surfaces, local temperatures can exceed 10,000 K. Thiessen distinguished between reactions occurring within the plasma medium and those occurring on the surfaces of particles that are highly excited within the plasma. This approach is significant in that it demonstrates that mechanically activated reactions are not governed by a single mechanism, but rather that multiple mechanisms may act simultaneously (Apaydin, 2010).

2.9.2 Thermodynamics in mechanochemistry

Chemical reactions occurring between solid materials are defined by the change in Gibbs free energy (ΔG), and the direction of a reaction depends on the sign of ΔG . If ΔG is negative, the reaction proceeds in the forward direction; if positive, it proceeds in the reverse direction; and at equilibrium, ΔG equals zero. According to the equation $\Delta G = \Delta H - T\Delta S$, since solids with ordered crystal structures have limited entropy contribution, ΔG is generally determined by the enthalpy change. In reactions, the activities of solids are typically assumed to be close to unity, and under these conditions, the standard free energy change (ΔG^0) is sufficient to determine the tendency of the reaction. Figure 2.24 illustrates the types and densities of defects formed through mechanical activation. These structural defects are among the primary factors that increase the total Gibbs energy of the system. In particular, for ionic crystals, surface energy is estimated to account for approximately 10% of the total Gibbs energy. In this context, the microstructural changes resulting from mechanical activation lead to the solid becoming thermodynamically unstable but chemically more reactive. This indicates that the evaluation of active solids must consider not only thermodynamic parameters but also structural characteristics (Baláz, 2008).

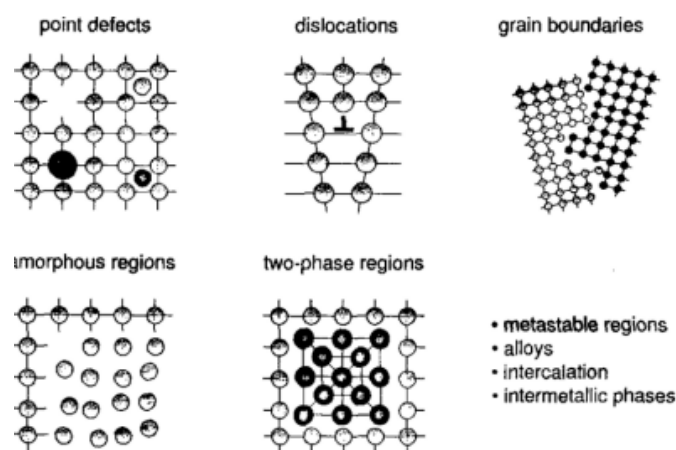


Figure 2.20: Structural imperfections induced by the mechanical activation of solids.

2.9.3 High-energy milling

Particle size reduction is a critical step in many technological operations and is defined as the mechanical separation of solids into smaller particles without agglomeration. This process aims not only to control particle size and shape but also to increase surface area and create defects on the surface for subsequent chemical reactions. Grinding not only increases the surface area but also enables the formation of highly active regions. Size reduction is an energy-intensive process; approximately 5% of the electricity produced globally is consumed for this purpose. Fine grinding refers to particle sizes below 100 μm , whereas ultra-fine grinding refers to sizes below 10 μm . In mechanochemistry, high-energy grinding refers to the characteristics of the grinding equipment (mill) used. During energy transfer, as illustrated in Figure 2.25, stress types such as compression, abrasion, impact, and collision are applied (Apaydın, 2010).

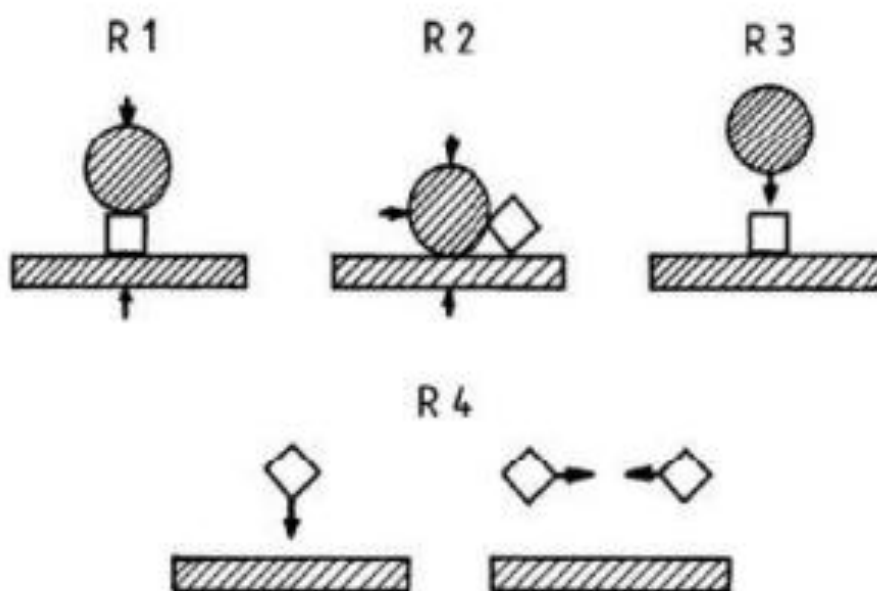


Figure 2.21: Main stress types observed in mills are as follows: R1 – compression, R2 – shear (attrition), R3 – impact (stroke), and R4 – impact (collision). The shaded area represents the mill wall, the square symbol indicates the mass of the material charge, and the spherical symbol indicates the mass of the milling media.

The multi-stage nature of mechanical activation necessitates the use of high-energy mills with different operating principles. The working principles of the most commonly used mills in high-energy grinding are illustrated in Figure 2.26 (Baláž, 2008).

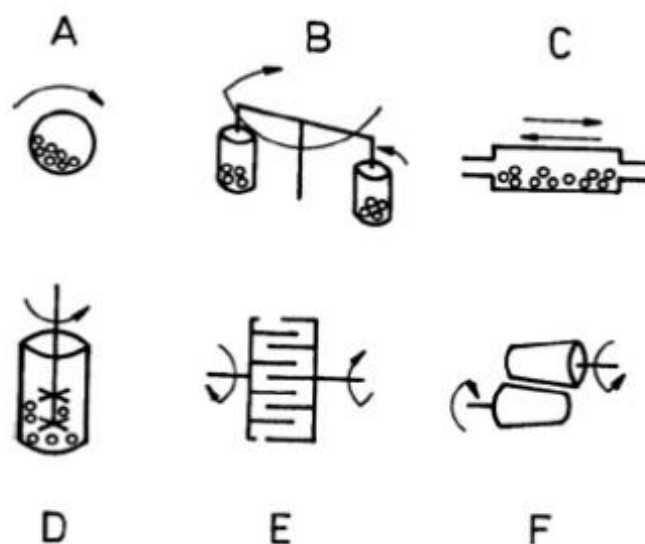


Figure 2.22: Mill types used in high-energy milling: (A) ball mill, (B) planetary mill, (C) vibrating mill, (D) attritor – stirring ball mill, (E) pin mill, (F) rolling mill.

In mills where balls are used as the grinding media, different types of ball movements can be observed (Figure 2.27). These movements can be classified as: cascading motion (A), cataracting or free-fall motion (B), and centrifugal motion (C) (Baláž, 2008).

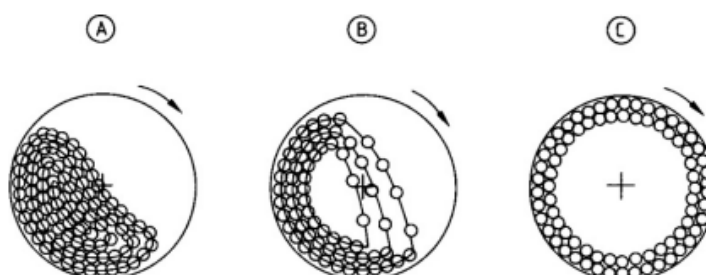


Figure 2.23: Types of motion in a ball mill: (A) cascading, (B) falling or cataracting, (C) centrifugal.

2.9.3.1 Vibrating mills

Vibrating mills are grinding devices with a tank-like structure that contain material and grinding media either in dry or wet form. In these mills, the chamber moves along a circular or elliptical trajectory due to the rotation of unbalanced masses. The three-dimensional vibrational motion is defined by four parameters: vibration speed, horizontal amplitude, vertical amplitude, and phase angle. The acceleration of the vibrational motion depends on amplitude and frequency. In laboratory-scale mills, high frequencies up to 25 Hz and low amplitudes of around 2–4 mm are typically observed, while industrial mills operate at frequencies between 16–19 Hz and generate

amplitudes below 6 mm. In some designs, the amplitude is increased up to 7–10 mm in order to enhance energy transfer, thereby achieving accelerations of 12–20 g. While balls are commonly used as the grinding media, rods are preferred for coarse grinding and silpebs are used for pulverization. The filling ratio usually ranges between 70–80%. The theoretical foundations of vibrating mills were developed in the 1940s, and it has been recommended to prefer high-frequency vibration and to adjust the size of the grinding media according to the mechanical strength of the feed material. Vibrating mills are especially used for the production of nanoscale products and mechanical activation. However, in such mills, the grinding time is usually long and the operation is generally batch-wise. Recent studies have shown that mechanical activation is also possible with continuous systems, with residence times of less than 30 min. A significant disadvantage of these mills is the development of high temperatures inside the mill due to low throughput and high energy input. This temperature increase arises from the nearly full loading of the mill and the complex movement trajectory of the grinding media. New-generation vibrating mills operating in “eccentric mode” produce combinations of elliptical, linear, and circular movements rather than circular vibrations. This new motion type increases the amplitude and rotation speed of the grinding media, making mechanical activation more efficient. Using this technology, various nanomaterials have been synthesized. As grinding time increases, particle size decreases and nanocrystalline structures are formed (Baláž, 2008). Industrial rotary-vibrating mill MOW-H-200 consists of several components as shown in Figure 2.28 (Sidor, 2010).

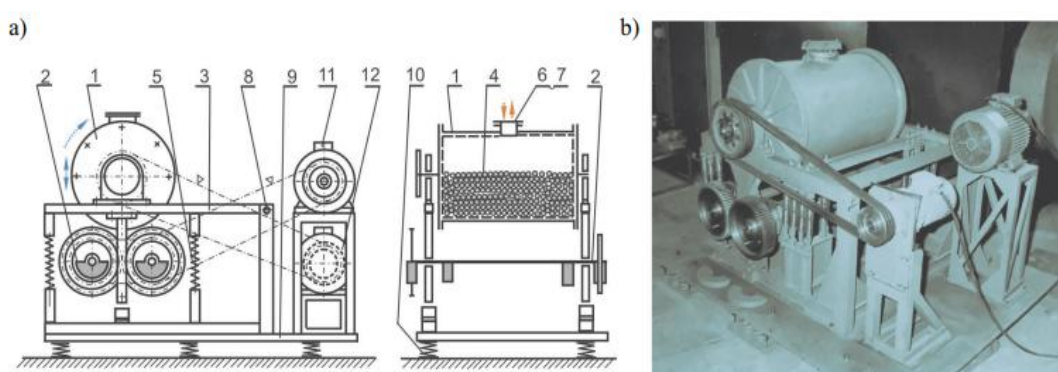


Figure 2.24: Industrial rotary-vibrating mill MOW-H-200 consists of several components as shown in (a), including the chamber (1), vibrator (2), rocker (3), load (4), elastic support (5), cover (6), feed inlet and grinding product outlet (7), joint (8), base (9), vibro-isolator (10), vibrator drive (11), and chamber drive (12), (b) shows the actual view of the MOW-H-200 mill.

2.9.3.2 Planetary mills

Planetary ball mills are high-energy grinding systems widely used in mechanical activation and mechanochemical processes. The fundamental characteristic of these mills is the simultaneous and counter-directional rotation of the grinding jars around their axes and a central rotating disk. This dual-axis movement causes the grinding balls within the mill to be subjected not only to gravitational forces but also to strong centrifugal and Coriolis forces. Under the influence of these forces, the balls detach from the jar walls and strike both the sample and the jar surface at high velocities, thereby generating intense impact energy and friction forces. Through this mechanism, it becomes possible to achieve significantly smaller particle sizes compared to conventional ball mills. The level of kinetic energy within the jars can increase by up to approximately 100 times relative to traditional systems. This high energy level not only leads to physical fragmentation but also induces disruptions in the crystal structure and facilitates chemical reactions. Therefore, planetary mills serve as effective tools in mechanochemical applications such as amorphous structure formation, synthesis of new phases, or enhancement of reactivity. Furthermore, since these mills can operate at low temperatures and in solvent-free conditions, they align well with environmentally friendly and sustainable processing methods (Pelitli et al., 2019). An image of a planetary-type ball mill is presented in Figure 2.29 (Nazik, 2013).



Figure 2.25: Planetary-type ball mill.

2.9.3.3 Attritors (Stirred ball mills)

Another mechanical activation mill is the attritor-type mill. It consists of a set of agitators positioned within a vertically oriented cylinder. These agitator elements, located inside the vertical cylinder, are rotated by a high-power motor, transferring kinetic energy to the grinding media (typically steel balls). The collisions between the

balls, the agitator shaft, the cylinder wall, and each other lead to the fragmentation of the powders being milled and the reduction of their particle size. Attritors are high-capacity systems that allow for the grinding of powder quantities ranging from 0.1 kg to 40 kg in a single run (Figure 2.30).

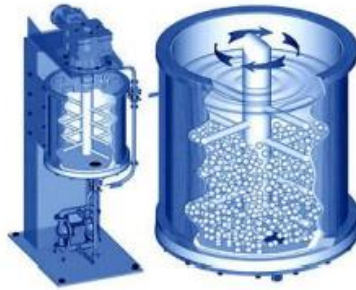


Figure 2.26: Attritor-type (vertical) ball mill.

2.9.4 Increase in dissolution efficiency through mechanical activation

The enhancement in dissolution efficiency via mechanical activation is achieved not only through the increase in specific surface area (surface area to mass ratio), but also by the formation of structural defects, amorphization of minerals, the emergence of crystal regions favorable for selective dissolution, and surface oxidation occurring on mineral particles during the activation process (Çemrek et al., 2022).

The effect of mechanical activation on the solubility of minerals has been investigated by many researchers. The primary reasons for the increased dissolution rate due to mechanical treatment can be summarized under the following points:

- Formation of morphological irregularities,
- Transformation of mineral grains into an amorphous structure,
- Development of specific crystal regions suitable for selective dissolution,
- Surface oxidation occurring during prolonged grinding.

During grinding, mechanical stress causes particles to break and be crushed. In this process, terraces and steps of various sizes and shapes form on the surfaces of the minerals (Figure 2.31). Compared to flat surfaces, the reaction rates at the edges of these steps are higher. The energy accumulated in the particles and amorphous–polymorphic transformations are among the key factors that enhance solubility (Korkut, 2022).

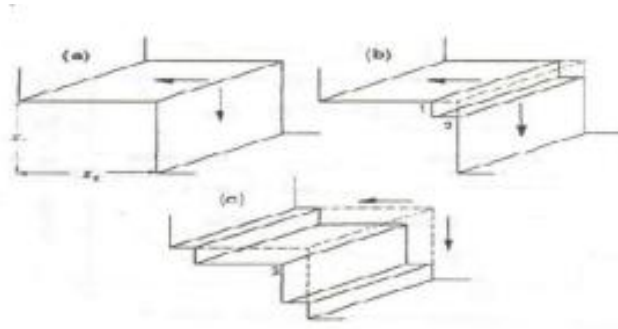


Figure 2.27: Dissolution at step edges; (a) dissolution area, (b) increase in the number of steps, (c) formation of new step edges (Korkut, 2022).

2.9.5 Industrial applications of mechanical activation

The industrial applications of mechanical activation are aimed at enhancing metal recovery efficiency through various processes.

2.9.5.1 Lurgi-mitterberg process

The leachability of chalcopyrite (CuFeS_2) was mechanically enhanced using a vibratory mill, achieving approximately 96% copper recovery. However, due to its high operational costs, the process was discontinued (Göktaş, 2018). A flow diagram explaining the Lurgi-Mitterberg process is presented in Figure 2.32 (Baláž, 2008).

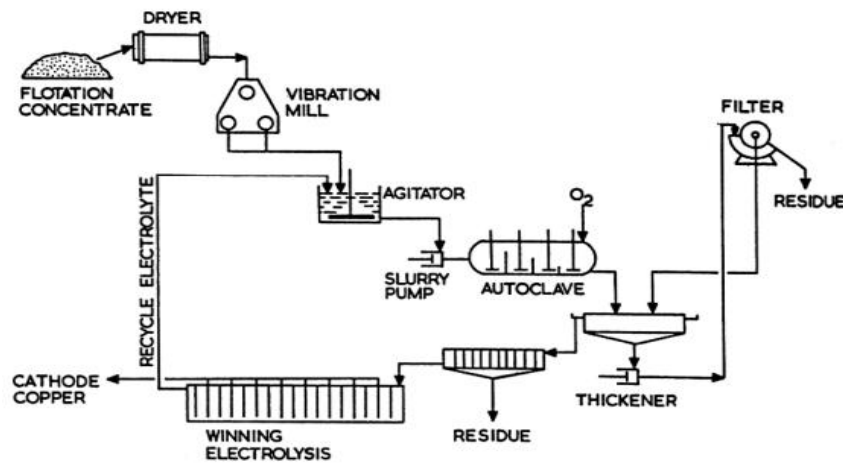


Figure 2.28: Flow diagram of the Lurgi-Mitterberg process.

2.9.5.2 Activox process:

Developed in Australia, this process replaces roasting with ultra-fine grinding and pressure oxidation in the treatment of sulfide ore concentrates. Mechanical activation generally occurs during the initial stage (Göktaş, 2018). A schematic representation of the Activox process is given in Figure 2.33 (Baláž, 2008).

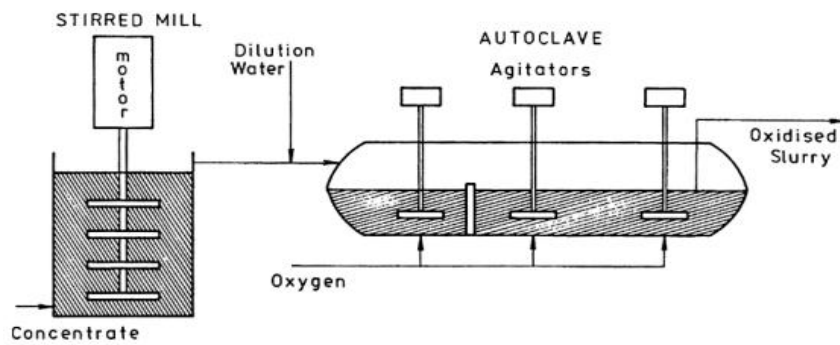


Figure 2.29: Schematic representation of the Activox process.

2.9.5.3 IRIGETMET process

In gold-bearing sulfide minerals, mechanical activation has shortened the cyanidation time and increased gold recovery by 11%. No increase in NaCN consumption was observed (Göktaş, 2018).

2.9.5.4 Sunshine process

In the hydrometallurgical processing of sulfide ores containing antimony, copper, and silver, oxygen pressure leaching with nitric and sulfuric acid was employed. For gold recovery, mechanochemical leaching was applied, providing a cost advantage (Göktaş, 2018).

2.9.5.5 MELLT process

The mechanochemical leaching of tetrahedrite minerals was tested on a semi-industrial scale in attritors by the Technical University of Berlin and the Slovak Academy of Sciences (Göktaş, 2018). A flow diagram of the MELLT process is presented in Figure 2.34.

2.9.5.6 Metprotech process:

This process, developed for gold recovery, applies mechanochemical leaching by adding cyanide during the grinding stage. Its first industrial application was carried out in 1988, and it was used until 1998 in South Africa, Australia, and New Zealand (Göktaş, 2018).

