

Article

Lithium Recovery from Smectite Clays via Sulphate Roasting and Water Leaching

Cara Philipa Haller * and Christie Dorfling

Department of Chemical Engineering, Stellenbosch University, Stellenbosch 7599, South Africa;
dorfling@sun.ac.za

* Correspondence: cbroeksma@sun.ac.za

Abstract

The growing lithium demand has led to increasing interest in low-grade clay deposits. In this study, a roast-leach process was investigated for the recovery of lithium from a Southern African smectite-rich clay deposit. Screening of various roasting additives showed that a binary system comprising sodium sulphate and calcium sulphate yielded the highest lithium dissolution during subsequent water leaching, and was therefore selected for optimisation tests. Roasting at 850 °C for 1.5 h, using a clay:total salt ratio of 2:1 and $\text{Na}_2\text{SO}_4:\text{CaSO}_4$ ratio of 1:2, followed by subsequent water leaching at 60 °C and 30% solids, resulted in 86.3% lithium dissolution after 2 h. Compared with direct acid leaching of the same clay deposit, the roast-leach process improved lithium selectivity over multivalent ions, modified the clay's swelling behaviour to enable leaching at higher solids content, and produced an alkaline leach solution, eliminating the need for neutralisation.

Keywords: leaching; lithium extraction; roasting; smectite clays

1. Introduction

Primary lithium resources can be broadly classified into three categories: (i) pegmatitic rock, (ii) brine, and (iii) sedimentary deposits, including clays. Historically, sedimentary lithium-bearing deposits, as well as low-grade pegmatitic rock and brine resources, were not considered economically viable for exploitation due to relatively low lithium grades. However, the rapid growth in lithium demand has driven renewed interest in the exploration and development of these lower-grade resources [1–3]. Lithium-bearing clay deposits have become a particular focus in North America, where a number of projects are under development for potential commercial extraction [4–7].

Exploration in Southern Africa has led to the identification of lithium-bearing clay deposits that exhibit geochemical similarities to some of the deposits in Western North America, with smectite identified as the predominant clay mineral. The general structure of smectite minerals has been described extensively in the literature [8–11].

Conventional methods for lithium recovery from clays consist of acid leaching using strong mineral acids, such as sulphuric acid. Sulphuric acid-based processing routes generally yield high lithium recoveries; however, drawbacks of this process include high acid consumption and complexity of downstream processing, since acid leaching is typically not selective towards lithium [12–14].

Sulphate roasting, followed by water leaching, has been proposed as an alternative process for lithium recovery from clay, to potentially reduce chemical requirements and

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minimise the co-dissolution of impurities during the leaching stage [13,15–18]. Sulphate roasting has traditionally been applied to pegmatitic ores, particularly those containing spodumene and lepidolite, where it has been shown to convert lithium into water-soluble lithium sulphate phases [19–22].

The roasting temperature plays an important role in the performance of the roast-leach process. Zhong et al. [18] investigated the leaching of lithium from kaolinite roasted with sodium sulphate for 1.5 h; the lithium dissolution increased from 36% to 84% as the roasting temperature was increased from 600 °C to 800 °C. Further increasing the temperature to 1000 °C caused lithium dissolution to decrease to 12%. The authors proposed that, as the calcination temperature increases from 600 °C to 800 °C, larger surface pores develop, increasing the specific surface area of the clay and allowing Na⁺ to diffuse into the mineral structure and exchange with Li⁺, thereby promoting higher lithium extraction. At higher temperatures (900–1000 °C), the pore structure collapses as metakaolinite transforms into mullite, restricting Na⁺ diffusion into the particle interior and reducing lithium recovery. It is further suggested that Li⁺ released from the structure reacts with SO₄²⁻ at the particle surface to form Li₂SO₄.

Feng et al. [15] observed that lithium recovery from chlorite-illite clay increased markedly between 600 °C and 800 °C during sodium sulphate roasting, followed by a gradual improvement up to 1000 °C, the highest temperature investigated.

The effect of roasting duration on lithium extraction varies across studies but generally shows that prolonged roasting can be detrimental. Qiu et al. [16] reported that, for illite-smectite roasted with sodium sulphate at 750 °C and a clay:salt ratio of 1:1, lithium extraction increased with increasing roasting duration up to 2 h, but decreased thereafter. When less sodium sulphate was used, extraction improved with roasting duration up to 1 h and then declined at 1.5 h. This decrease in recovery was attributed to the formation of mullite at 750 °C, which traps lithium within the lattice. This effect was more pronounced at higher salt dosages, as sodium sulphate promoted mullite formation. Under optimal roasting conditions (clay:salt ratio of 1:1, 750 °C, 1 h), a maximum lithium extraction of 94% was achieved. In contrast to the findings of Qiu et al. [16], Feng et al. [15] reported a consistent increase in lithium extraction from chlorite-illite clays as the roasting time increased from 0.5 to 4 h.

Qiu et al. [16] investigated the effects of solids content, leaching temperature, and leaching duration on lithium extraction during water leaching of illite clay roasted at 750 °C, with a clay:sodium sulphate ratio of 1:1. Increasing the leaching temperature from 25 °C to 90 °C at 17% solids and 120 min had little effect on lithium dissolution. Extending the leaching time from 30 to 180 min at 33% solids and 25 °C also had minimal impact on lithium extraction. According to Qiu et al. [16], lithium recovery was primarily governed by the roasting step, which explains the limited influence of leaching temperature and duration. Increasing the solids content from 17% to 33% did not significantly affect lithium extraction; however, a further increase to 50% solids led to a noticeable decrease in recovery.

The sulphate roast-leach process typically exhibits high selectivity towards lithium, with minimal co-dissolution of aluminium, iron, and magnesium. Zhong et al. [18] reported that iron and aluminium do not form water-soluble phases, while Feng et al. [15] observed that magnesium was incorporated into an insoluble silicate phase.

While most studies on sulphate roasting for lithium recovery from clays have focused on single-salt systems, American Lithium Corp. [23] indicated that using a mixture of gypsum with sodium salts (sodium chloride and sodium sulphate) increased lithium dissolution from clays by 10% relative to gypsum alone. Similarly, Vieceli et al. [21] reported that roasting lepidolite at 850 °C for 2 h with gypsum alone yielded 50.4% lithium recovery, whereas using a 1:1 mixture of sodium sulphate and gypsum increased lithium recovery to 77.3%. The use of limestone as an additive to sulphate salts has also been reported to

enhance lithium recovery; it reacts with free silica to form calcium silicate, thereby preventing the reverse reaction of lithium sulphate with silica and the formation of water-insoluble lithium silicate [24,25].

Studies on the sulphate roast–leach process for lithium extraction have typically focused on clay types other than smectites. Lithium leaching efficiencies and optimal conditions are strongly influenced by clay type, lithium grade, and the nature and concentration of impurities. Consequently, experimental studies are often required to identify the most suitable processing route, as the characteristics of individual deposits can vary considerably. This study contributes to the field of knowledge by experimentally evaluating the applicability of sulphate roasting followed by water leaching for extracting lithium from a low-grade smectite-rich clay deposit, and by directly comparing the performance of the roast–leach process against lithium dissolution achievable with direct acid leaching with mineral acids (sulphuric acid) and organic acids (oxalic acid).

2. Materials and Methods

2.1. Materials

The feed material consisted of particles with 100% passing 2.5 mm and a d50 of 470 µm. The crystalline phases identified in the feed material by X-ray diffraction (XRD) analysis are presented in Table 1. The phase composition reported in Table 1 is normalised to the crystalline fraction of the sample. As XRD does not quantify any amorphous material that may be present, the reported values do not represent the bulk phase composition of the feed material. The elemental composition of the feed material is reported in Table 2. Major elements were analysed using X-ray fluorescence (XRF), while the lithium concentration was determined by aqua regia digestion followed by inductively coupled plasma–optical emission spectroscopy (ICP-OES).

Reagent-grade sodium sulphate (99%), calcium sulphate dihydrate (98%), calcium carbonate (99%) and calcium chloride (99%) were used for the respective roasting tests, as per the experimental design. Water purified via reverse osmosis was used for leaching.

Table 1. Normalised crystalline phase composition of the feed material determined by XRD.

Phase Amount (wt%)						
Dolomite	Calcite	Quartz	Orthoclase	Smectite	Muscovite	Anorthite
38.6	16.3	5.3	4.5	18.0	2.5	15.0

Table 2. Metal composition of the feed material.

Metal Composition (wt%)						
Al	Ca	Fe	K	Li	Mg	Na
2.3	8.2	1.5	1.7	0.065	10.1	2.2

2.2. Experimental Design

Unless otherwise specified, roasting was carried out at 850 °C for 1.5 h using a clay:total salt ratio of 2:1 and, for binary salt systems, a 1:1 ratio between salts, followed by leaching at 60 °C with a maximum theoretical lithium concentration of 220 mg/L. The maximum theoretical lithium concentration corresponds to the concentration in solution that would be obtained if 100% lithium dissolution from the roast product is achieved. During roasting, excess salt was used to compensate for its consumption in side reactions, to maintain a high sulphate activity throughout the process, and to minimise kinetic limitations.

Repeat experiments were performed only at selected conditions due to practical constraints. Consequently, experimental variability could only be quantified for those conditions and is indicated by error bars on the respective figures.

2.2.1. Screening Tests

Screening tests were conducted to identify suitable additive systems for enhancing lithium extraction. In the initial screening phase, sodium sulphate was selected as the primary sulphate salt and combined with various co-additives to assess the influence of additive composition on lithium recovery. Five systems were evaluated, comprising a baseline test without additives, a single-salt system (Na_2SO_4), and three binary mixtures ($\text{Na}_2\text{SO}_4 + \text{CaSO}_4$, $\text{Na}_2\text{SO}_4 + \text{CaCO}_3$, $\text{Na}_2\text{SO}_4 + \text{CaCl}_2$). A clay:total salt ratio of 4:1 was used for the single-salt system and 2:1 for binary systems, with a 1:1 ratio between salts. Leaching was performed at 80 °C with a maximum theoretical lithium concentration of 110 mg/L.