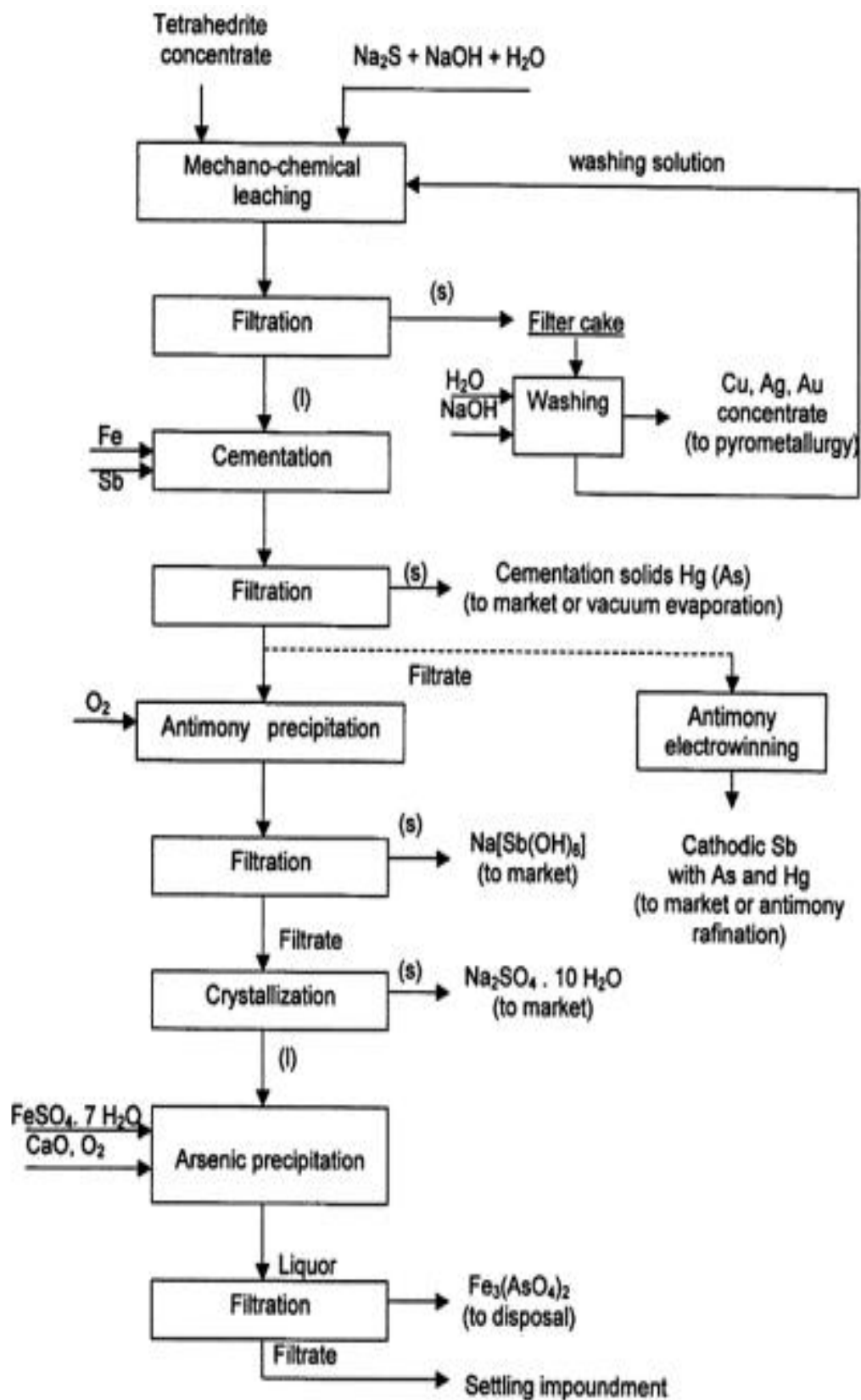


Figure 2.30: Flow Diagram of the MELLT Process.



3. EXPERIMENTAL STUDIES

3.1 Materials and Methods

3.1.1 Materials

In this thesis study, the solid wastes from the Eskişehir Kırka Boron Plant (Penta 4) were utilized to recover lithium from lithium-bearing clay structures. In this facility, as illustrated in Figure 3.1, the run-of-mine boron ore undergoes a series of processes including hot water leaching (96 ± 2 °C), precipitation, and sequential decantation and crystallization for solid–liquid separation. The dissolved boron minerals are processed in two stages by leaching sluices and decanter centrifuges, separating the dissolved boron components from the undissolved solid-phase minerals. The slurry in the form of a thick mud obtained from the leaching sluices and decanter centrifuges are then combined and discharged into the waste storage area.

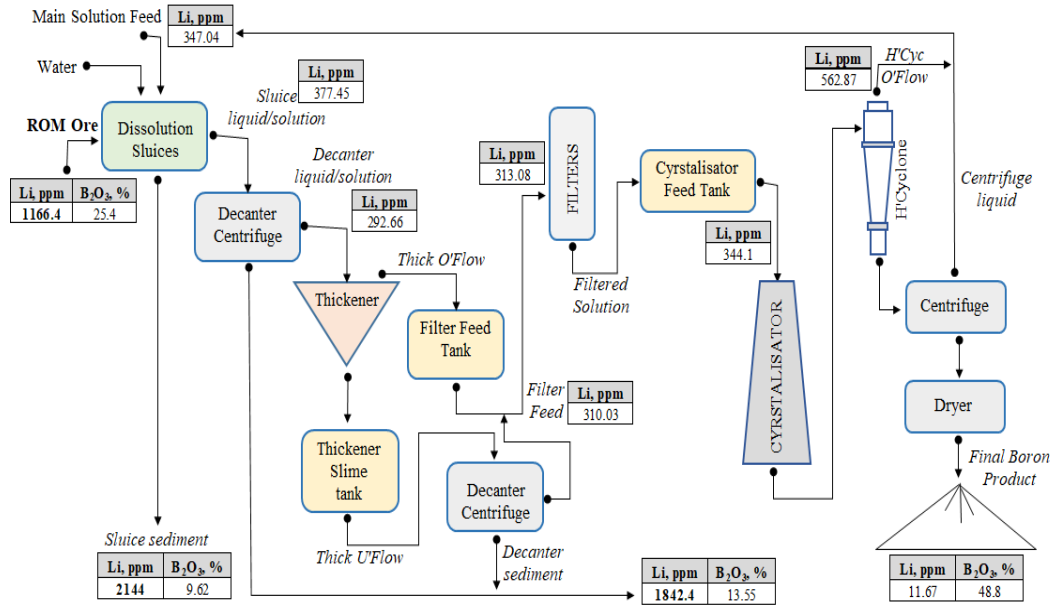


Figure 3.1: Flow diagram of the boron production plant and discharged lithium contents.

Representative samples in thick slurry form (mud) were collected from the waste storage area of the facility and transported to the Mineral Processing Engineering Laboratories at Istanbul Technical University (ITU). The samples were air-dried to

remove moisture prior to crushing. Before the drying process, the samples were subjected to three to four cycles of mixing and wet sieving to separate them into various particle size fractions, on which lithium analyses were conducted. The results of the fractional lithium contents are presented in Table 3.1, along with the cumulative undersize curve shown in Figure 3.2.

Table 3.1: Undersize distribution of the representative run-of-mine sample after drying.

Particle Size, (mm) (-)	Particle Size, (mm) (+)	Wt. (%)	Σ Under Size (%)	Li (ppm)
30.000	19.000	1.93	100.00	900.00
19.000	13.000	3.87	98.07	800.00
13.000	9.000	3.31	94.20	1100.00
9.000	5.600	4.28	90.89	1300.00
5.600	3.350	5.75	86.61	1300.00
3.350	2.000	5.06	80.86	1000.00
2.000	0.841	9.30	75.79	1200.00
0.841	0.595	2.12	66.50	1100.00
0.595	0.150	4.56	64.38	1100.00
0.150	-	59.83	59.83	1500.00
Total		100.00		1348.14

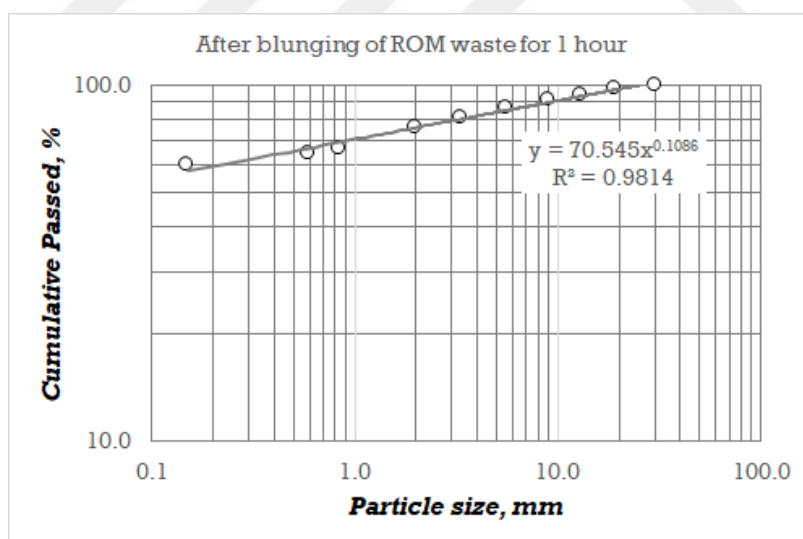


Figure 3.2: Cumulative undersize curve of the dried sample.

As presented in Table 3.1 and Figure 3.2, the sample, which is completely -30 mm in size, consisting of approximately 60% particles at the -150 μm size fraction, shows a relative increase in lithium content as the particle size decreases. It has been reported that the lithium source in the waste sample originates from clay minerals, which constitute approximately 20-30% of the material. Therefore, the relative increase in

lithium content in the finer fractions after the dispersion process is attributed to this fragmentation behavior.

In the mechanical activation tests, the particle size of the processed raw sample is required smaller than the size of the mechanical activation grinding media, i.e. balls. Considering that the smallest ball size used in the stirred mill is 3 mm, the sample thus was reduced to below 2 mm prior to mechanical activation (Figure 3.3).

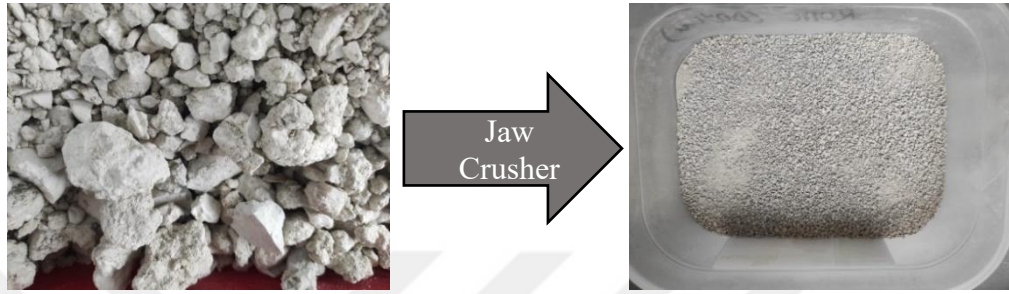


Figure 3.3: Sample crushed from -30 mm to -2 mm.

The chemical analysis results of the waste material from the boron plant, determined via ICP-OES, are presented in Table 3.2. The results indicate that the sample contains high levels of Mg (10.16%) and Ca (11.16%), as well as a high loss on ignition (LOI) value of 34.08%. These findings, further confirmed by XRD analyses, demonstrate that dolomite is the dominant mineral in the waste sample. The Na and K contents were determined as 2.15% and 0.62%, respectively. Considering the presence of a small amount of Al (0.69%), it can also be inferred that the sample contains a minor proportion of clay minerals.

Table 3.2: Chemical analysis of the boron plant waste sample.

Element	Value
Li, ppm	900
K, %	0.62
Na, %	2.15
Ca, %	11.16
Mg, %	10.16
SiO ₂ , %	16.34
Al, %	0.69
Fe, %	0.25
LOI, %	34.08

*LOI: Loss on ignition

The mineralogical analysis results of the waste sample are presented as an XRD pattern in Figure 3.4. The XRD analysis revealed that the tested sample is predominantly

composed of dolomite (>85%) and contains less than 15% in total of illite, clinochlore, montmorillonite, clinoptilolite, tinalconite, and similar minerals. The presence of dolomite is corroborated by the high Ca and Mg contents shown in Table 3.2. It is noteworthy that the waste sample possesses a highly complex structure, consisting mainly of dolomite along with various clay and boron mineral formations. The Na (2.15%) and K (0.62%) contents are associated with the minor amounts of halite, zeolite, muscovite, and illite minerals (Figure 3.4).

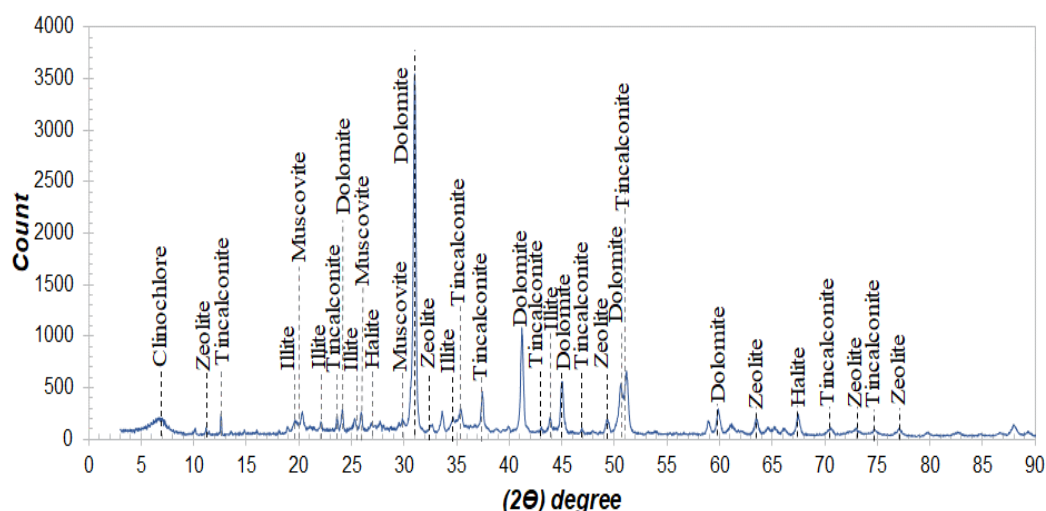


Figure 3.4: XRD analysis results of the sample used in the experimental studies.

In the leaching processes, commercial/technical-grade pickle salt was used instead of the table salt recommended by Tesla Group (2021) to facilitate isomorphic ion-exchange reactions between the sodium (Na) derived from the salt and the lithium (Li) originating from the waste material (Figure 3.5).



Figure 3.5: Commercial/technical-grade pickling salt.

The ion release properties of the pickle salt were evaluated based on the additive ratio used in the experimental studies conducted within the scope of this thesis (10% of the sample weight), the liquid-to-solid (L/S) ratio of 5:1, and the leaching temperature of 80 °C. The ions released into the medium under general leaching conditions due to the

use of this salt, along with their respective amounts, are presented in Table 3.3. The concentration of Na^+ is considerably higher than that of Mg^{2+} and Ca^{2+} , which is expected to contribute positively to the ion-exchange mechanism. Additionally, the use of commercial salt offers the advantages of being both economical and readily available.

Table 3.3: Ion release of pickling salt in water (at 80 °C Washing Temperature and L/S Ratio: 5:0.1).

Element	Value (ppm)
K^+	10,19
Na^+	9628
Ca^{+2}	19,01
Mg^{+2}	7,04
Fe^{+3}	0,0
Al^{+3}	0,0

Tesla patent combining mechanical activation with saline water leaching, states that the structural changes occurring in the crystalline lattice of the material after mechanical activation facilitate the transition of ions into the solution and, with the contribution of high Na^+ availability, promote Li^+ – Na^+ ion-exchange reactions. Mechanical activation disrupts the crystal structures of minerals, thereby enhancing ion dissolution. These structural modifications allow replacement of Li^+ ions by Na^+ ions present in the environment or introduced into the system. This type of ion exchange is particularly effective in minerals or structures with high Na content. Moreover, the presence of other cations (such as K^+ , Ca^{2+} , and Mg^{2+}) in the structure or the medium at low temperatures reduces competition with Li^+ and renders Na^+ ion exchange dominant. For mechanical activation, various mills, namely planetary mill (Figure 3.6), stirred media mill (Figure 3.7), and vibratory mills (Figure 3.8), were employed.



Figure 3.6: Planetary mill used in mechanical activation tests.

3.1.2 Methods

The representative sample, delivered in slurry form from the Kirka Boron Plant wastes, was first air-dried and subsequently oven-dried at 105 °C. The dried material was then crushed to below 2 mm using a combination of laboratory-scale jaw crusher and pulverizer. The sized sample was mechanically activated using a planetary mill (PM), stirred mill (SM), and vibratory mill (VM), and subsequently subjected to a water leaching process (Figure 3.9).

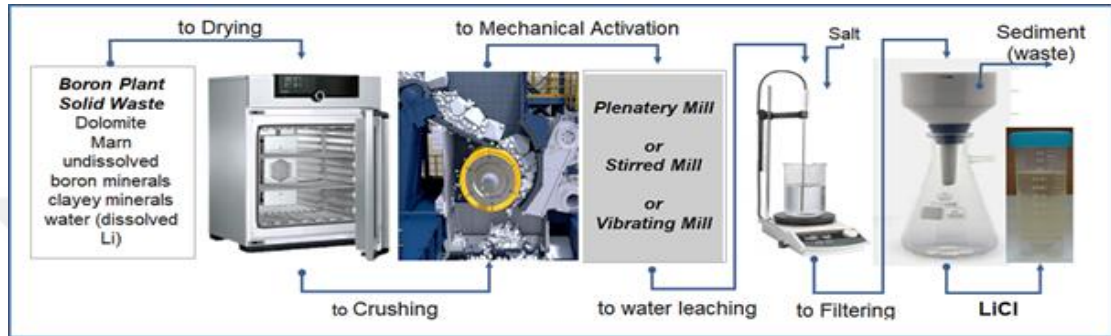


Figure 3.9: Experimental flow diagram of mechanical activation combined with water/acid leaching.

The variables for the mechanical activation optimization tests are provided in Table 2.4, while the operational parameters for the leaching (dissolution) process were selected as presented in Table 3.5. In addition, water leaching was also carried out using Mediterranean seawater as an alternative to salt addition.

Table 3.5: Operational parameters and working ranges for the leaching (dissolution) process.

Variables	Salt Leaching	Acid Leaching
Salt Addition, %	0-25 % (w/w)	-
Acid Concentration, mol/L	-	0 - 1.75 mol/L
Leach time, min.	0 -150	0 -150
Leach Temperature, °C	25 - 90	25 - 90
Liquid to solid ratio (L/S)	2.5:1 – 100:1	2.5:1 – 100:1

Detailed examinations were conducted on the activated powders, and residues obtained after leaching to determine the surface morphology and elemental composition of the raw material (untreated solid waste: ROM) using a scanning electron microscope (SEM, HITACHI SU3500), and surface elemental analyses performed via energy-dispersive spectroscopy (EDS, Oxford AZtech). Additionally,

all samples were characterized using X-ray diffraction (XRD, RIGAKU Miniflex 600). XRD analyses were carried out within a scanning range of 3° to 90°, with a wavelength of 1.5406 Å (λ) and a step size of 0.02°. The liquids obtained after leaching were separated from the solids using a vacuum pump, and lithium analyses were performed on the leachate using an Atomic Absorption Spectrometer (AAS). The leach solutions were also subjected to elemental ion analyses using ICP-OES at the NUMLab laboratories.

3.2 Mechanical Activation

3.2.1 Optimization of mechanical activation conditions

The mechanical activation conditions were first optimized with water leaching, and the effects of variable parameters were evaluated based on lithium leach recoveries. Optimization of mechanical activation conditions, along with the corresponding lithium leach recoveries, are presented for the planetary mill, stirred mill, and vibratory mill in Tables 3.6, 3.7, and 3.8, respectively. A comparative overview of the mechanical activation conditions for these three mills is shown in Figure 3.10.

Table 3.6: Optimization of mechanical activation conditions using the planetary mill.

Variable	Ball Charge (g)	Sample Mass (g)	BPR	Mech act. time, (min)	Shaft speed (rpm)	Li Conc. (ppm)	Leach Rec., (%)
Ball Charge (g)	70	30	2.33	60	1500	20.79	11.55
	140	30	4.67	60	1500	30.58	16.99
	280	30	9.33	60	1500	37.68	20.93
Sample Mass (g)	280	50	5.60	60	1500	31.57	17.54
	280	40	7.00	60	1500	29.56	16.42
	280	15	18.67	60	1500	58.14	32.30
Mech. Act. Time (min)	280	15	18.67	60	1500	58.14	33.22
	280	15	18.67	90	1500	60.16	34.38
	280	15	18.67	120	1500	81.90	46.80
	280	15	18.67	150	1500	90.01	51.44
Shaft speed (rpm)	280	15	18.67	60	500	26.20	14.97
	280	15	18.67	60	750	32.00	18.28
	280	15	18.67	60	1000	52.00	29.71
	280	15	18.67	60	1250	85.00	48.57
	280	15	18.67	60	1500	101.00	57.71
	280	15	18.67	60	1750	83.00	47.42
	280	15	18.67	60	2000	90.90	51.94
<i>Without mechanical activation</i>					0	9.00	5.14

Table 3.7: Optimization of mechanical activation conditions using the stirred mill.

Variable	Ball Charge (g)	Sample Mass (g)	BPR	Mech act. time, (Min)	Shaft speed (rpm)	Li Conc. P (ppm)	Leach Rec., (%)
Ball Charge (g)	700	40	17.50	60	700	29.8	16.56
	800	40	20.00	60	700	29.5	16.39
	900	40	22.50	60	700	30.0	16.67
	1000	40	25.00	60	700	41.7	23.17
	1100	40	27.50	60	700	43.2	24.00
	1200	40	30.00	60	700	45.5	25.28
Sample Mass (g)	1100	16	68.75	60	700	79.7	44.28
	1100	22	50.00	60	700	62.0	34.44
	1100	28	39.29	60	700	53.9	29.94
	1100	34	32.35	60	700	39.3	21.83
	1100	46	23.91	60	700	33.8	18.78
	1100	52	21.15	60	700	30.5	16.94
Mech. Act. Time (min)	1100	16	68.75	30	700	50.25	30.89
	1100	16	68.75	45	700	63.64	36.77
	1100	16	68.75	75	700	81.2	45.11
	1100	16	68.75	90	700	75.8	42.11
	1100	16	68.75	120	700	91.2	50.67
	1100	16	68.75	150	700	93	51.67
Shaft speed (rpm)	1100	16	68.75	150	400	89.1	49.50
	1100	16	68.75	150	450	89.4	49.67
	1100	16	68.75	150	500	86.1	47.83
	1100	16	68.75	150	550	91.2	50.67
	1100	16	68.75	150	600	92.0	51.11
	1100	16	68.75	150	650	85.3	47.39
	1100	16	68.75	150	700	93.0	51.67

As illustrated in Figure 3.10, dissolution efficiency increases with increasing the Ball-to-Powder Ratio (BPR). On a per-unit BPR basis, the planetary mill achieved higher dissolution efficiencies even at lower BPR values compared to the other mills (Figure 3.10A). Considering that the cell volumes of these three laboratory-scale mills are in the range of 300–750 mL, with ball fillings of approximately 35–45%, the amount of material processed per unit time (in a single run) remains relatively small. Therefore, 15 g of material was deemed appropriate for all mechanical activation devices.