Based on the results of this initial screening, chloride- and carbonate-containing additives were excluded from further investigation. Subsequent screening therefore focused exclusively on sulphate salts and their binary combinations. Six sulphate systems were studied, comprising three single-salts (Na_2SO_4 , K_2SO_4 , CaSO_4) and three binary mixtures ($\text{Na}_2\text{SO}_4 + \text{CaSO}_4$, $\text{Na}_2\text{SO}_4 + \text{K}_2\text{SO}_4$, $\text{CaSO}_4 + \text{K}_2\text{SO}_4$). A clay:total salt ratio of 2:1 was used for both single- and binary-salt systems, with a 1:1 ratio between salts. Preliminary tests on the effect of leaching conditions showed no significant difference in lithium dissolution when the leaching temperature was reduced from 80 °C to 60 °C; therefore, 60 °C was used for all subsequent sulphate screening tests and as a baseline condition for optimisation tests. In addition, the maximum theoretical lithium concentration was increased to 220 mg/L to enhance lithium concentration in solution.

2.2.2. Optimisation Tests

Based on the outcomes of the screening tests, the binary salt mixture of sodium sulphate and calcium sulphate was selected for further optimisation tests to evaluate the impact of clay-salt ratios, roasting temperature and duration, as well as leaching conditions on lithium extraction.

A full factorial design was used to assess the effect of clay:total salt ratio (1:1, 2:1, and 4:1) and the Na_2SO_4 : CaSO_4 ratio (2:1, 1:1, and 1:2). The influence of roasting temperature was investigated by varying the temperature between 650 °C and 1100 °C, while roasting duration was varied between 0.5 h and 2.5 h.

Leaching conditions were evaluated by varying the leaching temperature (25 °C, 40 °C, 60 °C) and the solid:liquid ratio, expressed in terms of the maximum lithium concentration (220 mg/L, 440 mg/L) achievable at 100% leaching efficiency. These leaching tests were performed on mixtures roasted using a clay:total salt ratio of 2:1 and Na_2SO_4 : CaSO_4 ratio of 1:2.

2.3. Equipment and Procedures

Roasting tests were conducted in a muffle furnace open to the atmosphere, with a maximum operating temperature of 1200 °C. The required mass of clay and salt(s) was mixed manually and added to cylindrical mullite crucibles (100–150 g per crucible). The crucibles were placed in the furnace at ambient temperature, after which heating was initiated. The furnace temperature was maintained within ± 5 °C of the setpoint using feedback control. The duration of the test was measured from the time instance that the setpoint temperature was reached. At the end of the test, the furnace was left to cool to ambient temperature overnight. Once cooled, the crucibles were removed, and the roast product was collected and split into representative samples using a rotary sample splitter.

Leaching was performed in a 1.5 L jacketed glass reaction vessel equipped with an overhead stirrer and a Teflon anchor impeller. The solution temperature was maintained within ± 2 °C of the setpoint using a hotplate and PT1000 sensor. Where necessary, cooling was achieved by circulating water at approximately 12 °C through the vessel jacket. The vessel lid was fitted with a condenser to minimise vapour losses, a sampling port for solids

addition, and an additional port for the pH probe. The required volume of water was added to the reaction vessel, and heating and stirring were initiated. Once the setpoint temperature had been reached, the required mass of roast product was added to the reaction vessel, with this time instance marking the start of the test. Solution samples (2 mL) were taken at predetermined intervals, filtered through 0.45 µm syringe filters, and the pH was recorded. At the end of the test, the solution was cooled to room temperature, and solid–liquid separation was achieved via vacuum filtration.

2.4. Analytical

XRD of the feed material and roast product was performed using a Malvern Panalytical Aeris diffractometer equipped with a PIXcel detector, fixed slits, and Fe-filtered Co-Kα radiation. Phases were identified using X'Pert Highscore Plus software and the PAN-ICSD database, and relative phase amounts were estimated via Rietveld refinement, with a detection limit of 0.5–3 wt%. The major elemental composition was determined by XRF using an ARL ADVANT'X Series spectrometer.

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were used to evaluate the thermal behaviour of the feed material prior to roasting. The analyses were conducted on a Netzsch STA 449 F3 instrument coupled to a Bruker Optik gas chromatography–mass spectrometry (GC-MS) system to identify evolved gases. Samples (10 mg) were heated from 20 °C to 900 °C at a rate of 10 °C/min under a nitrogen atmosphere.

Solution samples were analysed using ICP-OES (PerkinElmer Avio 500) to determine metal concentrations.

2.5. Thermodynamic Modelling

Thermodynamic modelling was conducted using FactSage version 8.2 to predict the equilibrium phases formed during roasting in air at 1 atm. The input phases and quantities were based on XRD results presented in Table 1, with smectite approximated as Li-montmorillonite [$\text{Li}_{0.3}(\text{Al,Mg})_2\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot 6\text{H}_2\text{O}$]. Since thermodynamic data for Li-montmorillonite are not available in the standard FactSage databases, these properties were estimated using the Cp Estimate module in HSC Chemistry version 9.4.1 and subsequently incorporated into the FactSage database. Thermodynamic data for the remaining input phases were obtained from the FactPS, FToxid, and FTSalt databases, while the FToxid-SLAGA solution model was used to predict the formation of any liquid phases during roasting.