In the experimental studies examining the effect of mechanical activation duration (Figure 3.10B), it was observed that, for all mechanical activation devices, structural modifications in the material increased linearly with longer activation times, leading to progressively higher leaching efficiencies. This linear trend persisted even at extended activation durations, such as 150 minutes, indicating that structural transformations and the associated dissolution efficiencies continued to improve

without reaching a plateau. However, considering potential industrial applications, activation durations of approximately 120–150 minutes were deemed more practical; therefore, experimental work was not extended beyond this range.

Table 3.8: Optimization of mechanical activation conditions using the vibratory mill.

Variable	Ball Charge (g)	Sample Mass (g)	BPR	Mech act. time, (min)	Li Conc. (ppm)	Leach Rec., (%)
Ball Charge (g)	600	25	24.00	60	25.1	13.94
	800	25	32.00	60	21.5	11.94
	1000	25	40.00	60	24.2	13.44
	1200	25	48.00	60	27.3	15.17
	1400	25	56.00	60	31.5	17.50
	1600	25	64.00	60	26.1	14.50
	1800	25	72.00	60	37	20.56
	2000	25	80.00	60	35.9	19.94
Sample Mass (g)	2000	15	133.33	60	52.4	29.11
	2000	20	100.00	60	30.2	16.78
	2000	30	66.67	60	36.5	20.28
	2000	40	50.00	60	31.4	17.44
Mech. Act. Time (min)	2000	15	133.33	30	39	21.67
	2000	15	133.33	60	52.4	29.11
	2000	15	133.33	90	52.9	29.39
	2000	15	133.33	120	76.6	42.56
	2000	15	133.33	150	70.95	39.42

The effect of rotational speed, expressed as either stirring speed or shaft speed, on the transfer of motion to the grinding media (Figure 3.10C), increasing the shaft speed in the planetary mill enhanced the mechanical activation effect, with an optimum value observed at 1500 rpm. In contrast, for the stirred mill, adjusting the stirring speed within the range of 400–700 rpm (its maximum operating speed) had only a marginal influence on activation and leaching efficiency, indicating that activation duration was a more critical factor than rotation speed. Accordingly, an average speed of 550 rpm was selected as the optimum for the stirred mill. For the vibrating mill, rotational speed was not evaluated, as its vibration frequency and amplitude are fixed and cannot be altered.

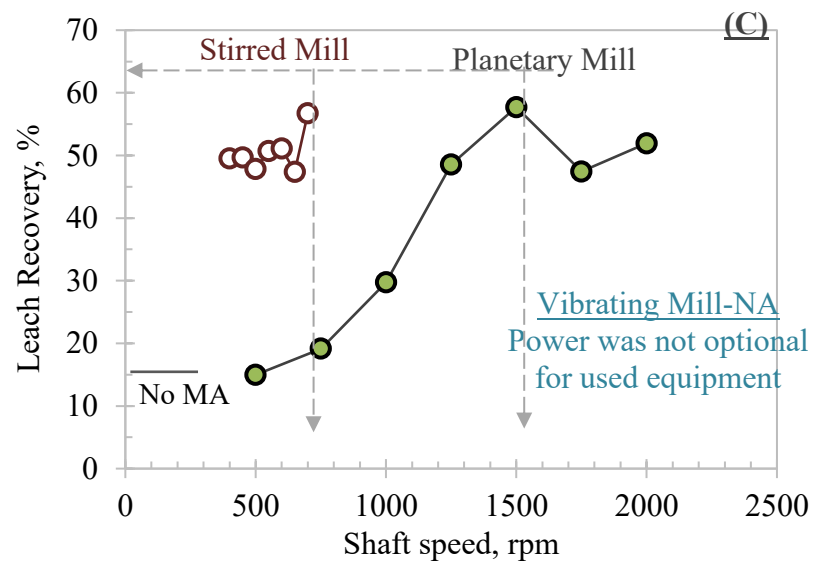
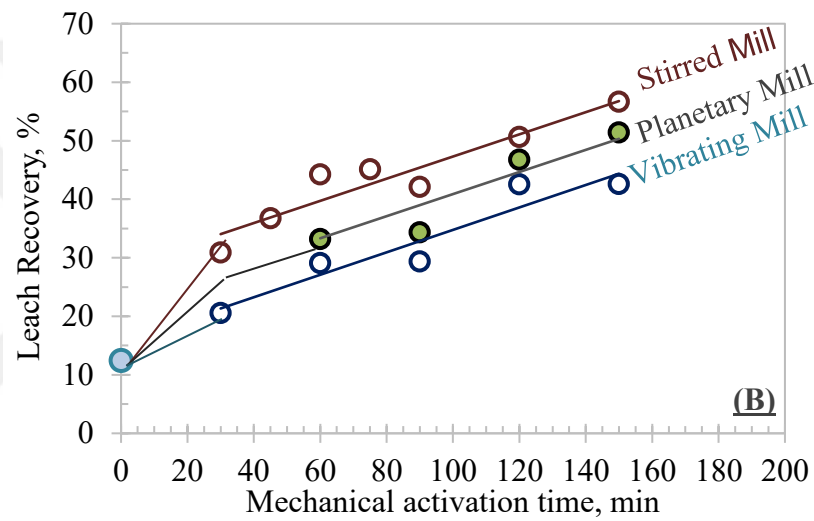
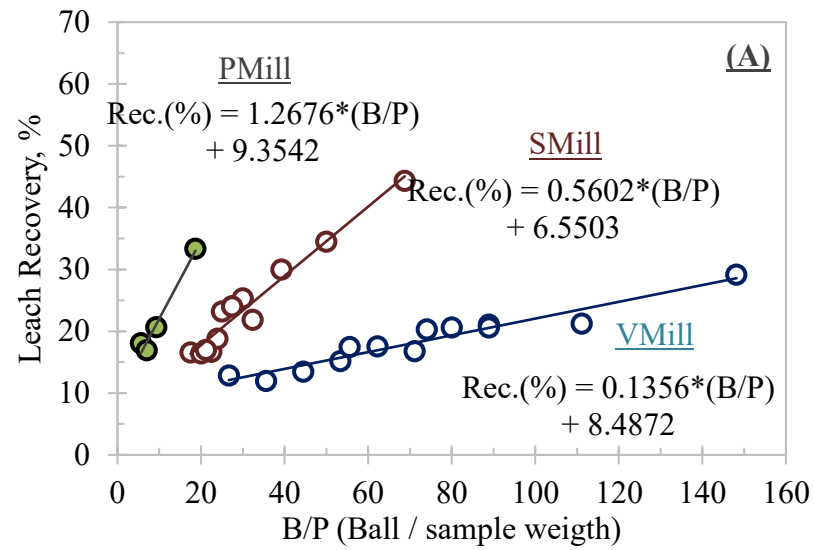


Figure 3.10: Optimization of mechanical activation conditions (A) Ball/sample Weight, (B) Mechanical activation time, (C) Shaft speed (NA: Not Available).

3.2.2 Structural changes as a function of mechanical activation intensity

The structural changes found on the material as a function of the degree of mechanical activation are presented in detail for the planetary mill in Figures 3.11–3.14.

3.2.2.1 XRD analysis

Figure 3.11 presents the XRD patterns of samples activated at different shaft speeds. As shown, in Figure 3.11, the mechanical activation process caused the peaks of certain minerals such as clinocllore, muscovite, illite, tincalconite, and halite to collapse and broaden, while the intensity of the dolomite peak decreased.

As reported by Manosa et al. (2023), mechanical activation induces substantial changes in particle morphology, resulting in a transition from crystalline to amorphous structures. During this process, hydroxyl groups are released from the crystal lattice, weakening the overall bonding framework. In the present study, these structural modifications as evidenced by changes in peak intensities increased proportionally with stirring speed and reached their maximum at 1500 rpm. As illustrated in Figure 3.10, the highest lithium leach recovery was also obtained at this speed, indicating a clear correlation between XRD pattern alterations and lithium dissolution performance.

3.2.2.2 FTIR analysis

To investigate the changes in FTIR characteristics as a function of mechanical activation intensity, a series of FTIR analyses was performed on the active powders (activated samples) (Figure 3.12). As shown in Figure 3.12, the O–H stretching peaks associated with crystalline and adsorbed water, along with the B–O–H, B–O/C–O, and CO₃ bands, progressively diminished or completely disappeared with increasing mechanical activation intensity. This attenuation occurred proportionally to the applied activation level. Specifically, as the stirring speed of mechanical activation applied to the run-of-mine material increased, structural bands such as O–H, B–O–H, Al–O–H, and CO₃ exhibited consistent weakening and spectral shifts. This phenomenon, as also reported by Yao et al. (2019) and Manosa et al. (2023), is attributed to partial amorphization, loss of crystallinity, and the transformation of structural hydroxyl groups into adsorbed water.

Mechanical activation is known to significantly alter the FTIR spectra of minerals, particularly clays, carbonates, and phyllosilicates, due to induced structural disorder, particle size reduction, and changes in hydrogen bonding. Literature studies have demonstrated that increasing mechanical activation intensity reduces the intensity of characteristic bands (O–H, B–O–H, CO₃, Al–O–H, Al–O–Si, Si–O–Si) as a result of structural degradation processes, including partial amorphization and hydroxyl group transformation (Yao et al., 2019; Manosa et al., 2023).

Henmi and Yoshinaga (1996) reported that dry grinding disrupts the tubular structure of imogolite, breaks Si–O–Al bonds, and removes structural hydroxyl groups. Similarly, Christidis et al. (2004) observed that grinding decreases crystal size, alters Si–O–Mg and Mg–O bonds, and increases the cation exchange capacity of talc and smectite. Aglietti et al. (1996) found that grinding and pressure treatment lower the crystallinity of kaolinite, promote earlier dehydroxylation, and introduce structural defects. Finally, Johnston et al. (2008) confirmed that grinding induces structural disorder in kaolin group minerals, manifested in FTIR spectra as shifts in OH stretching and Al–OH bending regions.

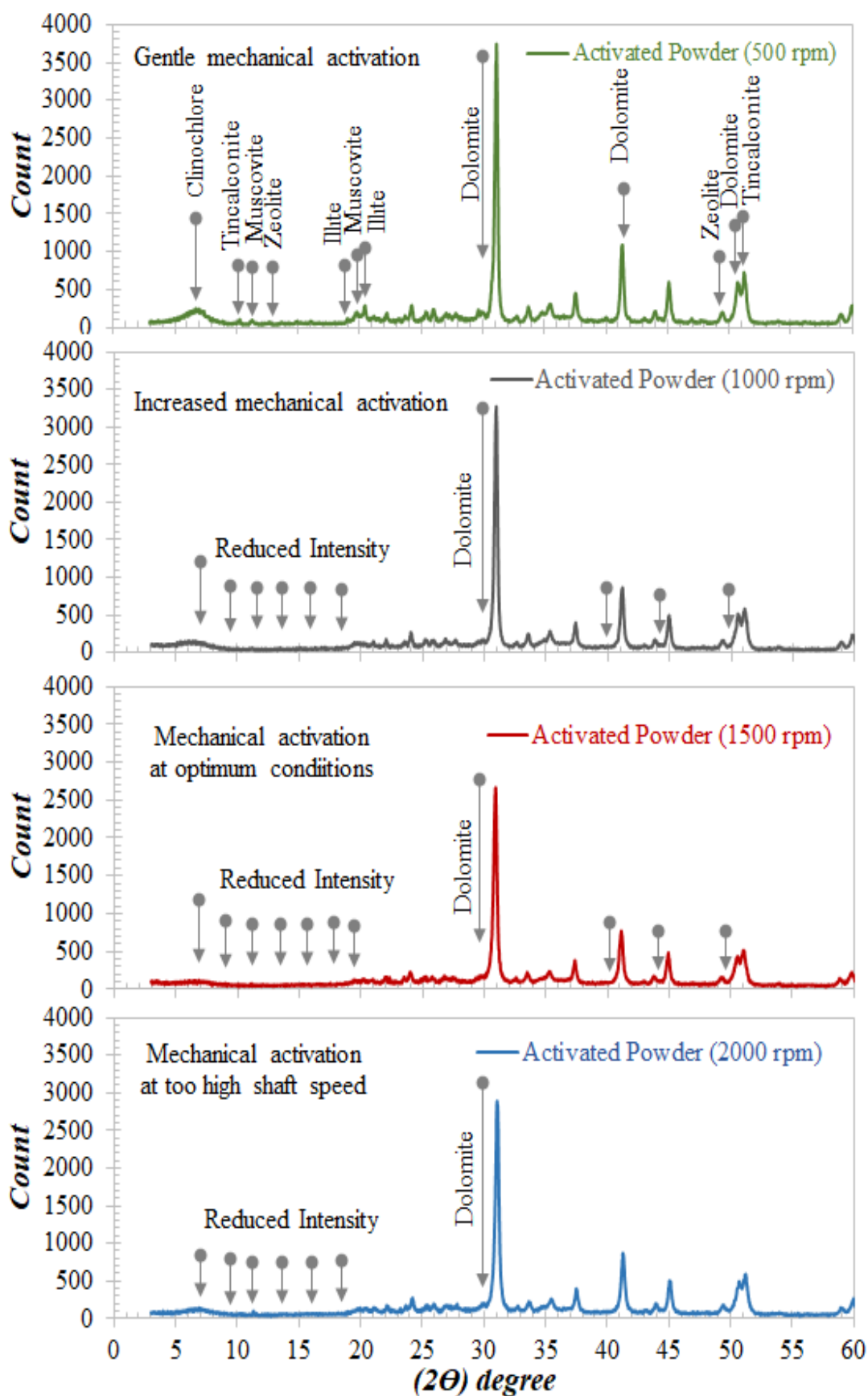


Figure 3.11: XRD Patterns of materials activated at different stirring speeds in the planetary mill: (a) 500 rpm, (b) 1000 rpm, (c) 1500 rpm, and (d) 2000 rpm.

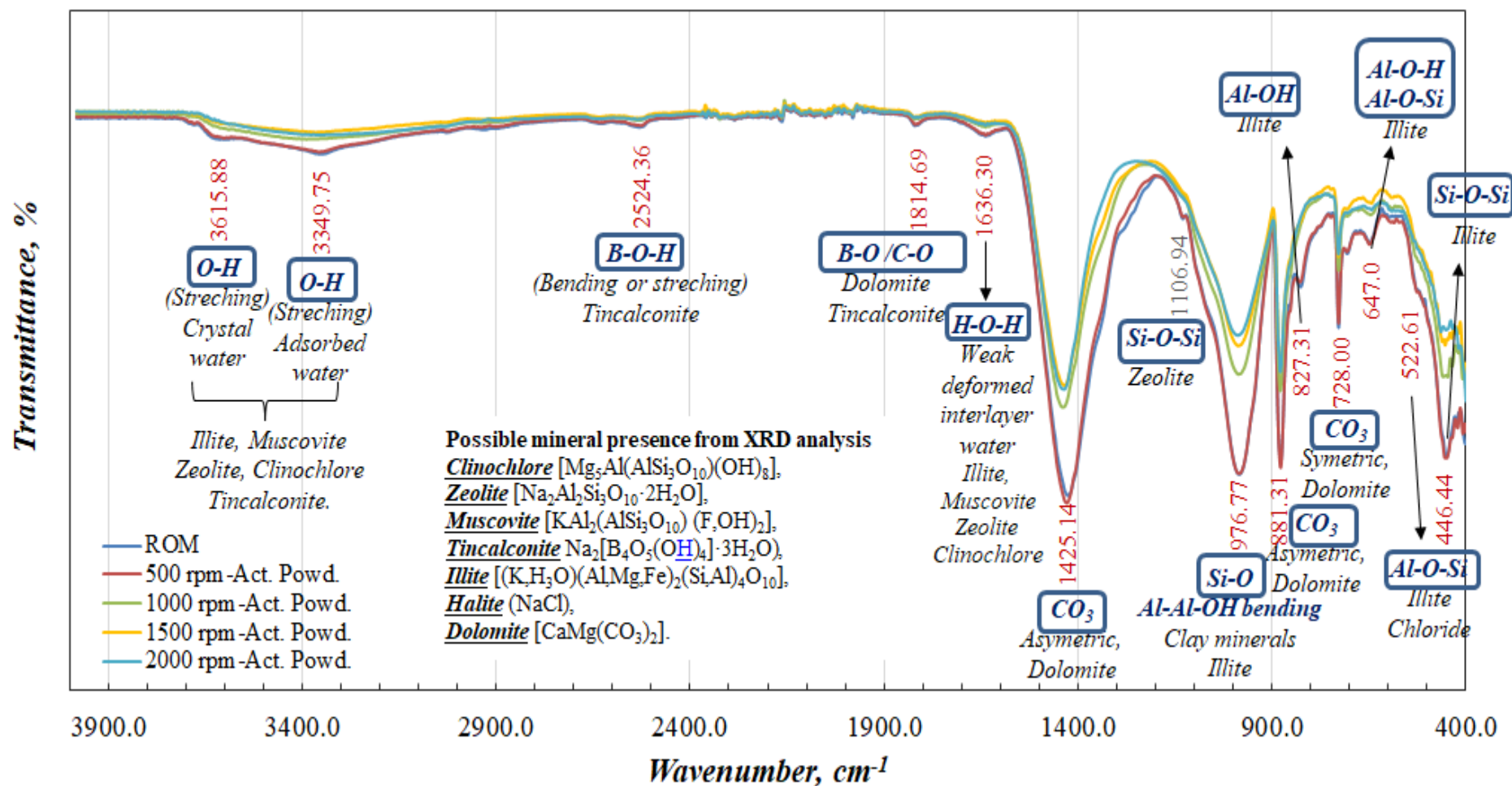


Figure 3.12: FTIR spectra of minerals activated at different stirring speeds in the planetary mill.

3.2.2.3 Morphological changes

The SEM images of the waste samples activated at different stirring speeds are shown in Figure 3.13. As clearly illustrated in Figure 3.13, the mechanical activation caused significant disruption of the crystalline structure, leading to its transformation into an amorphous form. This was accompanied by increased particle surface roughness and irregularity. Moreover, the amorphized structure, resulting from the breakdown of the crystalline lattice, exhibited enhanced reactivity in ion-exchange processes during the leaching stage, consistent with the trends observed in the leaching experiments.

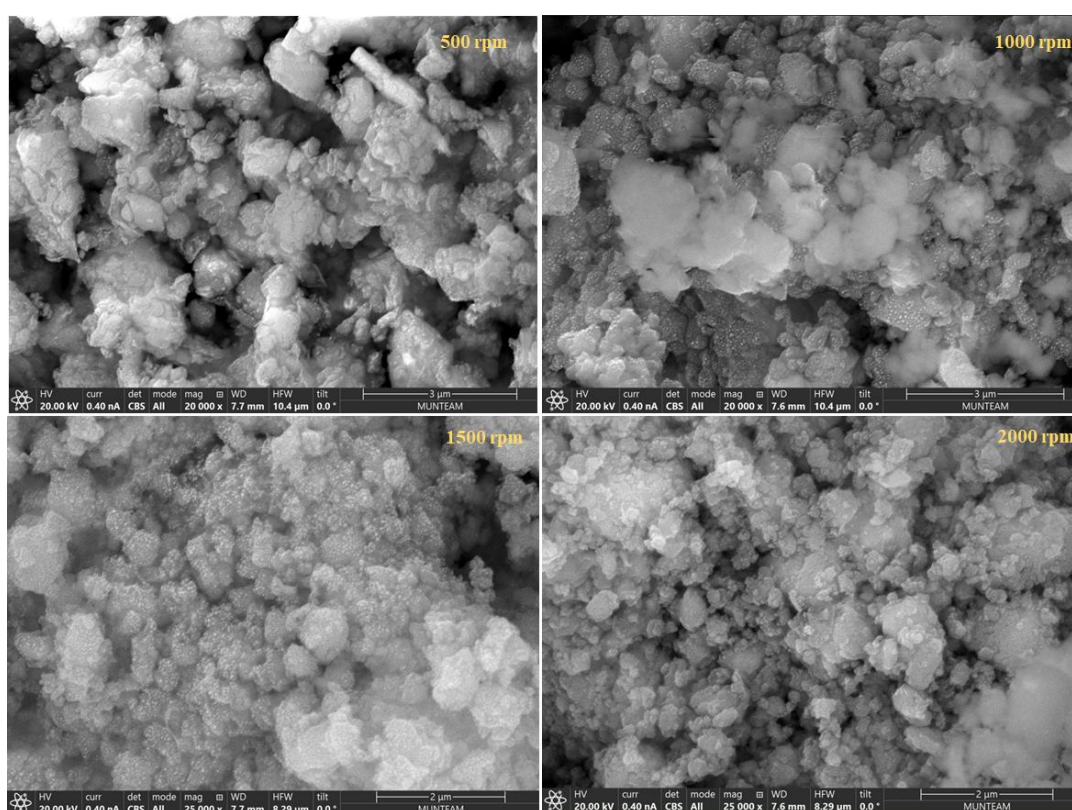


Figure 3.13: SEM images of materials activated at different stirring speeds in the planetary mill.

3.2.2.4 EDS/EDX analyses

Energy-Dispersive X-ray Spectroscopy (EDS/EDX) is a valuable technique for analyzing the elemental composition and assessing structural transformations in clay minerals subjected to mechanical activation. EDS analysis offers insights into elemental distributions, phase transformations, and potential contamination effects arising during the activation process. Mechanical activation can generate surface defects, reactive sites, and free radicals (Manosa et al., 2023), which in turn influence

surface charge, cation-exchange capacity, and adsorption behaviour particularly in minerals such as illite and tincalconite.