3. Results and Discussion

3.1. Screening Tests

3.1.1. Effect of Additive Composition

Figure 1 shows the percentage lithium dissolution as a function of leaching time for different additive compositions, including a baseline (no additives), a single-sulphate system, and mixed additive systems. Roasting without additives resulted in less than 5% lithium dissolution after 120 min. Using sodium sulphate alone (4:1 clay:total salt ratio) increased lithium dissolution to 43.8%, while the addition of a second sulphate, calcium sulphate, in a binary sulphate system (2:1 clay:total salt ratio) further increased lithium dissolution to over 80%.

The single- and binary-sulphate systems in this initial screening study were evaluated at different clay:total salt ratios; therefore, the observed differences reflect the combined effects of additive composition and total salt addition. However, as shown in Section 3.2.1, reducing the clay:total salt ratio from 4:1 to 2:1 increased lithium extraction by a maximum of 8%. This is substantially lower than the nearly 40% increase observed for

the binary-sulphate systems in the initial screening tests, suggesting that the enhanced lithium extraction cannot be attributed solely to the higher total salt addition.

As shown in Figure 1, the addition of calcium carbonate to sodium sulphate during roasting did not improve lithium dissolution compared to sodium sulphate alone. This contrasts with reports in the literature that calcium carbonate additives can enhance lithium recovery by decomposing to CaO and then reacting with free silica to form calcium silicates, thereby preventing the reverse reaction between lithium sulphate and silica [24,25]. However, Obut et al. [26] suggested that the presence of dolomite and calcite in the feed can eliminate the need for additional carbonate additives. Since the feed material in this study contains dolomite and calcite as major phases (Table 1), this may explain why calcium carbonate addition did not increase lithium recovery. Furthermore, it is possible that increased formation of calcium silicates could inhibit leaching through the encapsulation of lithium, as reported in the literature [27].

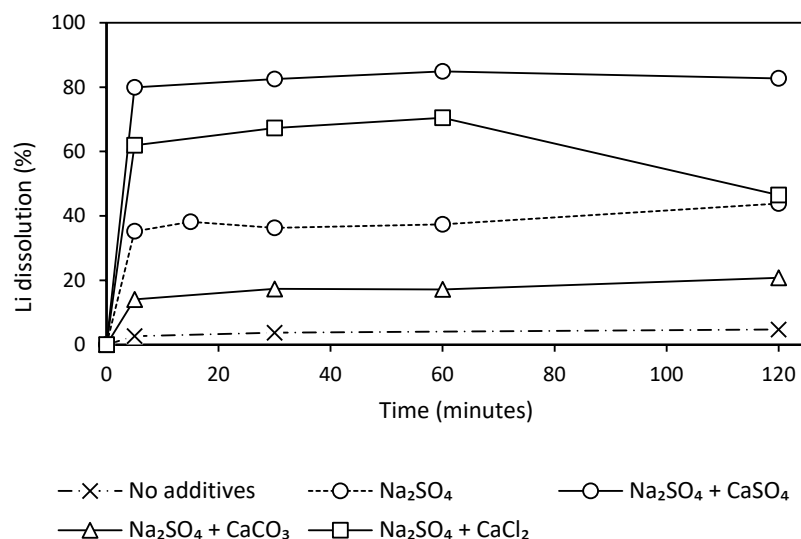


Figure 1. Effect of additive composition on lithium dissolution.

3.1.2. Effect of Sulphate Salt Systems

Figure 2 shows the percentage lithium dissolution as a function of leaching time for different sulphate salt systems. All sulphate salt systems were evaluated using a 2:1 clay:total salt ratio, allowing direct comparison of the single- and binary-sulphate systems. Of the single-salt systems tested, calcium sulphate yielded the highest leaching efficiency, while the binary system of sodium sulphate and calcium sulphate showed the best overall performance. For the single-salt systems, a possible reason for improved roasting performance observed with calcium sulphate is the higher cation charge-to-size ratio (z/r) of Ca^{2+} compared with Na^+ and K^+ . Using ionic radii for coordination number VI, the calculated z/r values are $\text{Ca}^{2+} = 2.00$, $\text{Na}^+ = 0.98$, $\text{K}^+ = 0.72$ [28], with the order $\text{Ca}^{2+} > \text{Na}^+ > \text{K}^+$. A higher z/r allows the cation to polarise anions more strongly, making the solid lattice more reactive. This trend is consistent with the pattern observed for the individual salts in this study. For binary-salt systems, adding sodium sulphate to calcium sulphate improved lithium recovery relative to calcium sulphate alone, consistent with the literature [21–23].

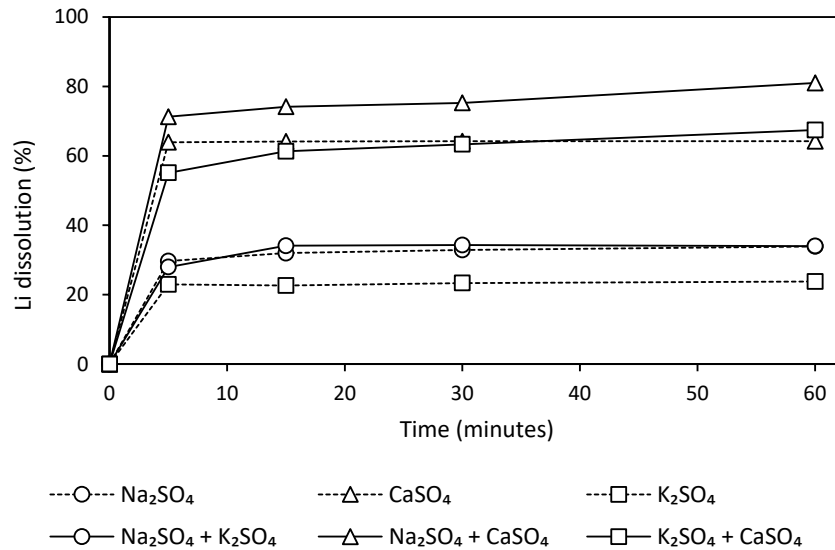


Figure 2. Effect of different sulphate salt systems on lithium dissolution.

For the sulphate-based screening tests (Figure 2), aluminium, iron, silicon and magnesium concentrations remained consistently below 5 mg/L, indicating limited co-dissolution of gangue elements. The PLS was alkaline, with a measured pH of 10.2 ± 0.2 for all tests, most likely due to partial dissolution of carbonate minerals present in the feed material.

The thermodynamic modelling results indicated that, in the absence of salt, an insoluble lithium aluminium oxide phase is formed. In the presence of sulphate salts, lithium is converted to water-soluble lithium phases, including $\text{KLi}(\text{SO}_4)$ and $\text{LiNa}(\text{SO}_4)$. Aluminium, iron and magnesium were not predicted to form any water-soluble phases under the roasting conditions evaluated.

XRD analysis showed no detectable lithium sulphate in the roasted product, likely due to lithium-bearing phases being present below the detection limit. The higher lithium extractions observed with additives compared to the baseline test (no additives) do, however, confirm the formation of a water-soluble lithium sulphate phase during roasting.

In the Na_2SO_4 - CaSO_4 system, XRD analysis of the roast product (Figure 3) detected ellestadite $[\text{Ca}_{9.94}(\text{SiO}_4)_3(\text{SO}_4)_3(\text{Cl}_{0.32})(\text{O}_{1.7}\text{H}_{1.2})]$, a calcium silicate sulphate mineral. Formation of ellestadite coincided with the highest lithium dissolution. Ellestadite may host lithium in its structure, but it is generally insoluble in water and is therefore unlikely to contribute to lithium in solution; rather, its presence may indicate extensive reaction among Ca-, Si-, and S-bearing phases [29].

In addition, water-soluble aluminium, iron, and magnesium phases were not detected by XRD in the roast product.