In this study, the effect of mechanical activation stirring speed was comprehensively assessed using planetary mill experiments. The influence of stirring speed on material structure, as revealed by EDS/EDX analysis, is presented in Figure 3.14.

Mechanical activation induced structural transformation and amorphization of the material, making it impossible to obtain highly comparable or detailed images at an extremely fine measurement scale. Nevertheless, although these images lack sharp microscopic detail, the mosaic surface views effectively illustrate changes in surface morphology. Therefore, the images in Figure 3.14 were evaluated at a 100 μm scale. As shown in Figure 3.14, mechanical activation caused a redistribution of alkali and other ions on the material's surface. With increasing activation intensity, the dominant alkali ion Mg^{2+} was progressively replaced by Na^+ ions. At the optimal rotational speed of 1500 rpm for lithium recovery, surface Mg^{2+} ions (indicated in green) were largely substituted by Na^+ ions (indicated in pink/purple), corresponding to enhanced lithium recovery. Additionally, mechanical activation generated surface defects, reactive sites, and free radicals, which influenced the key properties such as surface charge and cation-exchange capacity.

In the solid residues after water leaching of the active powders, the surfaces were again dominated by Mg^{2+} ions, similar to the raw material. These results indicate that Na^+ ions, originating from minerals such as halite, tincalconite, and zeolite, migrated to the surface during activation, becoming available for isomorphic ion exchange with lithium. The disappearance of Na^+ ions from the surfaces after leaching confirms their transfer into the liquid phase and subsequent removal through solid–liquid separation. To validate this mechanism, ion analyses of the leach solutions were conducted, with results presented in the following section of this study.

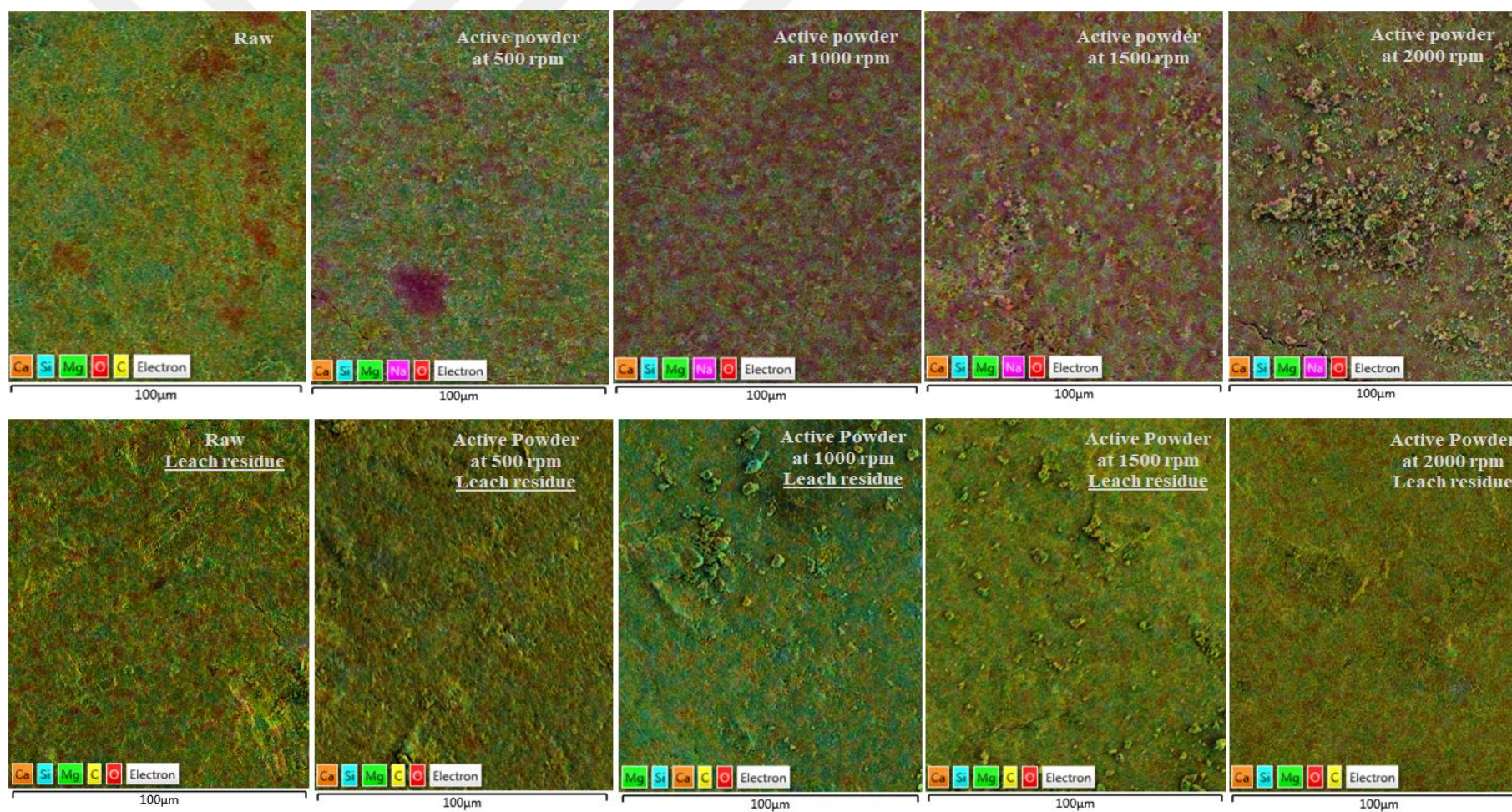


Figure 3.14: EDS images of materials activated at different stirring speeds in the planetary mill (Top: Activated powders; Bottom: Leaching residues of these powders).

As shown in Figure 3.15, the difference observed in the two experiments, e.g., activated powder with 0.2 g NaCl and 2 g NaCl; saline-water leaching; 20 min quiescent settling can be explained by the surface modified upon by mechanical activation and the solution's ionic strength. According to Manosa et al. (2023), mechanical activation generates surface defects, reactive sites, and free radicals, thereby increasing the surface charge density and cation-exchange capacity; consistent with the EDS/EDX results in Figure 3.14, activation leads to surface Na^+ enrichment and a $\text{Mg}^{2+} \rightarrow \text{Na}^+$ redistribution. Under low ionic strength (0.2 g NaCl), the high surface charge maintains a thick electrical double layer and persistent interparticle repulsion; the suspension remains colloidally stable and settling is limited. In contrast, at 2 g NaCl the ionic strength increases substantially; Na^+ compresses the double layer, lowers the zeta potential, and suppresses interparticle electrostatic repulsion. Simultaneously, the elevated $[\text{Na}^+]$ facilitates rapid exchange of replaceable surface cations, which promotes flocculation/agglomeration. Consequently, larger and denser flocs form and settle rapidly, and the supernatant clarifies (good settling in the right beaker), whereas at 0.2 g NaCl the flocs remain small and fragile, producing an opalescent/turbid supernatant and poor settling. This behaviour indicates that activation redistributes surface ions and that, in saline-water leaching, higher NaCl concentrations promote rapid settling through double-layer compression and cation exchange by mitigating repulsive forces; indeed, the reappearance of Mg^{2+} -dominated surfaces in the water-leached residues confirms the migration of Na^+ from the surface to the liquid phase, consistent with the EDS/EDX and ion-analysis results of this study.



Figure 3.15: Salt-induced enhanced settling rate of the activated powder (Left is with 0.2 gr salt, Right is with 2 gr salt).

As also evidenced by the XRD, FTIR, and EDS results, mechanical activation disrupts the carbonate (CO_3^{2-}) structure of the sample; accordingly, the characteristic peak/band intensities assigned to carbonate phases decrease. In equation (2.3) and

(2.4), the reactions of carbonate minerals with H_2SO_4 as reported in the literature (Mäkinen et al., 2022) are as follows:



These reactions lead to CO_2 evolution and, consequently, bubble/foam formation. Indeed, as seen in Fig. 3.16(a), bubble formation is limited in the PM-activated powder, whereas in Fig. 3.16(b) the untreated (ROM) sample exhibits pronounced and intense foaming. This visual observation is consistent with the analytical evidence that mechanical activation weakens/deconstructs the CO_3 bonds—and thus the carbonate matrix. In sum, the experimental observations and structural analyses are in agreement; mechanical activation disrupts the carbonate structure and thereby relatively reduces CO_2 evolution during acid leaching (Mäkinen et al., 2022).

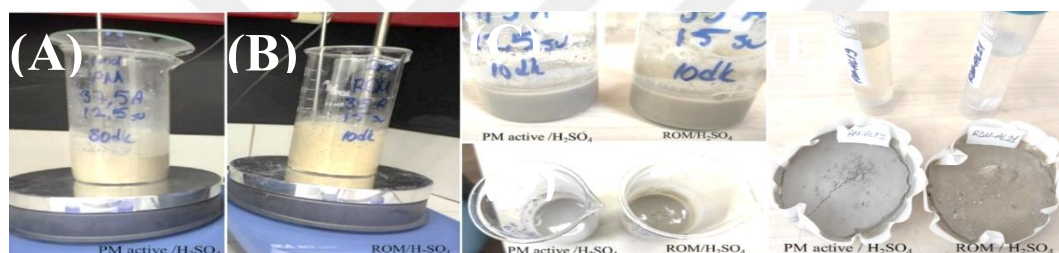


Figure 3.16: Acid leaching behaviour of activated powder vs. ROM (Left is PM active powder and right is ROM in figures).

As observed in Fig. 3.16(c–e), the PM-activated powder exhibits a greyish appearance during leaching, whereas the filtrate becomes yellowish after filtration. In contrast, the ROM sample displays the opposite behaviour. As shown in Table 3.21, the PM-activated powder was leached with $0.75 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$, while the ROM sample was leached with $1.45 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$. Under these conditions, Fe(III) species entering solution under PM conditions (approx. pH 5–8) rapidly undergo hydrolysis to form poorly soluble ferric hydroxide/oxyhydroxide colloids ($\text{Fe(OH)}_3/\text{FeOOH}$); free ionic Fe(III) is thermodynamically stabilised primarily under strongly acidic media (pH < 3) (Hem, 1959; Health Canada, 2020). These hydrolysis/complexation products can impart a yellow–amber hue to the liquid; however, if samples are not immediately acidified to pH < 2 prior to analysis, such colloids are not counted within the “dissolved Fe” fraction and the measured Fe may be reported as low/not detected (LibreTexts, 2023). And, as commonly recommended in Standard Methods and EPA Method 200.8, samples should be preserved immediately at pH < 2 to quantify dissolved metals

(APHA, 2017; U.S. EPA, 1994). Under ROM conditions, the lower pH increases the solubility of Fe and Al, while the concurrent reaction of carbonates with H_2SO_4 yields gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$); the intrinsically white gypsum and light scattering by fine crystals (Tyndall effect) render the filtrate opalescent/white (Booth et al., 1997; Encyclopaedia Britannica, 2025). This framework consistently explains the observations that the PM filtrate appears yellow, although Fe is not detected, whereas the ROM filtrate is white, while Fe/Al are measurable (Hem, 1959; Health Canada, 2020).

3.2.3 Characterization of powders activated by different mechanical activators

The XRD, FTIR, and EDS/EDX analyses of the products activated under optimum conditions using different mechanical activation devices, along with the untreated material for comparison, are presented in Figures 3.15, 3.16, and 3.17, respectively.

3.2.3.1 XRD analysis

Figure 3.15 presents the XRD patterns of products activated under optimum conditions using different mechanical activation devices, alongside the untreated material for comparison. As seen in Figure 3.15, the peaks corresponding to clinochlore, tinalconite, illite, muscovite, and dolomite in the untreated material either decreased in intensity or shifted (e.g., dolomite), while some peaks, such as those of clinochlore, disappeared completely. Additionally, the products activated with the stirred mill and the planetary mill exhibited similar XRD patterns, indicating comparable effects on the crystalline structure under the applied activation conditions.

3.2.3.2 FTIR analysis

Figure 3.16 presents the FTIR patterns of active powders obtained under optimum conditions using different mechanical activation devices, compared to the untreated (raw) material.

As shown in Figure 3.16, mechanical activation caused a reduction or complete disappearance of the O–H stretching peaks related to crystalline and adsorbed water, as well as the B–O–H, B–O/C–O, and CO_3 bands. These structural changes were more pronounced in the stirred mill than in the planetary mill, indicating a greater degree of alteration in the material's structure under the applied activation conditions.

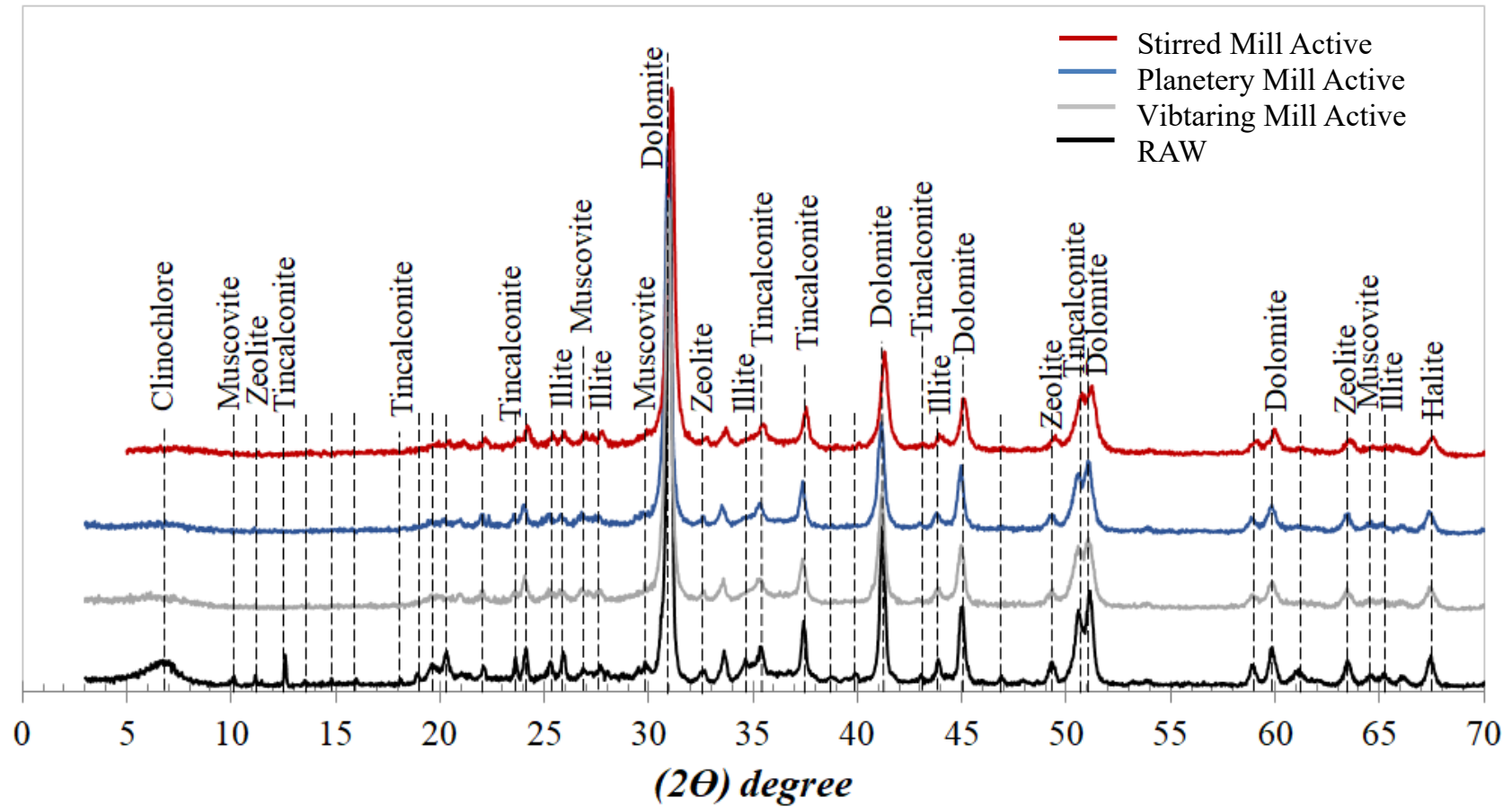


Figure 3.17: XRD patterns of powders activated under optimum conditions using different mechanical activation devices.

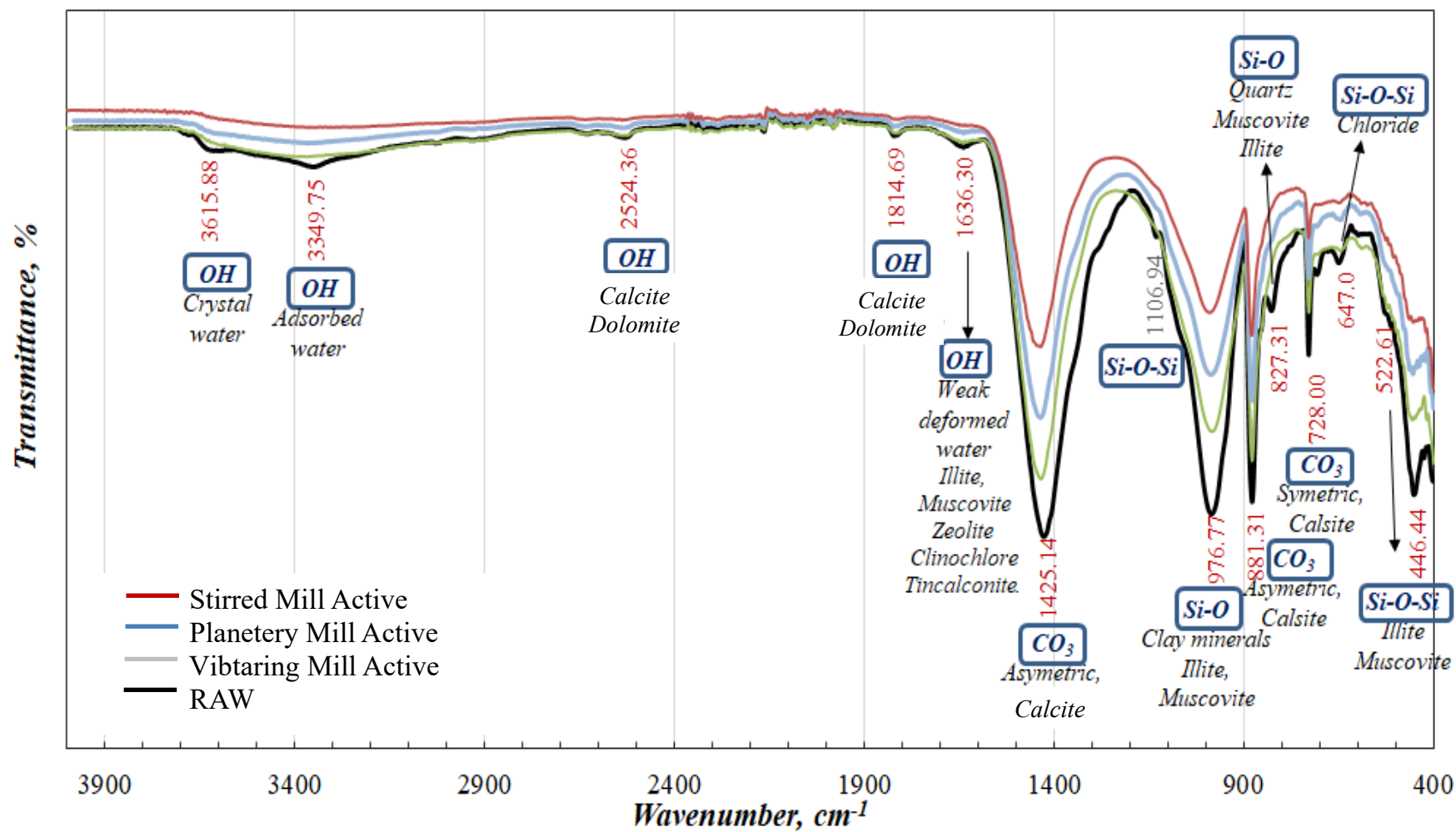


Figure 3.18: FTIR patterns of powders activated under optimum conditions using different mechanical activation devices.

3.2.3.3 EDS/EDX analysis

Figure 3.19 shows the surface morphology (EDS/EDX) of products activated under optimum conditions using different mechanical activation devices, compared to the raw material. As seen in Figure 3.19, mechanical activation caused changes in the distribution of ions on the material surface. In the application of planetary mill, Na^+ ions predominantly accumulated on the surface, whereas in the stirred and vibratory mills, the activation process led to the accumulation of a mixture of Na^+ , Ca^{2+} , and Mg^{2+} ions on the surface.

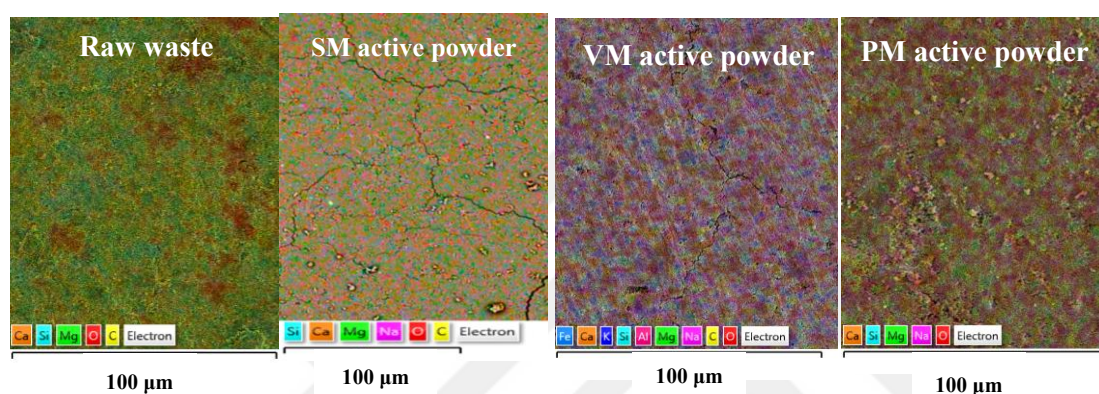


Figure 3.19: EDS/EDX images of powders activated under optimum conditions by different mechanical activation devices.