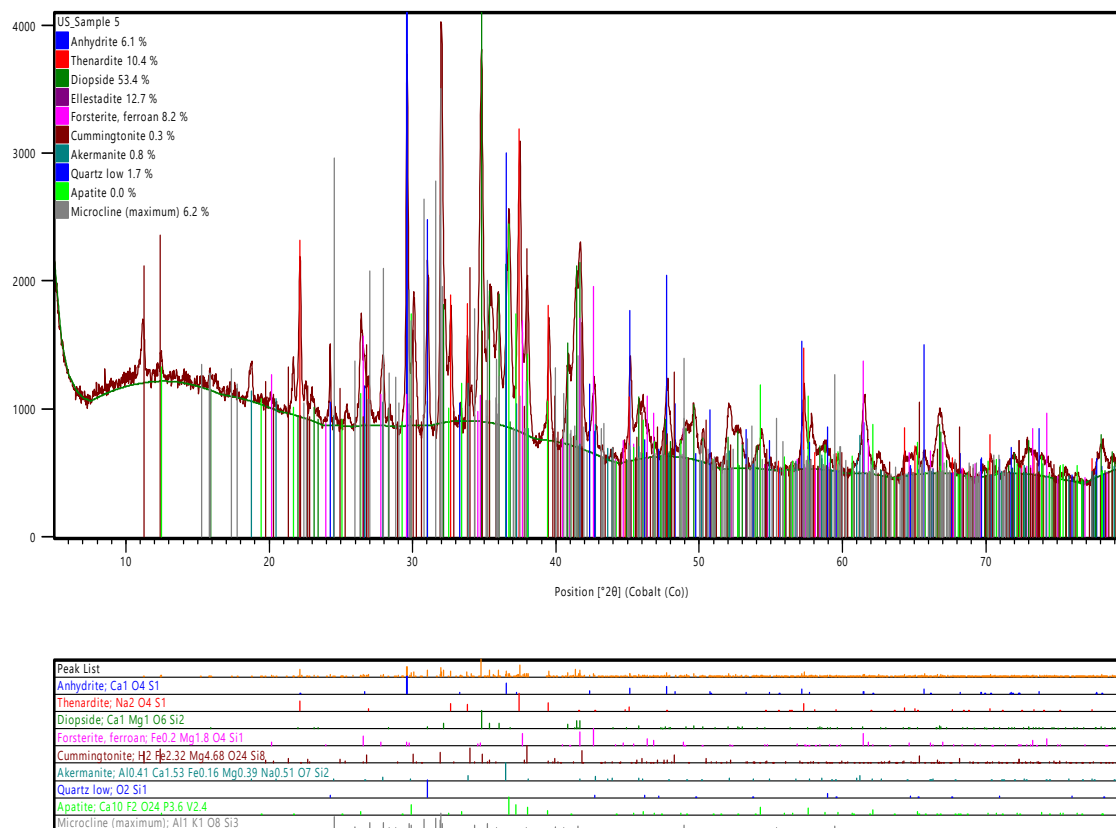


Figure 3. XRD diffractogram of the roast product from the $\text{Na}_2\text{SO}_4 + \text{CaSO}_4$ system.

3.2. Optimisation Tests

The $\text{Na}_2\text{SO}_4 + \text{CaSO}_4$ system was selected for optimisation tests based on the highest lithium extraction efficiency achieved in the screening tests.

3.2.1. Effect of Clay-Salt Ratio

Figure 4 shows the effect of the $\text{Na}_2\text{SO}_4:\text{CaSO}_4$ ratio on lithium dissolution at varying clay:total salt ratios after 120 min of leaching. The leaching test at a clay:total salt ratio of 1:1 and a $\text{Na}_2\text{SO}_4:\text{CaSO}_4$ ratio of 1:1 was not performed, as roasting produced very hard agglomerates, likely from sintering, in which particles fuse at high temperature. At the same clay:total salt ratio, but a $\text{Na}_2\text{SO}_4:\text{CaSO}_4$ ratio of 1:2, hard agglomerates were also formed, but these could still be broken up by hand.

At the highest $\text{Na}_2\text{SO}_4:\text{CaSO}_4$ ratio of 2:1, lithium dissolution decreased progressively with increasing clay:total salt ratio. At a 1:1 $\text{Na}_2\text{SO}_4:\text{CaSO}_4$ ratio, the clay:total salt ratio appeared to have little effect on lithium dissolution. At the lowest $\text{Na}_2\text{SO}_4:\text{CaSO}_4$ ratio of 1:2, lithium dissolution exhibited a non-linear response: similar values were observed at the highest and lowest clay:total salt ratios (1:1 and 4:1), while an intermediate ratio (2:1) produced the highest dissolution. A multiple linear regression analysis performed at a 95% confidence level confirmed that both the clay:total salt ratio ($p = 0.026$) and the $\text{Na}_2\text{SO}_4:\text{CaSO}_4$ ratio ($p = 0.028$) had statistically significant effects on lithium dissolution after 2 h, consistent with the experimental trends.

At the lowest $\text{Na}_2\text{SO}_4:\text{CaSO}_4$ ratio (1:2) and an intermediate clay:total salt ratio of 2:1, both sodium and calcium sulphates are present in sufficient amounts to react with the lithium-bearing phases in the clay. As the clay:total salt ratio increases, the relative amount of available sulphate per unit of clay decreases, limiting the reaction and lowering

lithium extraction. Conversely, when the clay:total salt ratio is too low, excess calcium sulphate hinders lithium dissolution. Although direct evidence in lithium-bearing clay and ore systems is limited, sintering and densification of anhydrite (CaSO_4) at elevated temperatures ($>800^\circ\text{C}$) have been shown to reduce the reactivity of the material [30].

At the highest $\text{Na}_2\text{SO}_4:\text{CaSO}_4$ ratio of 2:1, the progressive decrease in lithium dissolution with increasing clay:total salt ratio suggests that calcium sulphate becomes the limiting reagent when the clay content is sufficiently high. These observations are consistent with Vieceli et al. [21], who reported improved lithium extraction when the proportion of gypsum was increased relative to sodium sulphate.

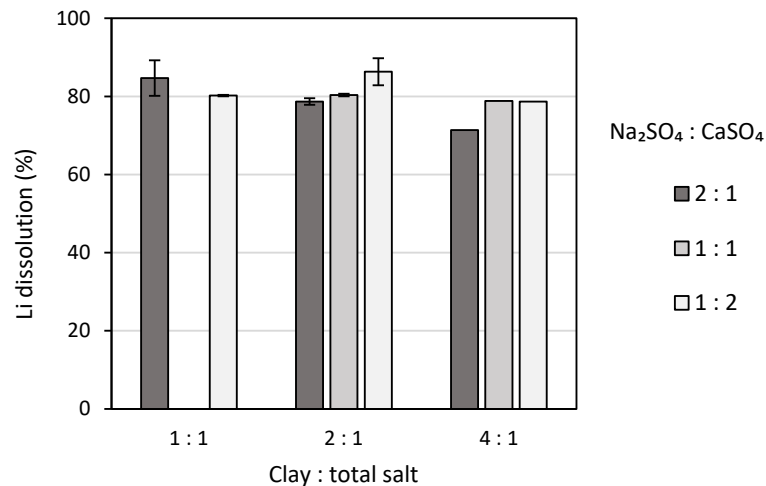


Figure 4. Effect of clay-salt ratios on lithium dissolution after 120 min of leaching. Error bars represent the standard deviation of duplicate tests.

3.2.2. Effect of Roasting Temperature and Duration

Figure 5 shows the effect of roasting temperature on lithium dissolution as a function of time at a clay:total salt ratio of 2:1 and $\text{Na}_2\text{SO}_4:\text{CaSO}_4$ ratio of 1:1. Increasing the roasting temperature from 650°C to 850°C significantly increased lithium dissolution, from 23.8% to 80.3% after 2 h. A further increase in temperature to 950°C resulted in only a slight rise in lithium dissolution to 84.8%, whereas heating to 1100°C caused a larger increase, reaching 93.3% lithium dissolution after 2 h.

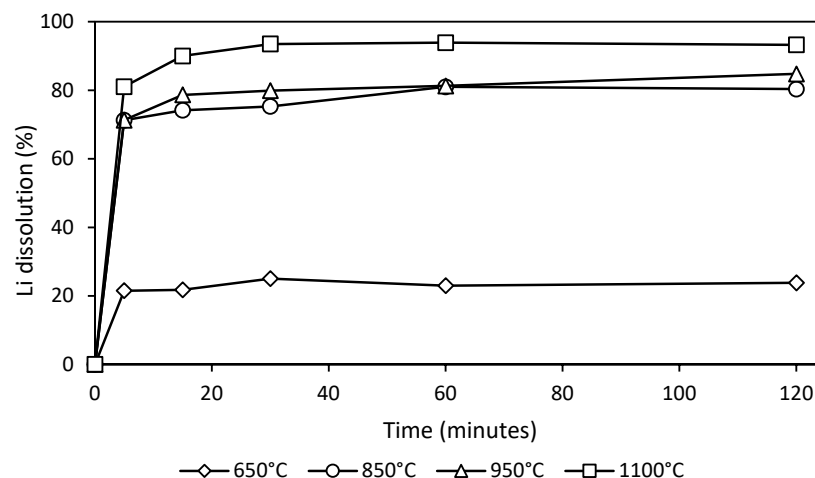


Figure 5. Effect of roasting temperature on lithium dissolution.

The TGA/DSC profile of the raw clay (Figure 6) showed an initial mass loss up to ~200 °C, corresponding to smectite dehydration. Between 450 °C and 700 °C, continuous mass loss occurred, likely due to structural water release from smectite (dehydroxylation) and decomposition of dolomite and calcite, releasing CO₂. Decomposition of calcite and dolomite in clay matrices has been reported to begin between 600 °C and 700 °C [31,32]. GC-MS confirmed the evolution of H₂O and CO₂ during heating. Above 700 °C, the mass stabilised, with an exothermic peak at ~750 °C likely associated with recrystallisation of new phases, including forsterite and diopside, which were detected by XRD at 850 °C, but not at 650 °C.

The low lithium extraction observed at 650 °C is consistent with these TGA/DSC trends, which indicate only partial smectite dehydroxylation and limited carbonate decomposition at this temperature. At higher temperatures, more extensive mass loss and the exothermic recrystallisation at ~750 °C facilitate phase transformations that promote the release of lithium from the clay structure and its subsequent conversion into water-soluble sulphate phases predicted by the thermodynamic modelling (Section 3.1.2), resulting in significantly higher lithium extraction.

The melting points of the individual salts are 884 °C for Na₂SO₄ and 1450 °C for CaSO₄, with the eutectic point of the mixture lying between 890 °C and 918 °C [21]. Reactions at 850 °C are therefore predominantly solid-state, whereas, at 1100 °C (Figure 4), melting may enhance ion mobility, contributing to the further increase in lithium extraction observed between 950 °C and 1100 °C.

The effect of roasting duration on lithium dissolution after 120 min of leaching was negligible. The percentage lithium dissolution achieved following roasting at 850 °C (clay:total salt ratio of 2:1 and Na₂SO₄:CaSO₄ ratio of 1:2) were 88.1%, 86.3% and 88.8% for roasting durations of 0.5 h, 1.5 h and 2.5 h, respectively.