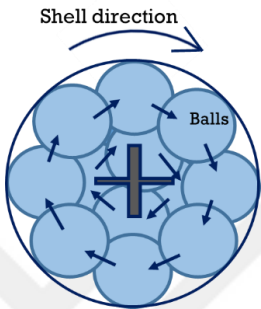
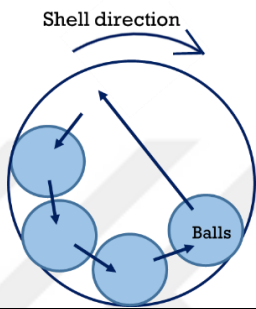
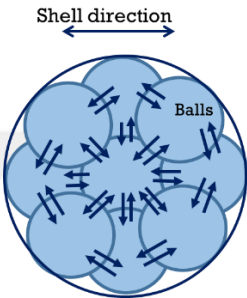
The data obtained from activation processes using different mechanical activation devices reveal differences in the resulting products, including structural changes, amorphization due to crystal structure breakdown, changes in particle size (either reduction or growth), surface roughening, and variations in the ions accumulated on the surface. These differences are reflected to some extent in the subsequent leaching processes, as the mechanical activation devices differ in their operating mechanisms. A comparative summary of these differences based on the activation device is presented in Table 3.9.

Both planetary and stirred mills are classified as high-energy mills but differ in their operating principles. In planetary mills, grinding jars mounted on a rotating central disk simultaneously revolve around their axes and the central axis. This complex motion generates high-energy impact and friction forces. Centrifugal acceleration in such mills can reach up to 50 g (gravitational acceleration) (Baláž, 2008).

In vibrating mills, energy is transmitted to the grinding media (usually balls) through vibrational motion applied to the chamber, with grinding or activation occurring

mainly through impact mechanisms. In contrast, stirred mills have a stationary grinding chamber while a rotating agitator transfers energy to the grinding media. Energy transfer in stirred mills primarily occurs through shear and attrition forces.

Table 3.9: Comparison of mechanical activation devices.

Feature	Stirred Mill	Planetary Mill	Vibrating Mill
	Medium–High (via rotating impeller shaft)	Very High (combined centrifugal and rotational motion; >50 g)	High (via high-frequency vibrations and dynamic impacts)
Energy Transfer			
Main Mechanism	Shear, impact, compression	Strong impact, friction, high centrifugal force	Impact, friction, resonance-induced collisions
Activation Efficiency	Moderate (requires longer grinding time)	Very High (rapid amorphization possible in minutes)	High (effective surface activation)
Collision frequency	High	Moderate-High	Very high
Energy density	Medium-High (depending on impeller speed and media)	High (>50 g acceleration in typical setups)	Medium
Crystal Structure Alteration (Amorphization)	Moderate	Very High	High
Surface Area Increase	Slow but steady increase	Rapid increase	Fast increase
Operational Scalability	Suitable for pilot and industrial scale	Mostly laboratory scale	Lab to pilot scale
Post-activation Reactivity	Moderate to High	Very High	High

Similar to vibrating mills, planetary mills generate very high impact energy, which leads to amorphization, reduction in crystal size, and even mechanochemical reactions. In contrast, stirred mills primarily rely on shear forces and moderate impact energy, making them more suitable for surface activation and fine grinding rather than complete mechanochemical transformations.

When considering the energy transferred per unit mass of material, planetary mills outperform stirred mills. However, from a processing capacity standpoint, stirred mills have an advantage for large-scale operations.

3.2.4 Dissolution of mechanically activated products

3.2.4.1 Water leaching in the presence/absence of salt

Water leaching on raw (untreated) material

To better understand the effect of mechanical activation, dissolution experiments were conducted on untreated solid waste (raw) samples (without mechanical activation) at dissolution temperatures of 25 °C, 50 °C, and 80 °C, with and without salt addition, and leaching durations ranging from 60 to 120 minutes (liquid/solid ratio: 5). The comparative results are presented in Table 3.10 and Figure 3.20.

Table 3.10: Leaching parameters of the raw material with and without salt addition.

	Salt Addition (%)	Leach temp (°C)	Leach time (min)	Li Conc. (ppm)	Leach Rec. (%)
ROM-@25°C	0	25	120	21.9	12.17
ROM-@50°C	0	50	120	22.1	12.28
ROM-@80°C	0	80	60	23.7	13.17
ROM-@25°C (+salt)	10	25	120	19.2	10.67
ROM-@50°C (+salt)	10	50	120	19.7	10.94
ROM-@80°C (+salt)	10	80	60	22.5	12.50

According to the findings, without salt addition, lithium recovery ranged between 12.17% and 13.17% after 120 min of leaching at temperatures between 25 °C and 80 °C, with lithium concentration in the solution varying from 21.9 to 23.7 ppm. In contrast, experiments with 10% salt addition (NaCl) showed lower recovery and lithium concentrations compared to the salt-free leaching. For instance, in the Rom-25 sample (rom defines the raw waste sample), lithium recovery decreased from 12.17% to 10.67%, and lithium concentration dropped from 21.9 ppm to 19.2 ppm.

These results indicate that direct salt addition without mechanical activation does not effectively promote ion exchange of lithium ions within the matrix structure with Na⁺, limiting the ion exchange mechanism. Therefore, salt addition alone does not enhance lithium solubility in the run-of-mine material, highlighting the importance of pretreatments such as mechanical activation to improve leaching efficiency.

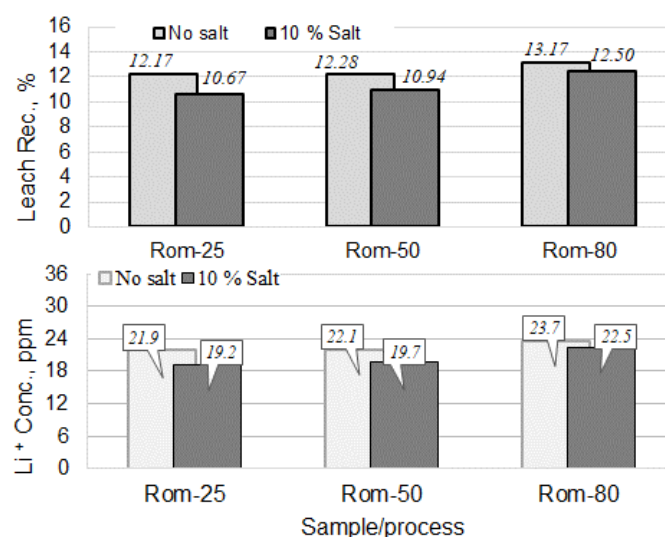


Figure 3.20: Lithium dissolution efficiency and ion concentrations in leaching of raw material with and without salt addition.

Even without mechanical activation and salt addition, the raw material achieved lithium dissolution efficiencies of 12–13% through hot water leaching. This can be attributed to several factors, the most significant being the lithium content in the main process solution circulating within the plant. The primary circulating solution in the plant contains lithium at concentrations of 300–350 ppm. After hot water leaching of the raw boron ore, the undissolved solid residues are separated as sludge, which retains some of the main solution. During storage and drying of this sludge, lithium ions remaining in the solid waste can re-dissolve into the solution upon subsequent hot water treatment.

The fact that lithium dissolution efficiencies remain around 10–12% in the water leaching of unactivated solid waste—even with salt addition—indicates that no significant isomorphic substitution occurs between Na^+ and Li^+ ions within the solid structure.

Furthermore, the alkali ions, Fe^{3+} , Al^{3+} , and B_2O_3 contents transferred into the solution during water leaching of the untreated material, with and without salt addition, are presented in Figure 3.21.

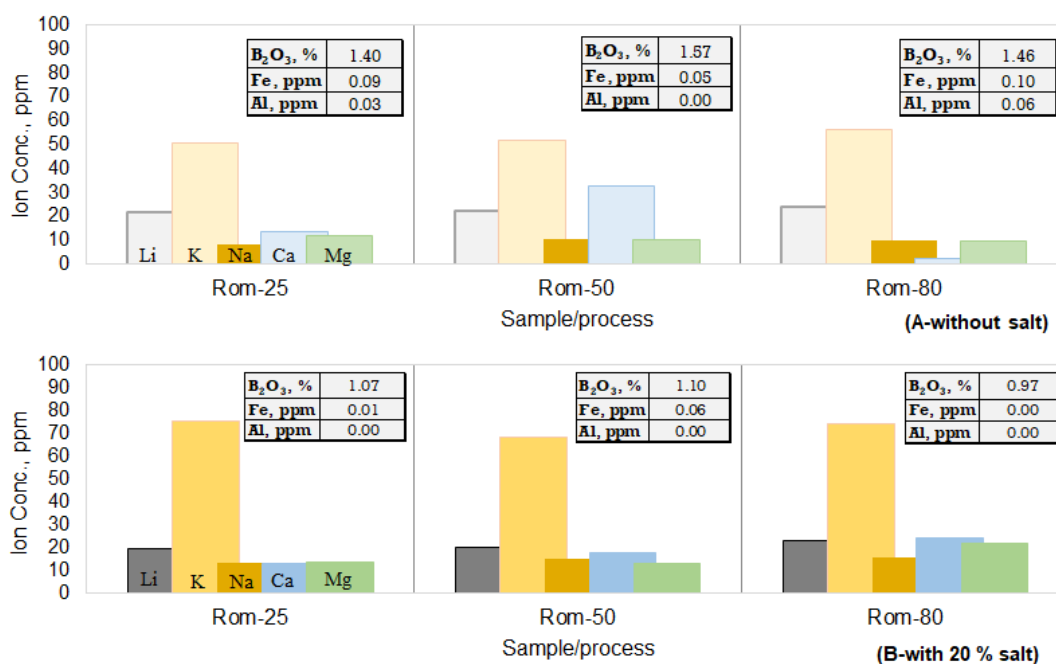


Figure 3.21: Dissolution tendency of other ions in salted/unsalted leaching processes of the raw material (Na⁺ ion *1000) A-without B-with salt should be for all.

As observed in Figure 3.21, an extremely high concentration of Na⁺ ions (10,000–14,000 ppm) released into the solution, likely originating from halite minerals present in the material or from the PAC (Polyacrylamid) flocculant used during solid-liquid separation at the plant. Concentrations of Ca²⁺ and Mg²⁺ ions were below 20 ppm, while K⁺ ion concentrations ranged between 50 and 70 ppm. Another ion dissolved into the solution during water leaching of the raw solid waste was boron (probably in B₂O₃²⁻ form), believed to originate from a boron mineral that remained undissolved during the boron leaching process that exhibited water-soluble properties.

Water leaching of mechanically activated powder

Salt addition in mechanical activation/leaching

As stated in the Tesla patent, approximately 10% salt by sample weight is added in mechanical activation combined with water leaching to facilitate a substitution reaction with lithium. Preliminary tests were carried out to determine whether the salt should be added during mechanical activation or during the water leaching stage.

Lithium concentrations and recovery efficiencies obtained from material activated in a planetary mill at stirring speeds ranging from 500 to 2000 rpm, then leached at 80 °C for 120 min (when salt was added during activation) or for 60 min (when salt was

added during leaching), either without salt or with 20% salt addition, are presented in Table 3.11 and Figure 3.22.

Table 3.11: Leaching parameters of salted/unsalted samples ground in planetary mill.

	Shaft Speed, (rpm)	Leach Temp. (°C)	Leach Time, (min)	Li Conc. (ppm)	Rec., (%)
Salt in Mechanical Activation	500	80	60	18.63	10.64
	750	80	60	34	20.07
	1000	80	60	56.8	32.45
	1250	80	60	87.9	50.22
	1500	80	60	88.6	50.62
	1750	80	60	73.9	42.22
	2000	80	60	84.8	48.45
Salt in Leaching	500	80	120	26.2	14.97
	750	80	120	32.00	19.14
	1000	80	120	52.00	29.71
	1250	80	120	85.00	48.57
	1500	80	120	101.00	57.71
	1750	80	120	91.00	50.56
	2000	80	120	90.90	51.94

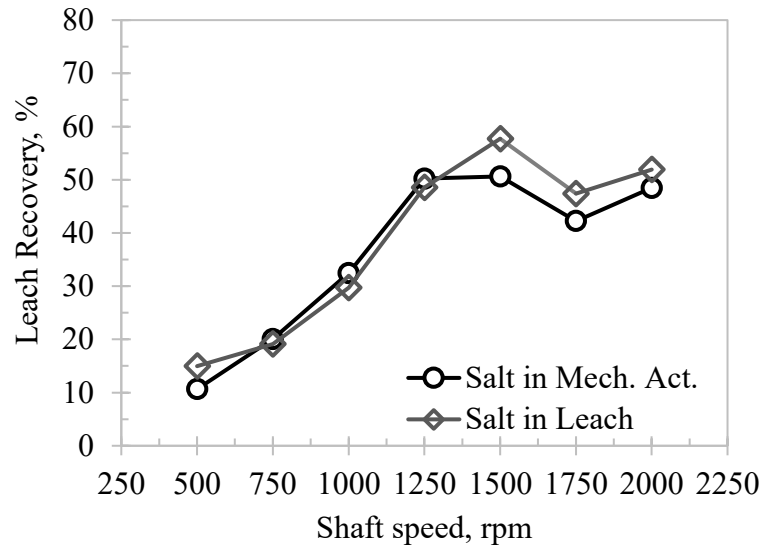


Figure 3.22: Salted/unsalted leaching processes of the active powders in the planetary mill.

As seen in Table 3.11 and Figure 3.22, adding salt during the leaching stage is more advantageous for achieving higher leaching efficiencies. This is especially true for mechanical activation performed at the optimum stirring speed of 1500 rpm, where salt addition during leaching increased leaching efficiency by approximately 7%.

The ball-to-powder ratio in mechanical activation is a critical parameter. It was found that adding salt during mechanical activation reduces the effective ball-to-powder

weight ratio, with part of the activation energy consumed in grinding the salt, which consequently lowers the leaching efficiency.

Optimization of leaching conditions after mechanical activation

As a result of the optimization experiments on mechanical activation conditions, the optimum operating parameters for each mechanical activation device are summarized in Table 3.12. Based on these optimized mechanical activation settings, studies on the optimization of leaching conditions have been conducted and are presented in this section. The variable parameters examined during leaching optimization include salt concentration, leaching time, leaching temperature, and liquid-to-solid ratio.

Table 3.12: Optimization of mechanical activation conditions; the most suitable operating conditions for each mechanical activation device.

	Vcell (cm ³)	Ball Mass, (g)	Sample Mass, (g)	BPR	Mech. Act. Time (min)	Shaft Speed (rpm)
Planetary Mill	300	280	15	18.67	150	1500
Stirred Mill	750	1100	15	68.67	150	550
Vibrating Mill	750	2000	15	133.3	150	-

Effect of salt concentration on leaching efficiency

Pickle salt was used as the source of Na⁺ ions, which act as exchangeable cations in lithium ion displacement reactions. The experimental results on the effect of salt concentration on leaching efficiency are presented in Figure 3.23.

The experiments showed that, even without salt addition, significant lithium dissolution was achieved through hot water leaching after mechanical activation, with leaching efficiencies of 53.37%, 41.41%, and 34.1% for stirred, planetary, and vibratory mills, respectively. This is attributed to the presence of Na⁺ ion sources (originating from halite or flocculants used in the plant) within the material structure.

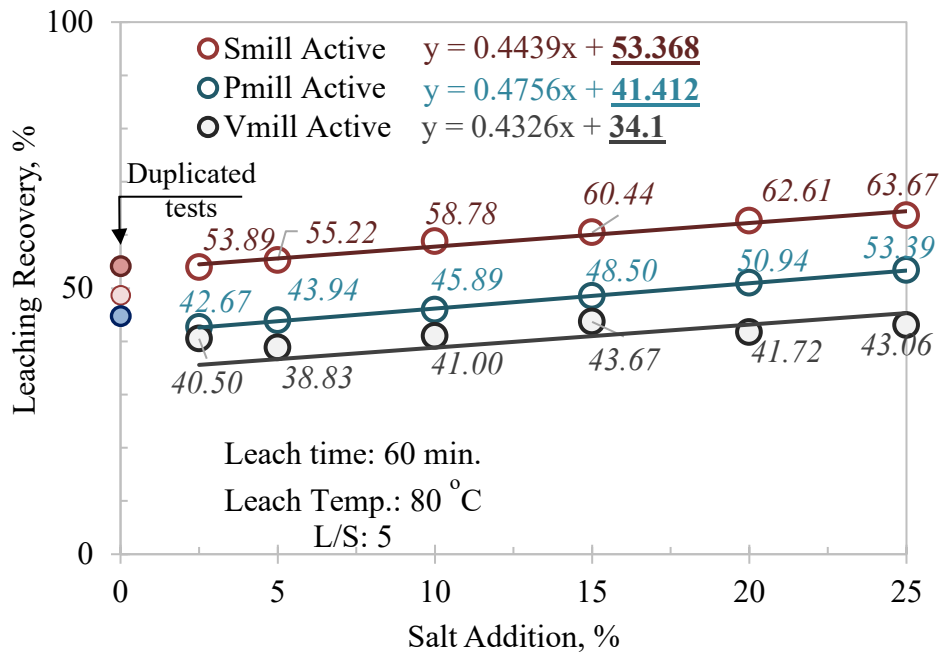


Figure 3.23: The effect of salt addition on leaching efficiency in water leaching of mechanically activated solid waste samples.

However, 25% salt addition is considered a high dosage, and the excessive Na^+ ion concentration in the leaching solution may cause problems in subsequent lithium recovery processes. Therefore, a salt concentration of around 10% was chosen as optimal. At 10% salt addition, lithium leaching efficiencies of 58.78%, 45.89%, and 41.00% for the stirred, planetary, and vibratory mills, respectively were obtained.

Effect of leaching time on leaching efficiency

The effect of leaching time on leaching efficiency is presented in Figure 3.24. As clearly shown in Figure 3.24, leaching time does not significantly influence leaching efficiency; high dissolution rates can be achieved even with very short leaching durations of 3–5 min. This behavior was consistent across all solid waste products activated by different mechanical activation devices. Given that 3–5 minutes is a very short period for a typical chemical reaction, it is considered that the dissolution process during leaching primarily occurs through a cation exchange mechanism.

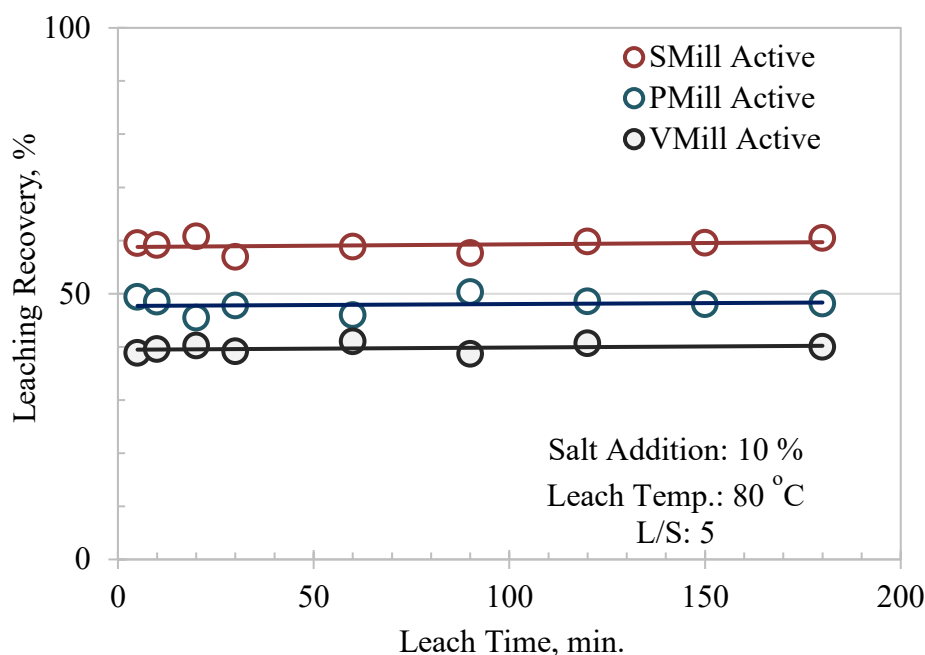


Figure 3.24: The effect of leaching time on leaching efficiency in water leaching of mechanically activated waste sample.

Effect of leaching temperature on leaching efficiency

It is well known that temperature acts as a catalyst in chemical reactions. Therefore, a series of tests was conducted to evaluate the effect of leaching temperature on leaching efficiency, and the results are shown in Figure 3.25.

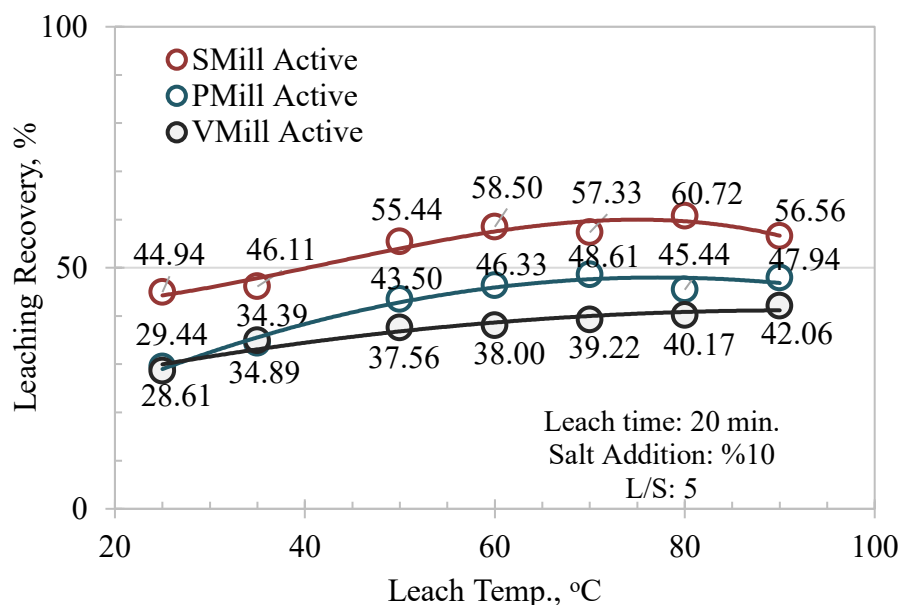


Figure 3.25: Effect of leaching temperature on leaching efficiency during aqueous leaching of mechanically activated solid waste samples.

As shown in Figure 3.25, increasing the leaching temperature from room temperature to 60°C significantly improved the leaching efficiency for all activated products processed by different mechanical activation devices. However, leaching at temperatures above 60°C resulted in nearly the same efficiency. Thus, the optimum operating temperature was determined to be 60°C. Leaching conducted at this temperature yielded 14–16% higher efficiencies compared to those performed at room temperature. The recommended working temperature of 65°C in the Tesla patent aligns closely with the optimum temperature identified in this study.

Effect of liquid/solid ratio on leaching efficiency

In leaching processes, the liquid-to-solid ratio, or the solids content in the pulp, directly influences both leaching efficiency and the capacity of the leaching unit. Therefore, a series of experiments was conducted to investigate the effect of the liquid-to-solid ratio on leaching efficiency. The results, including both leaching efficiency and lithium ion concentration in the solution, are presented in Figures 3.26 and 3.27, respectively.

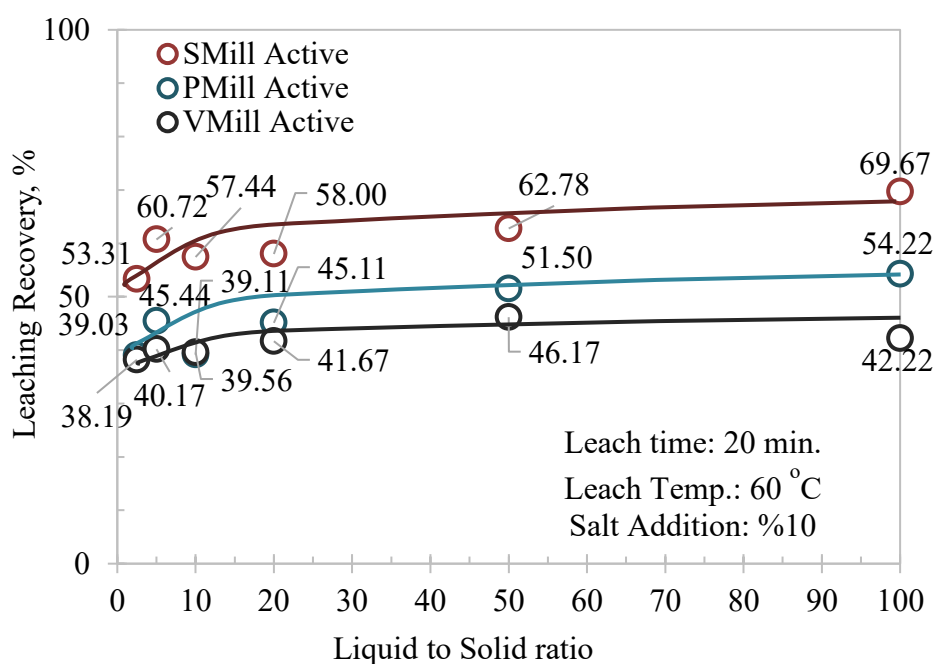


Figure 3.26: Effect of liquid/solid ratio on leaching efficiency during aqueous leaching of mechanically activated solid waste samples.

Consistent with previous tests on salt concentration, leaching time, and temperature, products activated by different devices showed similar dissolution behavior. Leaching efficiency increased at higher liquid-to-solid ratios, reaching approximately 70% at a 100:1 ratio for the product activated in the stirred mill. However, considering industrial

applications and plant capacity, operating at a 5:1 liquid-to-solid ratio was deemed more practical, and evaluations were made based on this ratio.

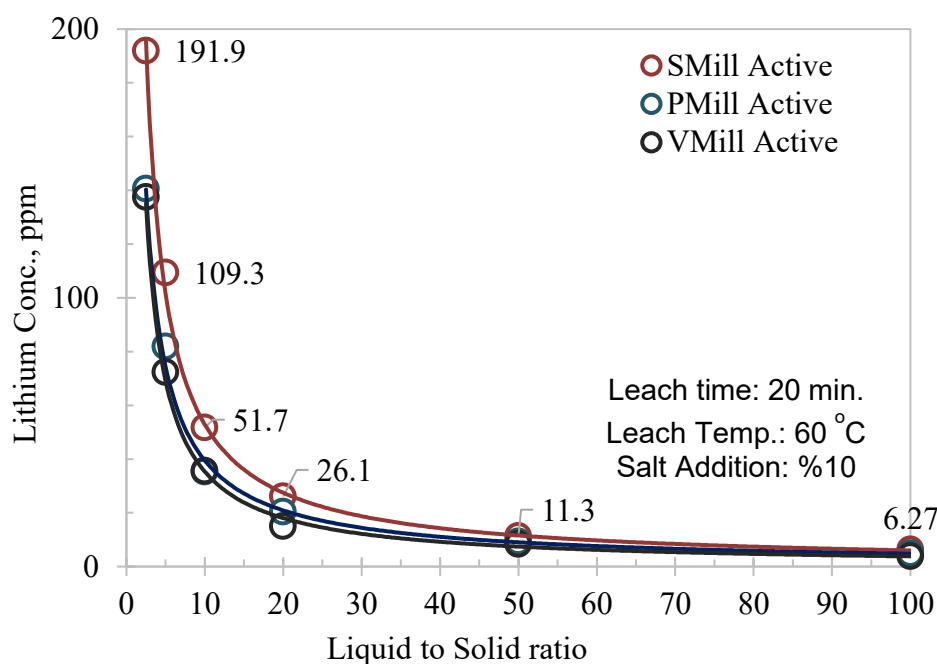


Figure 3.27: Effect of the liquid-to-solid ratio on the concentration of lithium ions transferred into the solution during water leaching of mechanically activated solid waste sample.

Leaching in seawater medium

The limited availability of freshwater resources and the need for sustainable approaches provided an incentive to conduct leaching experiments with Mediterranean seawater using mechanically activated samples in a stirred mill. Leaching was performed at 80°C L/S ratio of 5 and a stirring time of 20 min, both without additional salt and with 10% salt added in the seawater environment. This section evaluates the lithium recovery efficiencies obtained and explores the potential of seawater as an alternative to both freshwater and supplementary salt.

Table 3.13 presents the average concentrations of major ions in Mediterranean seawater, compiled from two key literature sources (Besson et al., 2013; Hainbucher et al., 2020). These data are essential for assessing the concentrations of ions such as Mg^{2+} and Ca^{2+} in the saltwater leaching experiments following mechanical activation.

Since distilled water was used in most of the experimental studies, the ions required for ion exchange were supplied through the addition of salt or acid. As presented in Table 3.13, the dissolution behavior of the activated material was also examined in the

presence of certain ions naturally found in seawater. The results are presented in Table 3.14. Seawater leaching was applied to products activated in a stirred mill at 550 rpm for 150 min, and these results were compared with those from experiments conducted using distilled water, as summarized in Table 3.14 and Figure 3.28.

Table 3.13: Mineral composition of seawater from the Mediterranean region.

Ion	Concentration	Source
Mg ²⁺	54 .10 ⁻³ mol/L (~1,310 mg/L)	Besson et al. (2013)
Ca ²⁺	10.5 .10 ⁻³ mol/L (~420 mg/L)	Besson et al. (2013)
Na ⁺	455.4 . 10 ⁻³ mol/L (~10,480 mg/L)	Besson et al. (2013)
K ⁺	10.2 . 10 ⁻³ mol/L (~400 mg/L)	Besson et al. (2013)
Cl ⁻ , SO ₄ ²⁻ and others	≈ Total: 35 g/kg	Hainbucher et al. (2020)

Table 3.14: Lithium recovery yields (%) and lithium concentrations using seawater and pure water leaching (Leaching temperature: 80 °C, Leaching time: 20 minutes (seawater) and 60 min (pure water), liquid-to-solid ratio: 5:1).

	Salt Addition (%)	Li Conc, (ppm)	Li Rec., (%)
Seawater (Saline water)	0	113.0	62.78
Seawater (Saline water)	10	112.70	62.61
Distilled water	0	84.96	47.20
Distilled water	10	97.24	54.02
Distilled water	20	112.7	62.61
Distilled water	25	114.6	63.67

According to the results presented in Figure 3.26, leaching experiments conducted with seawater and pure water demonstrate that seawater provides significantly higher lithium content (ppm) and leaching efficiency (%) compared to pure water.

Specifically, in the absence of additional salt, leaching efficiency reached 62.78% with seawater, while it was only 47.20% with pure water. Adding 10% salt to pure water increased lithium dissolution, raising efficiency to 54.02%; however, in seawater, which already has high salinity, additional salt had no significant effect. Similar efficiencies to those obtained with seawater were achieved using pure water containing 20–25% salt.

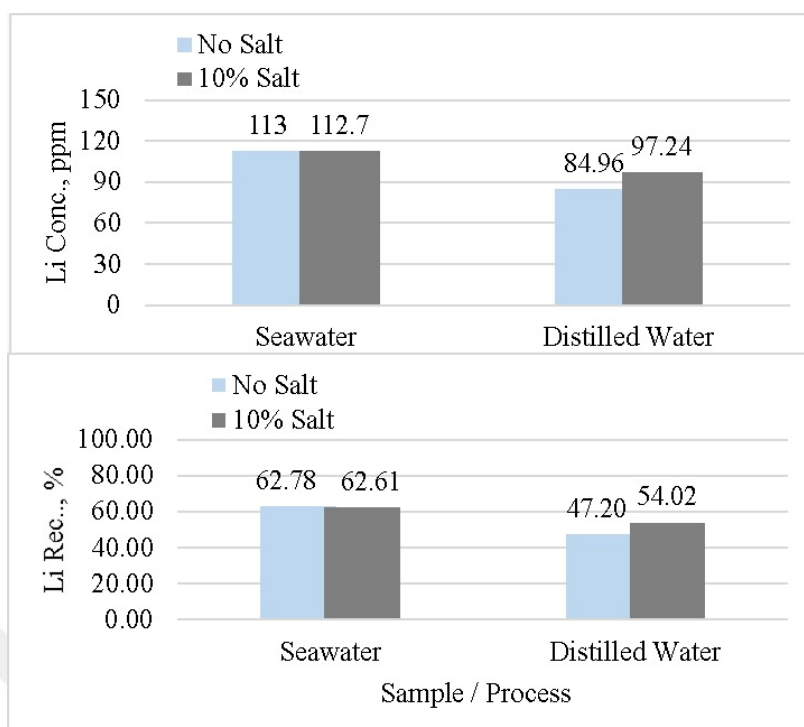


Figure 3.28: Lithium leaching efficiencies and lithium contents in solution for seawater/distilled water leaching.

These findings indicate that the natural ionic composition of seawater (particularly Na^+ , Mg^{2+} , Ca^{2+} , and Cl^-) supports lithium dissolution during leaching, eliminating the need for extra salt. This can reduce chemical consumption and help conserve freshwater resources. Therefore, seawater presents an environmentally friendly and sustainable alternative for lithium leaching.

Ions released alongside lithium in mechanical activation assisted water leaching processes

The solid waste from the Kirka Boron Processing Plant used in the experimental studies has a complex structure, predominantly composed of dolomite. It also contains various clay minerals and boron derivatives. Therefore, during mechanical activation of this material and subsequent water leaching processes, the presence of other alkali and boron ions alongside lithium significantly influences the selective recovery of lithium from the solution. For this reason, the analysis of ions released into the solution during water leaching of products using stirred and planetary mills is presented in Table 3.15.

Table 3.15: Ions Released into Solution Together with Lithium After Leaching (With and Without Salt Addition).

	Shaft Speed, (rpm)	Salt add., (%)	Leach Temp, (°C)	Leach Time, (min)	Li Conc., (ppm)	Rec., (%)	K (ppm)	Na (ppm)	Ca (ppm)	Mg (ppm)	Fe (ppm)	Al (ppm)	B ₂ O ₃ (ppm)
PLANETARY MILL	0	0	80	60	23.2	12.88	56.00	9759	2.50	9.80	0.10	0.06	14612
	500	0	80	60	22.5	12.50	78.36	7821	46.56	16.02	0.42	0.72	11520
	750	0	80	60	33.4	18.56	104.25	7190	34.35	4.65	0.06	0.13	10990
	1000	0	80	60	47.4	26.33	103.35	6498	27.09	6.63	0.19	0.25	10540
	1500	0	80	60	80.5	44.72	114.11	4431	19.70	7.03	0.18	0.07	9492
	2000	0	80	60	84.4	46.89	118.45	4168	16.58	8.85	0.21	0.08	9616
	0	20	80	120	22.5	12.50	74.01	15505	23.80	21.33	0.00	0.00	9647
	500	20	80	120	26.2	14.97	130.29	17357	12.60	7.87	0.03	0.00	8367
	750	20	80	120	32.00	19.14	165.41	14473	25.07	5.55	0.01	0.00	5810
	1000	20	80	120	52.00	29.71	200.93	16772	20.32	4.26	0.02	0.00	7300
	1500	20	80	120	101.00	57.71	252.05	19421	13.24	5.52	0.03	0.00	8390
	2000	20	80	120	90.90	51.94	226.37	17538	18.16	7.72	0.02	0.00	7680
STIRRED MILL	0	0	80	60	23.7	13.17	56.00	9759	2.50	9.80	0.10	0.06	14612
	30	0	80	60	42.6	23.67	98.90	4679	28.92	7.04	0.12	0.04	10600
	60	0	80	60	53.9	29.94	96.60	4392	19.14	7.51	0.17	0.08	9736
	90	0	80	60	69.6	38.67	111.16	4184	13.53	9.22	0.20	0.10	9725
	120	0	80	60	85.3	47.39	128.98	4038	10.00	8.44	0.12	0.03	9220
	150	0	80	60	87.6	48.67	145.02	6317	12.02	14.72	0.07	0.00	9670
	0	10	80	60	22.5	12.50	74.01	15505	23.80	21.33	0.00	0.00	9647
	30	10	80	60	50.25	30.89	159.80	11922	32.71	5.94	0.00	0.00	9548
	60	10	80	60	79.7	44.28	195.67	13425	20.88	8.75	0.06	0.00	10718
	90	10	80	60	85.8	47.67	191.55	11871	16.10	13.21	0.06	0.00	9270
	120	10	80	60	91.2	50.67	202.57	10997	15.37	14.55	0.06	0.00	8100
	150	10	80	60	102	56.67	224.58	11111	12.20	18.28	0.05	0.00	7044

Evaluation of Table 3.15 shows that a significant amount of Na ions entered the solution even without salt addition. Furthermore, as the intensity of mechanical activation increased, the dissolution of Ca and Mg ions was suppressed. Under optimal conditions, Ca ion concentrations remained below 20 ppm, while Mg ion concentrations stayed below 10 ppm. The particularly low Mg levels indicate that mechanical activation followed by water leaching is more advantageous than acid leaching. Meanwhile, K ion concentrations were relatively higher compared to other alkali ions (approximately 250 ppm), suggesting that clay minerals such as illite or muscovite were structurally disrupted by mechanical activation. Figure 3.27 illustrates the variation of alkali and boron ions in the solution relative to lithium concentration.

As shown in Figure 3.29, a linear correlation exists between K^+ and Li^+ ions, indicating that lithium concentration in the solution increases proportionally with potassium ion concentration. This suggests that lithium originates from illite or muscovite, which are potassium-bearing minerals. In contrast, the concentrations of other alkali and boron ions decrease as lithium concentration rises, indicating competition between these ions and Li^+ during the leaching process.

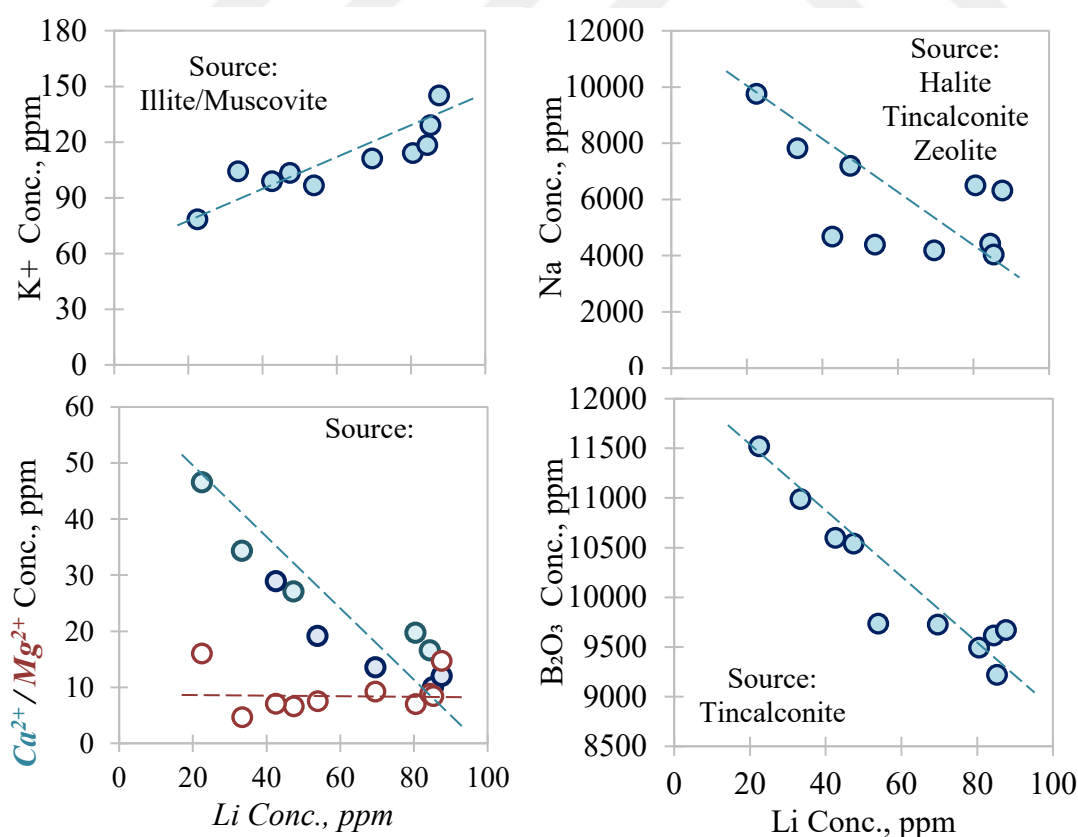


Figure 3.29: Lithium extraction efficiencies and lithium concentrations in solution.

Repeatability of tests performed with water leaching

After optimizing the mechanical activation and water leaching experimental conditions, repeatability tests were conducted solely on the mechanically activated product obtained using the stirred mill. These tests were performed under both 10% NaCl salt-added and salt-free conditions to assess the consistency of leaching efficiencies and lithium ion concentrations in the solution. The results are presented in Table 3.16.

Table 3.16: Lithium concentration and recovery consistency in repeated leaching tests under 0% and 10% NaCl conditions.

	Mech. Act. Time (min)	Shaft Speed (rpm)	Salt Add., (%)	L/S	Leach Temp., (°C)	Leach Time, (min)	Li Conc., (ppm)	Li Rec. (%)
Water/Saline water Leaching	150	550	0	5	80	60	86.10	47.83
	150	550	0	5	80	60	87.30	48.50
	150	550	0	5	80	60	85.40	47.44
	150	550	0	5	80	60	84.30	46.83
	150	550	0	5	80	60	81.70	45.39
	150	550	10	5	80	60	93.70	52.06
	150	550	10	5	80	60	99.70	55.39
	150	550	10	5	80	60	95.60	53.11
	150	550	10	5	80	60	97.30	54.06
	150	550	10	5	80	60	99.90	55.50

For these repeated experiments carried out under identical operational conditions, the averages and standard deviations of the solution lithium concentrations (ppm) were calculated to evaluate process reliability, as shown in Table 3.17 and Figure 3.30.

The standard deviation for the sample data was calculated using the classical formula:

$$s = \sqrt{\frac{\sum_{i=1}^n (x_i - \bar{x})^2}{n - 1}}$$

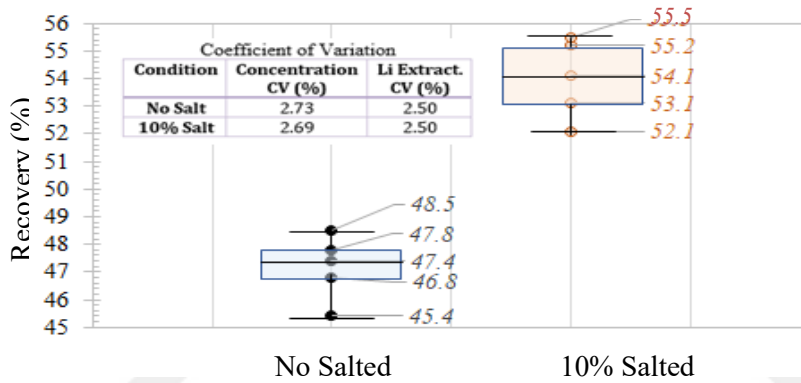
Where s is the sample standard deviation, n is the number of observations, x_i represents each individual observation, and $\bar{x}$ is the sample mean (NIST/SEMATECH, 2012; Montgomery & Runger, 2014).

These results present the average lithium concentrations (ppm) and standard deviations obtained from repeated leaching experiments with 0% and 10% NaCl. In the group with 10% NaCl addition, the average lithium concentration was 93.84 ppm, approximately 10% higher than the 85.24 ppm average in the salt-free group.

Table 3.17: Mean and standard deviation of measurement results, for Li contents.

Experimental Group	Measurements (Li, ppm)	Average (ppm)	Standard Deviation (ppm)
Without salt added	86.10, 87.30, 85.40, 84.30, 83.10	85.24	1.62
With 10% NaCl added	90.20, 92.30, 95.00, 97.80, 93.90	93.84	2.86

Additionally, the low standard deviation values in both groups (1.62 ppm and 2.86 ppm) indicate that the experimental results are consistent and reproducible. This low variation in repeated tests supports the reliability of the methodology.

**Figure 3.30:** Reproducibility tests, for Li recovery.

Development of the mechanical activation + water leaching process flow diagram

Following detailed mechanical activation and water leaching experiments, a process flow diagram was developed based on the material's general structure and its behavior during mechanical activation and leaching. This diagram is presented in Figure 3.31.

As shown in Figure 3.31, it is proposed that water-soluble boron ions in the solid waste from the Kirka Boron Plant can be removed or recovered primarily through stepwise hot water washing even at temperatures as low as 50 °C. This step helps prevent the dissolution of boron ions during the subsequent lithium leaching stage.

Alternatively, the solid waste disposed of in the landfill area can be air-dried and then mechanically activated using an industrial-scale stirred mill. Subsequently, water leaching can be conducted either without salt or with up to 10% salt addition, achieving lithium recovery efficiencies of 50–65%. As previously noted, mechanical activation combined with water leaching can largely suppress alkali ion dissolution, keeping Mg ion concentrations below 20 ppm.

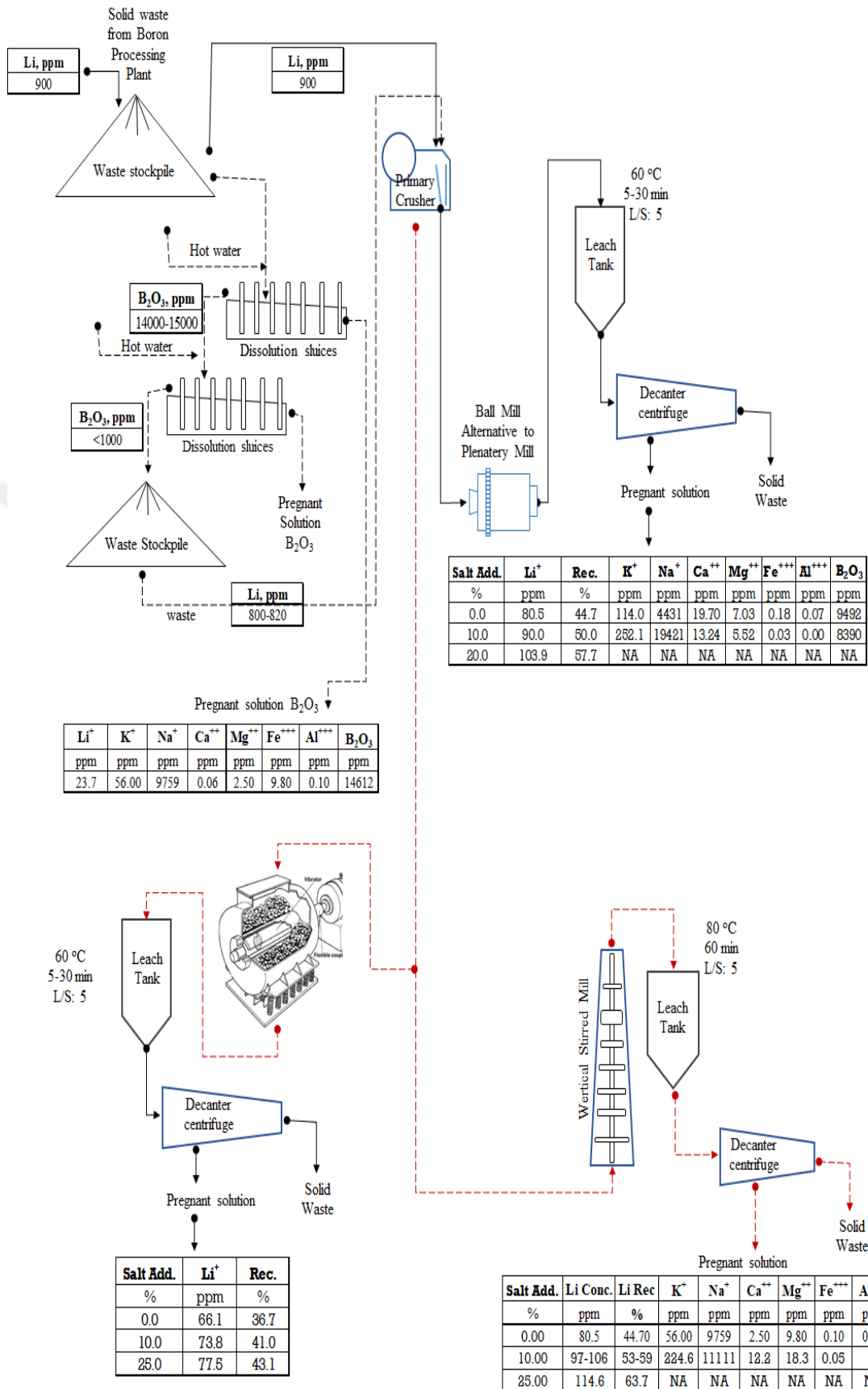


Figure 3.31: Proposed Process Flow Diagram of Mechanical Activation + Water Leaching for Lithium Recovery from Kirka Boron Plant Waste.

3.2.4.2 Acid leaching on mechanically activated powder

To optimize sulfuric acid (H_2SO_4) leaching conditions for the recovery of mechanically activated solid waste from the Kırka Boron Plant under optimum parameters, a series of leaching experiments was conducted. The variable parameters included acid concentration, leaching time, leaching temperature, and solid-to-liquid ratio (the latter only for samples activated using the stirred mill). The mechanical activation and leaching conditions for the raw (untreated) solid waste, as well as for samples processed with the planetary mill, stirred mill, and vibrating mill, are summarized in Tables 3.18, 3.19, and 3.20, respectively.

Table 3.18: Acid leaching test conditions, lithium recovery yields (%), lithium content, and solution pH for material ground in planetary mill.

Variable	Mech. Act.				Leaching					
	Act. Time (min)	Shaft Speed (rpm)	H ₂ SO ₄ , (mol/L)	L/S	Leach Temp (°C)	Leach time (min)	Li Conc., (ppm)	Rec. %	pH	
Planetary Mill	Acid Conc. Molar	150	1500	0.125	5	50	60	109.1	60.61	8.40
		150	1500	0.250	5	50	60	109.0	60.56	8.00
		150	1500	0.375	5	50	60	117.2	65.11	7.49
		150	1500	0.500	5	50	60	126.1	70.06	7.55
		150	1500	0.750	5	50	60	136.8	76.00	7.23
		150	1500	1.000	5	50	60	151.3	84.06	6.78
		150	1500	1.250	5	50	60	186.0	100.0	5.62
		150	1500	1.500	5	50	60	211.0	100.0	3.69
	Leach time	150	1500	0.750	5	50	10	135.0	75.00	7.33
		150	1500	0.750	5	50	30	123.5	68.61	7.36
		150	1500	0.750	5	50	60	136.8	76.00	7.23
		150	1500	0.750	5	50	90	133.0	73.89	7.48
		150	1500	0.750	5	50	120	135.5	75.28	6.94
		150	1500	0.750	5	50	150	132.0	73.33	7.47
	Leach Temp	150	1500	0.750	5	25	90	166.3	92.36	7.83
		150	1500	0.750	5	35	90	155.0	86.11	7.86
		150	1500	0.750	5	50	90	133.0	73.89	7.48
		150	1500	0.750	5	60	90	140.5	78.06	7.64
		150	1500	0.750	5	70	90	142.0	78.89	7.37
		150	1500	0.750	5	80	90	148.0	82.22	7.34
		150	1500	0.750	5	90	90	155.5	86.39	7.11

Table 3.19: Acid leaching test conditions, lithium recovery yields (%), lithium content, and solution pH for material ground in stirred mill.

	Variable	Mech. Act.			Leaching					
		Act. Time (min)	Shaft Speed (rpm)	H ₂ SO ₄ , (mol/L)	L/S	Temp, (°C)	Leach Time (min)	Li Conc, (ppm)	Rec. (%)	pH
Stirred Mill	Acid conc.	150	550	0.125	5	80	60	113.0	62.78	8.58
		150	550	0.250	5	80	60	121.3	67.36	8.34
		150	550	0.375	5	80	60	124.3	69.03	8.25
		150	550	0.500	5	80	60	129.8	72.08	8.10
		150	550	0.750	5	80	60	145.3	80.69	7.81
		150	550	1.000	5	80	60	159.5	88.61	7.45
		150	550	1.125	5	80	60	164.0	91.11	6.87
		150	550	1.250	5	80	60	180.5	100.0	6.58
	Leach time	150	550	0.600	5	80	10	139.8	77.64	7.97
		150	550	0.600	5	80	30	140.0	77.78	8.01
		150	550	0.600	5	80	60	135.0	75.00	8.00
		150	550	0.600	5	80	90	139.8	77.64	7.93
		150	550	0.600	5	80	120	135.0	75.00	8.02
	Leach Temp.	150	550	0.600	5	25	60	132.5	73.61	8.09
		150	550	0.600	5	40	60	134.5	74.72	8.11
		150	550	0.600	5	50	60	139.8	77.64	8.07
		150	550	0.600	5	60	60	135.0	75.00	8.00
		150	550	0.600	5	70	60	140.0	77.78	7.80
		150	550	0.600	5	80	60	141.5	78.61	7.67
		150	550	0.600	5	90	60	139.8	77.64	7.55
	Liquid to solid	150	550	0.600	2.5	80	60	231.0	64.17	7.76
		150	550	0.600	5	80	60	141.5	46.39	7.67
		150	550	0.600	10	80	60	83.5	73.89	7.00
		150	550	0.600	20	80	60	66.5	100.0	1.00
		150	550	0.600	50	80	60	28.0	100.0	<1
		150	550	0.600	100	80	60	19.0	100.0	<1

Table 3.20: Acid leaching test conditions, lithium recovery yields (%), lithium content, and solution pH for material ground in vibrating mill.

	Variable	Mech. Act. Time (min)	H ₂ SO ₄ , (mol/L)	L/S	Leach Temp., (°C)	Leach Temp., (°C)	Li Conc., (ppm)	Li Rec. (%)	pH
Vibrating Mill	Acid Conc., Molar	150	0.125	5	80	60	88.0	48.89	8.24
		150	0.250	5	80	60	95.5	53.06	8.07
		150	0.375	5	80	60	99.5	55.28	7.40
		150	0.500	5	80	60	111.7	62.06	7.65
		150	0.750	5	80	60	130.4	72.44	7.23
		150	1.000	5	80	60	165.0	91.67	7.33
		150	1.250	5	80	60	107.5	59.72	7.68
		150	0.75	5	80	10	136.3	75.7	7.21
	Leach Time	150	0.75	5	80	30	126.0	70.0	7.33
		150	0.75	5	80	60	130.4	72.4	7.41
		150	0.75	5	80	90	130.4	72.4	7.41
		150	0.75	5	80	120	106.8	59.3	7.30
		150	0.75	5	80	150	130.0	72.2	7.29
		150	0.75	5	25	60	130.0	72.2	7.83
	Leach Temp.	150	0.75	5	40	60	137.0	76.1	7.86
		150	0.75	5	50	60	119.0	66.1	7.48
		150	0.75	5	70	60	130.4	72.4	7.64
		150	0.75	5	80	60	97.0	53.9	7.37
		150	0.75	5	90	60	111.3	61.8	7.34

Effect of acid concentration on dissolution efficiency

In a series of experiments investigating the effect of acid concentration on dissolution efficiency, acid concentrations ranging from 0 to 2.0 mol/L were applied. The corresponding dissolution efficiencies and final solution pH values are presented in Figure 3.32.

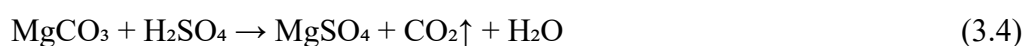
Lithium dissolution efficiency and final solution pH vary significantly among different process types, including ROM-AL (Run-of-Mine Acid Leaching), VM Act.-AL (acid leaching of powder activated in vibrating mill), PM Act.-AL (acid leaching of powder activated in planetary mill), SM Act.-AL (acid leaching of powder activated in stirred mill), and SM Act.-WL+AL (two-stage leaching of powder activated in vibrating mill: brine leaching followed by acid leaching). These differences impact both process efficiency and chemical sustainability.

In the ROM-AL process, where direct acid leaching was applied to the run-of-mine sample, lithium recovery showed limited improvement at low acid concentrations

(0.125–1.000 mol/L). However, at 1.250 mol/L, a marked increase in yield (32.89%) and a decrease in pH (to 5.81) were observed, indicating a critical threshold where dissolution accelerates. At acid concentrations of 1.500 mol/L and above, yield increased from 91.94% to 100%, while the pH dropped below 1, indicating near-complete dissolution and aggressive leaching conditions. However, such high acid doses must be carefully considered due to acid consumption and environmental impacts. From an optimization standpoint, the range of approximately 1.250–1.500 mol/L offers a balance of high yield and manageable pH.

For the PM-AL, VM-AL, and SM-AL samples activated by various mills, mechanical activation enhanced efficiency at lower acid concentrations, reducing the acid dose required to reach 100% efficiency. While 60–70% efficiency was achieved at 0.50 mol/L acid concentration across all activated samples, full efficiency (100%) was attained between 1.00 and 1.25 mol/L.

The most remarkable results were observed in the SM+WL+AL process; in this method, efficiency climbed to approximately 87.67% until the acid amount reached 1 mol/L. Afterwards, despite the presence of higher acid concentration, Li efficiency significantly decreased. On the other hand, the pH value was maintained at approximately 8.85 across all acid concentrations. This situation indicates that acid consumption during the process was minimal and that the alkaline environment was preserved, pointing to a highly sustainable process potential from an environmental perspective. This tendency of efficiency decrease after the optimum acid point has also been observed in previous studies on dolomitic and aluminosilicate-based clays (Obut et al., 2022; Zhong et al., 2024). Dolomitic clays contain significant amounts of CaCO_3 (calcite) and $\text{CaMg}(\text{CO}_3)_2$ (dolomite). When introduced into a sulfuric acid medium, it primarily reacts with these carbonates and is consumed, as illustrated in Equations (3.3) and (3.4):



As a result of these reactions, most of the acid is consumed before reaching the lithium-containing phases, leaving insufficient acid in the medium for effective lithium dissolution. This issue is commonly referred to in the literature as the "acid consumption problem" (Obut et al., 2022).

With increasing acid concentration, the amount of dissolved Ca^{2+} and Mg^{2+} ions in the solution also rises. These ions combine with sulfate ions to form soluble or insoluble phases such as CaSO_4 (gypsum). These phases can co-precipitate Li^+ ions, effectively removing them from the solution (Zhong et al., 2024).

Furthermore, in highly acidic environments, the aluminosilicate structure of clay minerals breaks down, leading to the formation of amorphous gel-like Al-Si phases in the solution. These gel phases adsorb Li^+ ions, further reducing their concentration in the leachate (Obut et al., 2022).

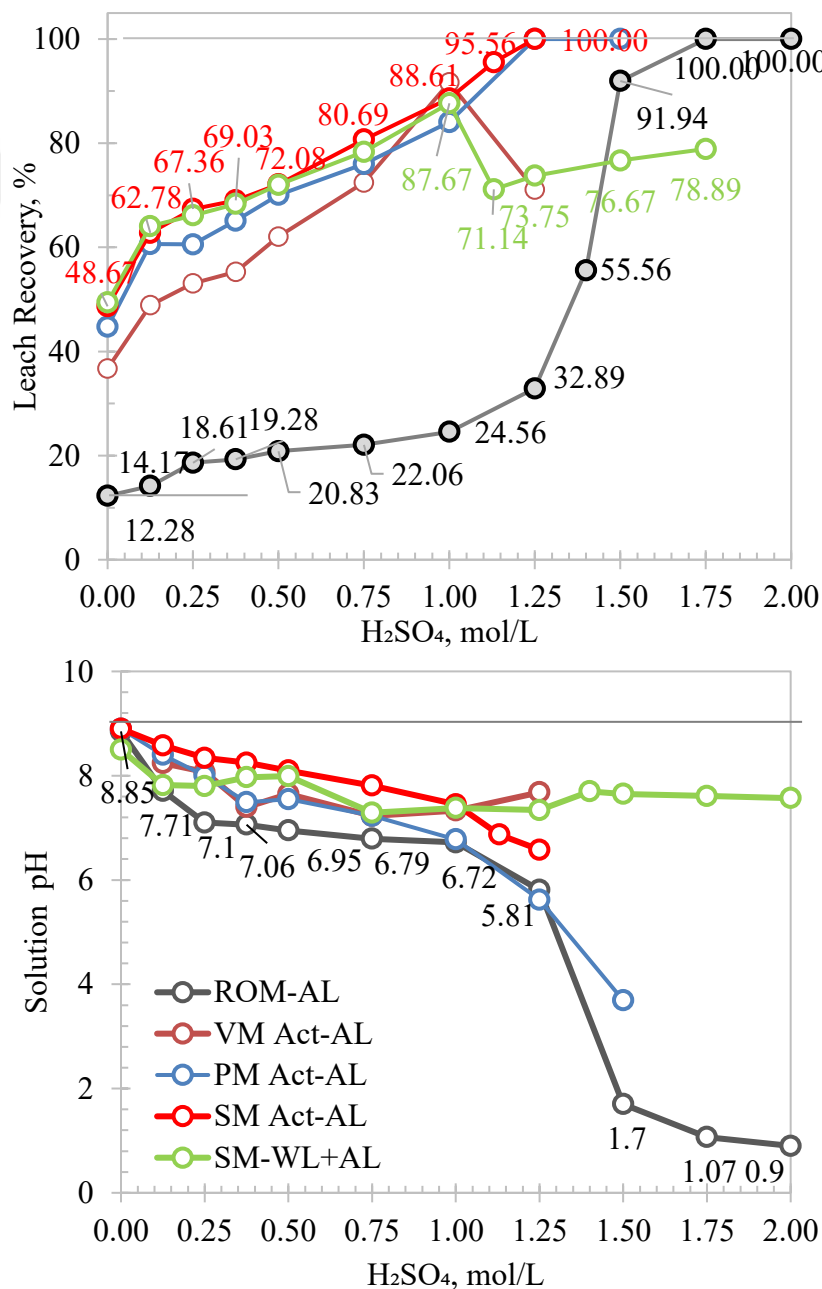


Figure 3.32: Leach recoveries against H_2SO_4 Concentration (Leaching time: 60 min, Leaching temperature: 50 °C, L/S:5).

The effect of dissolution time on dissolution efficiency

In a series of experiments investigating the effect of dissolution time on dissolution efficiency, leaching durations ranged from 5 to 150 minutes, and the resulting dissolution efficiencies are presented in Figure 3.33. Acid concentrations that previously provided approximately 75% dissolution efficiency were used for PM, SM, and VM samples, maintaining their dissolution efficiencies around this level. However, for the untreated solid (ROM), the 75% efficiency indicated from the curve was misinterpreted due to the broad parameter range and the sharp increase beyond a certain acid concentration; at the selected acid concentration, dissolution efficiency for ROM remained around 58%.

As seen in Figure 3.31, the ROM sample without mechanical activation exhibited a gradual increase in dissolution efficiency over time. In contrast, mechanically activated samples (PM, SM, and VM) reached maximum dissolution efficiency within the first few minutes and maintained this level without significant change over time. This demonstrates that mechanical activation significantly enhances the dissolution kinetics of lithium-containing structures, with dissolution completing rapidly due to crystal structure degradation and increased surface area.

Notably, SM and PM activation achieved a consistently high efficiency of approximately 77%, indicating that process duration can be shortened, thus minimizing energy and chemical consumption. In this regard, mechanical activation offers substantial advantages in both process efficiency and environmental sustainability.

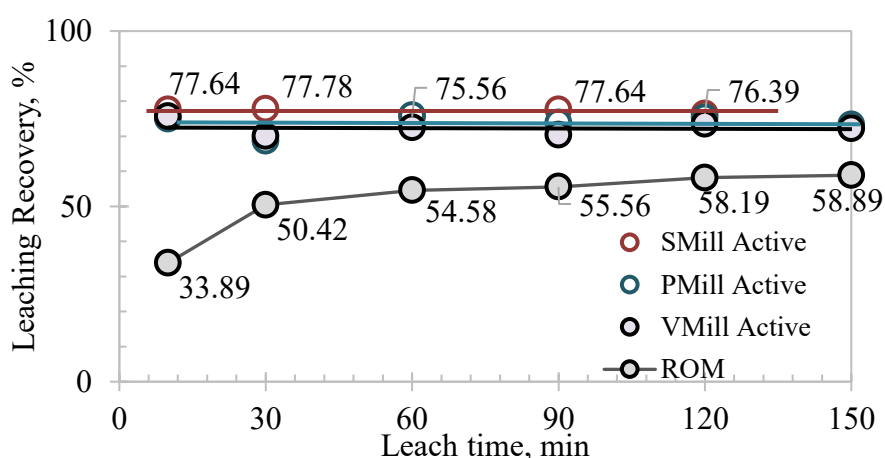


Figure 3.33: Dissolution efficiencies depending on dissolution time (Dissolution time: 60 min, Dissolution temperature: 50 °C, Liquid/Solid: 5, H₂SO₄ : 0.75 mol/L (for Smill, Pmill and Vmill) and 1.40 mol/L (for ROM)).

The effect of dissolution temperature on dissolution efficiency

In a series of experiments investigating the effect of dissolution temperature on dissolution efficiency, leaching was performed at temperatures ranging from 25 to 90 °C. The resulting dissolution efficiencies are presented in Figure 3.34. Mineral dissolution efficiency varied with temperature for the run-of-mine (ROM) sample and those subjected to different types of mechanical activation. While samples exhibited distinct behaviors up to 50 °C, their responses became more similar beyond this temperature.

For the ROM (non-activated) sample, temperature had a pronounced effect on increasing dissolution efficiency, indicating that temperature differences impact non-activated samples more significantly. Efficiency increased rapidly up to 50 °C, then the rate of increase slowed between 50 °C and 80 °C. Beyond 80 °C, temperature showed a reversible effect on efficiency.

Samples activated by the planetary mill (PM) and vibrating mill (VM) exhibited the highest dissolution efficiencies at low temperature (25 °C), with values of 92.36% and 82.22%, respectively. However, as the temperature increased, efficiency declined, suggesting that higher temperatures may degrade active surface properties and reduce dissolution efficiency. In contrast, samples activated by the stirred mill (SM) showed a more moderate increase in efficiency, generally maintaining dissolution efficiencies between 75% and 82% across the temperature range.

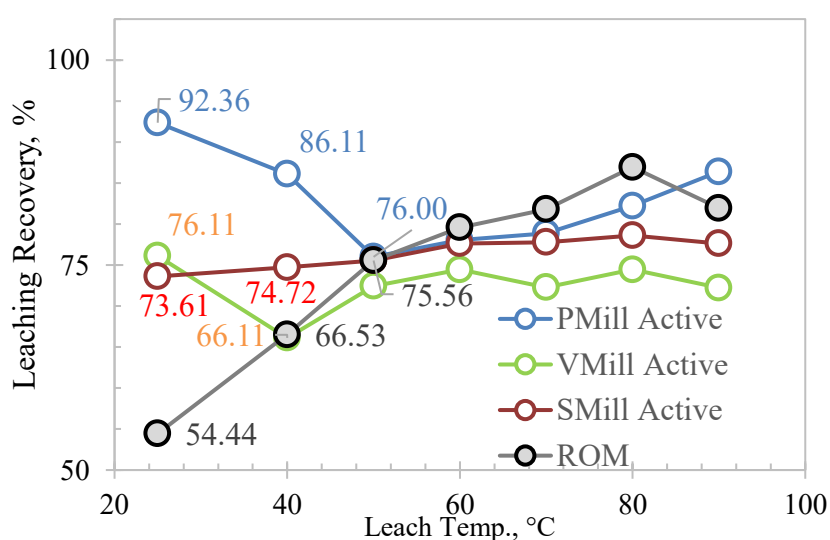


Figure 3.34: Variation of dissolution efficiencies on leaching temperature (Dissolution time: Vmill and Smill are 60 min, Pmill and ROM 90 min, Liquid/Solid: 5, H₂SO₄: 0.75 mol/L (for Smill, Pmill and Vmill) and 1.40 mol/L (for ROM)).

The effect of Liquid/Solid ratio on dissolution efficiency

In a series of experiments investigating the effect of the liquid-to-solid ratio on dissolution efficiency, leaching was performed with ratios ranging from 2.5 to 100. The corresponding dissolution efficiencies are presented in Figure 3.35. This parameter was tested only for samples activated using the stirred mill. Although dissolution efficiency reached 100% at a liquid-to-solid ratio of 20, this level is not considered practical from an industrial and economic perspective. For industrial applicability, a liquid-to-solid ratio of around 5 is regarded as more effective and feasible in balancing solid and liquid quantities.

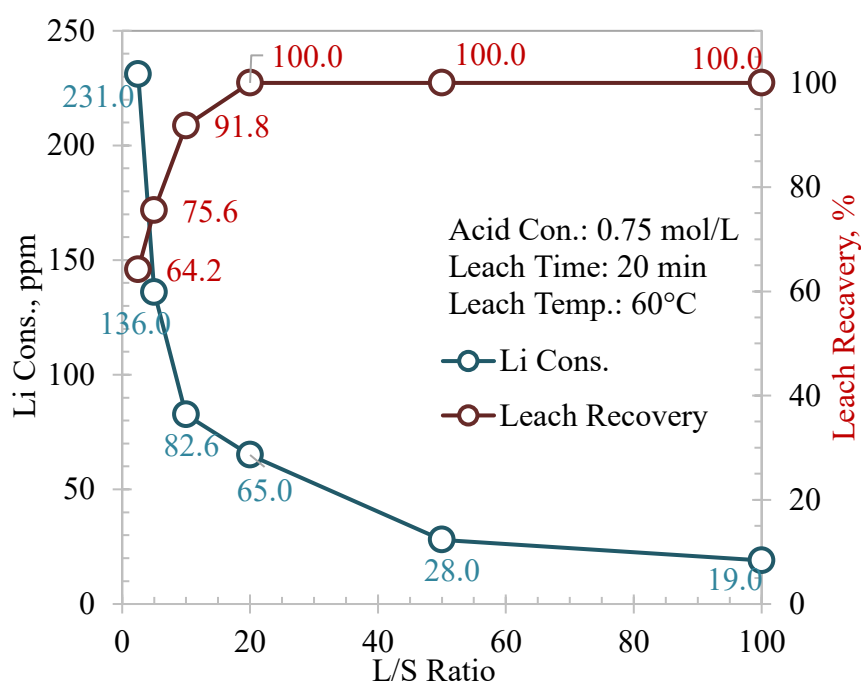


Figure 3.35: Dependence of dissolution efficiencies and released Li concentrations in solution depending on liquid/solid ratio (Dissolution time: 20 min, Dissolution temperature: 50 °C, Liquid/Solid: 5).

Evaluation of Acid leaching in terms of ions transferred into the solution

The concentrations of major ions (K^+ , Na^+ , Ca^{2+} , Mg^{2+} , Fe^{3+} , Al^{3+} , B_2O_3) released into the solution during acid leaching of run-of-mine (ROM), planetary mill, vibrating mill, and stirred mill activated samples at various acid concentrations are summarized in Table 3.21. According to the data, changes in ion concentrations are closely related to both the acid concentration (mol/L) and the activation state of the sample.

As the acid concentration increases, lithium concentration and dissolution efficiency also increase. In the ROM sample, dissolution remains limited at low acid

concentrations. However, at 1.50 mol/L H_2SO_4 , lithium solubility reaches 91.94%, with lithium ion concentration rising to 165.5 ppm. At this stage, significant increases in impurity ions such as Mg^{2+} , Ca^{2+} , Fe^{3+} , and Al^{3+} are observed (e.g., Fe^{3+} : 72.74 ppm, Al^{3+} : 201.57 ppm), indicating dissolution of gangue minerals in the acidic medium. When the acid concentration reaches 1.75 mol/L, the pH falls below 1.0, and impurity levels peak, potentially complicating the recovery of lithium salts from the leachate.

For the sample activated by the planetary mill, 70.06% dissolution efficiency is achieved at only 0.50 mol/L acid, demonstrating that high efficiency can be obtained at significantly lower acid doses compared to the ROM sample. This improvement highlights that mechanical activation increases surface area, accelerates reaction kinetics, and reduces acid consumption. Moreover, Fe^{3+} and Al^{3+} concentrations remain negligible (around 0.05 ppm or lower), indicating a more selective leaching process and a cleaner solution. Even at 1.25 mol/L acid concentration, the pH remains relatively high at 5.62, reflecting a much more controlled acidic environment compared to the ROM sample.

Overall, mechanical activation not only enhances lithium solubility but also limits the dissolution of unwanted gangue minerals, making the acid leaching process more environmentally friendly and economically sustainable.

Table 3.21: The effect of acid concentration on lithium dissolution efficiency in acid leaching of solid waste samples activated by different mechanical activation devices.

	Acid Conc (mol/L)	Leach Temp. (°C)	Leach Time (min)	Li Conc.. (ppm)	Rec. (%)	K ⁺ (ppm)	Na ⁺ (ppm)	Ca ²⁺ (ppm)	Mg ²⁺ (ppm)	Fe ³⁺ (ppm)	Al ³⁺ (ppm)	B ₂ O ₃ (ppm)	pH
RAW	0.00	80	20	22.5	12.50	56.00	9758.7	2.5	9.8	0.10	0.06	14612	8.85
	0.250	50	60	33.5	18.61	54.17	5101.5	531.6	1407.3	0.05	0.00	12510	7.10
	0.500	50	60	37.5	20.83	60.65	5460.3	558.7	4300.0	0.05	0.00	12000	6.95
	0.750	50	60	39.7	22.06	68.09	5402.3	561.5	6760.0	0.05	0.00	12630	6.79
	1.00	50	60	44.2	24.56	72.38	5316.5	564.5	9421.6	0.05	0.00	12285	6.72
	1.25	50	60	59.2	32.89	72.49	4984.1	541.0	13017.9	1.82	0.00	11690	5.81
	1.50	50	60	165.5	91.94	125.78	5511.8	564.1	17599.1	72.74	201.57	13160	1.70
	1.75	50	60	180.00	100.00	192.42	5700.2	548.3	21060.2	117.60	341.72	7890	< 1.0
PLANETARY MILL	0.125	50	60	109.1	60.61	156.90	4587.6	382.3	1203.6	0.02	0.00	6900	8.40
	0.250	50	60	109.0	60.56	184.50	4845.8	826.1	2602.6	0.03	0.00	8080	8.00
	0.375	50	60	117.2	65.11	186.06	5106.6	619.7	3840.3	0.00	0.00	9890	7.49
	0.500	50	60	126.1	70.06	203.30	4668.7	583.7	4832.9	0.05	0.00	10155	7.55
	0.750	50	60	136.8	76.00	212.34	5086.9	599.9	8233.1	0.05	0.00	10185	7.23
	1.00	50	60	151.3	84.06	230.61	4887.5	576.6	10602.9	0.03	0.00	10830	6.78
	1.25	50	60	180.0	100.00	262.80	5057.6	442.6	15112.9	1.65	0.00	11775	5.62
STIRRED MILL	0.25	50	60	121.25	67.36	300	5000	800	2900	0.00	0.00	NA	8.34
	0.50	50	60	129.75	72.08	300	4800	700	5200	0.00	0.00	NA	8.10
	0.75	50	60	145.25	80.69	300	5000	600	8200	0.00	0.00	NA	7.81
	1.00	50	60	159.50	88.61	300	4900	600	11100	0.00	0.00	NA	7.45
	1.25	50	60	180.00	100.0	300	5000	600	14300	0.00	0.00	NA	6.58
VIBRATING MILL	0.25	50	60	95.50	53.06	600	5800	600	2300	NA	NA	NA	8.07
	0.50	50	60	111.70	62.06	500	5400	600	5400	NA	NA	NA	7.65
	0.75	50	60	130.40	72.44	500	5500	700	9300	NA	NA	NA	7.23
	1.00	50	60	165.00	91.67	500	5500	600	12900	NA	NA	NA	7.33
	1.25	50	60	115.70	64.28	400	5300	700	6000	NA	NA	NA	7.68
SM+WL+ AL	0.25	50	60	18.61	66.11	100	1900	500	2500	0.00	0.00	NA	7.80
	0.500	50	60	20.83	72.00	200	2000	500	5600	0.00	0.00	NA	7.99
	0.750	50	60	22.06	78.33	300	5000	500	12500	0.00	0.00	NA	7.29
	1.000	50	60	24.56	87.67	300	4800	600	16200	0.00	0.00	NA	7.38



4. GENERAL COMMENTS AND CONCLUSIONS

Ion analyses conducted at the beginning and throughout the experimental studies revealed that the boron plant solid waste sample has a complex composition. It predominantly contains dolomite, along with 5–15% boron minerals and 5–15% of minerals such as illite, muscovite, zeolite, clinocllore, and halite.

In water leaching experiments performed on the untreated solid sample, lithium dissolution efficiencies of 10–13% were achieved. The significant dissolution of B_2O_3 indicated that both lithium and boron ions likely originated from the main process solution of the boron plant.

Mechanical activation tests utilized planetary, stirred, and vibrating mills, which differ in the intensity of this energy transferred from grinding media to the sample. These differences translated into varying degrees of mechanical activation. Among these devices, the planetary mill achieved similar or better mechanical activation even at much lower ball-to-powder ratios (BPR). However, from an industrial perspective, vibrating and stirred mills are more practical and should be considered accordingly.

The dissolution efficiencies obtained from leaching products activated under optimal conditions by different mills, in the presence of various salts, are summarized in Table 4.1. Although tests were not conducted at equal BPR values, it was found that the stirred mill provided more effective mechanical activation compared to the vibrating mill under selected conditions. For example, a dissolution efficiency of 63.67% was achieved with stirred mill activation followed by water leaching, while the vibrating mill activation resulted in approximately 41.0% dissolution efficiency.

When examining competing ions dissolved alongside lithium, such as alkali ions, Fe, Al, and B_2O_3 , it was observed that Ca, Mg, and K ion concentrations remained relatively low. Moreover, a linear correlation between lithium and potassium ions was identified, indicating that lithium primarily originates from potassium-bearing minerals such as muscovite or illite.

This dissolution behavior observed in water leaching after mechanical activation was similarly reflected in acid leaching processes. Direct acid leaching of run-of-mine solid waste required high acid concentrations (around 1.50 mol/L) to achieve high dissolution efficiency, whereas mechanically activated samples reached comparable efficiencies at much lower acid concentrations, between 0.75 and 1.00 mol/L.

Table 4.1: Summary results of mechanical activation + water/acid leaching application.

	Salt Conc., (ppm)	SALT Li Conc. (ppm)	Leach Rec., (%)	Acid Conc., (mol/L)	H ₂ SO ₄ Li Conc., (ppm)	Li Conc. (ppm)
RAW	0	23.7	13.17	-	-	-
	10	22.5	12.50	-	-	-
	-	-	-	0.75	39.7	22.06
	-	-	-	1.00	44.2	24.56
	-	-	-	1.25	59.2	32.89
	-	-	-	1.50	165.5	91.94
	-	-	-	1.75	180.0	100.00
Planetary Mill	0	80.5	44.72	-	-	-
	10	87.2	48.44	-	-	-
	25	96.1	53.39	-	-	-
	-	-	-	0.50	126.1	70.06
	-	-	-	0.75	136.8	76.00
	-	-	-	1.00	151.3	84.06
	-	-	-	1.25	180	100.00
Stirred Mill	0	97.4	54.11	-	-	-
	10	109.3	60.72	-	-	-
	25	114.6	63.67	-	-	-
	-	-	-	0.50	129.75	72.08
	-	-	-	0.75	145.25	80.69
	-	-	-	1.00	159.5	88.61
	-	-	-	1.25	172.0	95.56
Vibrating Mill	0	66.10	36.72	-	-	-
	10	73.80	41.00	-	-	-
	25	75.70	42.06	-	-	-
	-	-	-	0.50	111.70	62.06
	-	-	-	0.75	130.40	72.44
	-	-	-	1.00	165.00	91.67
	-	-	-	1.25	115.70	64.28

Although the use of lower acid concentrations such as 0.5–0.75 mol/L is less common, it is particularly important in terms of the disposal of resulting solid wastes. Additionally, in acid leaching applications at 1.25 mol/L and below, the pH of the medium remains above 5, whereas at higher acid concentrations of 1.50–1.75 mol/L,

the pH drops below 1. This highly acidic environment causes normally insoluble Fe and Al ions to dissolve into the solution.

However, although not to the same extent as direct acid leaching of the run-of-mine sample, it was observed that acid leaching following mechanical activation still resulted in significant dissolution of Ca, Mg (approximately 15,000–20,000 ppm), and Na ions. These ions are known to pose challenges in the subsequent recovery of lithium from the solution, especially during lithium carbonate precipitation.

Therefore, despite generally lower dissolution efficiencies compared to direct acid leaching, mechanical activation combined with water leaching offers advantages due to lower concentrations of competing ions in the solution, which remain within manageable limits.

To better illustrate the dissolution mechanism, Figure 4.1 has been prepared, showing the regional dissolution behavior of the boron plant solid waste. As seen in Figure 4.1, even stirring the solid waste sample in water at room temperature causes a significant amount of B_2O_3 to dissolve into the solution. This suggests that the B_2O_3 content does not originate from boron minerals but rather remains on the solid surface from the plant's main process solution (region A). Mechanical activation alters the chemical structure, leading to the dissolution not only of lithium but also small amounts of Ca and Mg (<20 ppm) due to crystal structure degradation and amorphization (regions B, C, and D). The variation in lithium dissolution observed across these regions corresponds to the degree of mechanical activation applied.

Direct acid leaching, in contrast, aggressively breaks down the chemical structure and reacts with dolomite, causing a significant release of Mg and Ca ions (region E), with concentrations increasing up to 20,000 ppm.

In summary, this study demonstrates that mechanical activation followed by either water or acid leaching can efficiently transfer lithium into solution with high dissolution efficiencies. However, water leaching offers a more selective dissolution process with fewer impurities.

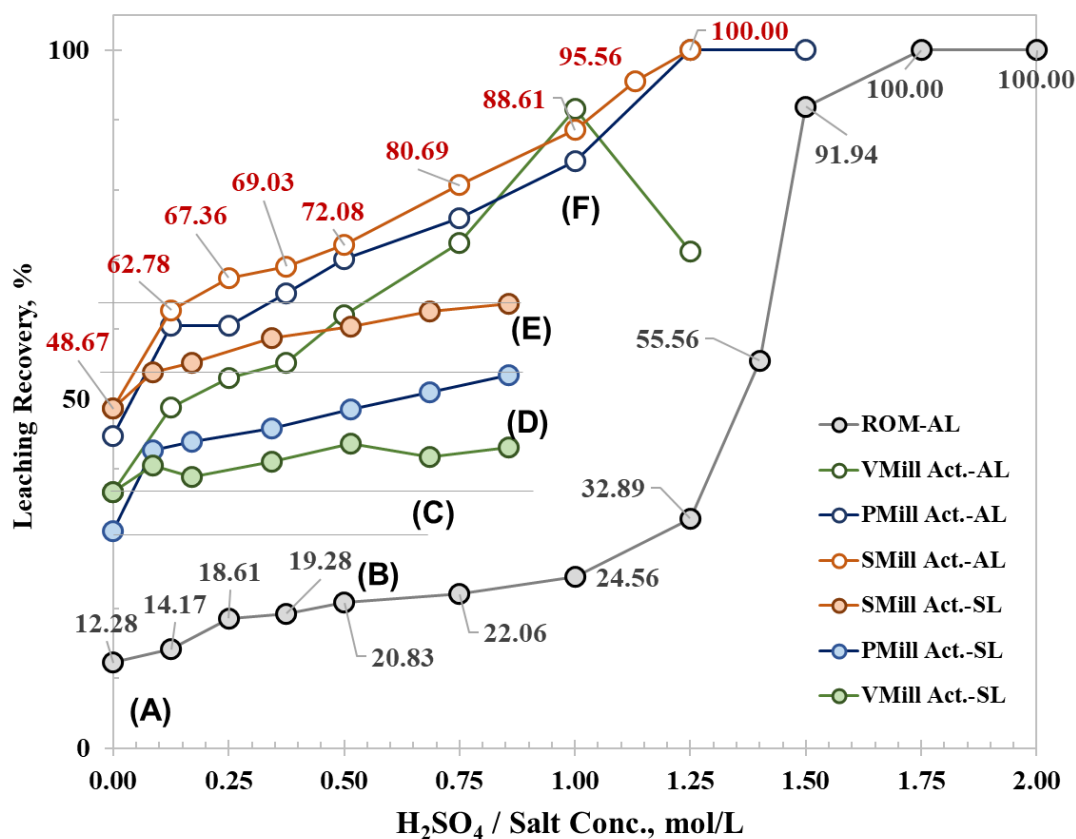


Figure 4.1: Dissolution mechanism.

(A: Lithium remaining on the waste sample originating from the main process solution. B: Cation exchange at a low level due to structural change in the waste sample as a result of mechanical activation. C: Cation exchange at a high level due to structural change in the waste sample as a result of mechanical activation. D: Increasing Na–Li cation exchange due to Na ion originating from salt. E: Decomposition of the chemical structure of the waste by acid after mechanical activation).

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