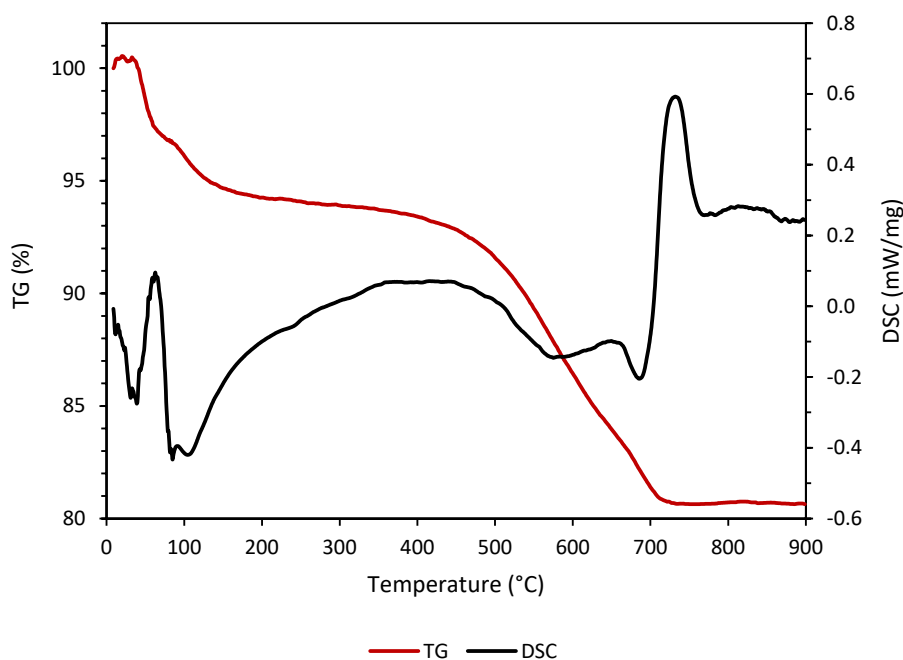


Figure 6. Thermal analysis of raw clay.

3.2.3. Effect of Leaching Conditions

Figure 7 shows the effect of leaching temperature and solid:liquid ratio (specified in terms of the maximum theoretical lithium concentration achievable at 100% leaching effi-

ciency) on lithium dissolution from the roast product after 120 min of leaching. At the lower solid:liquid ratio with a maximum theoretical lithium concentration of 220 mg/L, lithium dissolution increased only slightly, from 83.5% to 86.3%, as the leaching temperature was increased from 25 °C to 60 °C. At the higher solid:liquid ratio (maximum lithium concentration of 440 mg/L), lithium dissolution also increased only marginally, from 77.0% to 79.4% when the temperature was increased from 25 °C to 40 °C, with no further increase observed at 60 °C.

In contrast, increasing the maximum theoretical lithium concentration in solution (by increasing the solid:liquid ratio in the leaching step) from 220 mg/L to 440 mg/L led to a more significant change than that caused by temperature, with a 5–7% decrease in lithium dissolution at each of the three temperatures investigated. The maximum theoretical lithium concentrations of 220 mg/L and 440 mg/L corresponded to a solids content of approximately 30% and 46%, respectively, at the clay:total salt ratio investigated. Similarly, Qiu et al. [16] reported that the water leaching temperature did not affect lithium dissolution from a sodium sulphate roast product of lithium-bearing illite, whereas lithium extraction decreased with increasing solids content. The lower lithium extraction at higher solids content may be due to the reduced water-to-solid ratio, which limits the amount of lithium that dissolves, even though the solution remains well below the solubility limit of lithium sulphate.

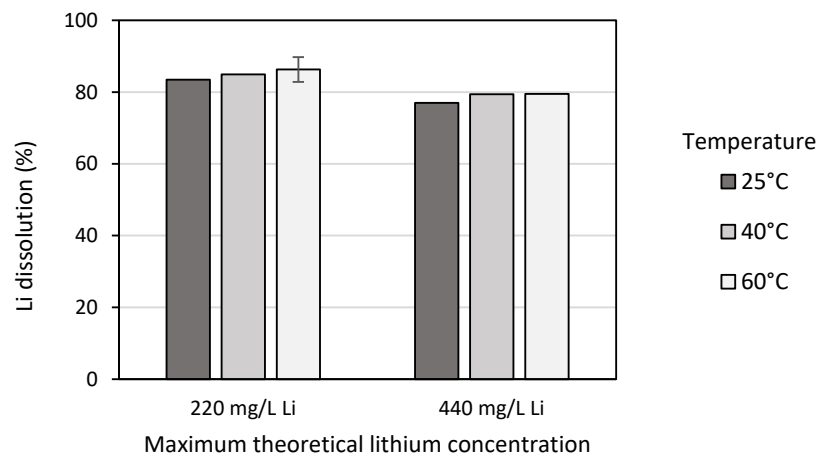


Figure 7. Effect of leaching conditions on lithium dissolution after 120 min of leaching. Error bars represent the standard deviation of triplicate tests.

3.3. Comparison to Acid Leaching

Table 3 compares the composition of the leach solution obtained from the roast-leach process with that obtained from direct sulphuric acid and oxalic acid leaching of the same clay deposit [12]. For the roast-leach tests, these results correspond to leaching tests performed using maximum theoretical lithium concentrations of 220 mg/L (30% solids) and 440 mg/L (46% solids) at 60 °C. For the direct acid leaching tests, the results correspond to the conditions that yielded the highest lithium concentrations in solution.

As shown in Table 3, 86.3% and 79.5% lithium dissolution was achieved for the roast-leach process using 30% solids and 46% solids, respectively. For direct acid leaching, 93% and 68% dissolution was achieved using sulphuric acid and oxalic acid, respectively, at 12% solids. Although lithium dissolution of up to 99% (sulphuric acid) and 82% (oxalic acid) was achieved under dilute conditions (8% solids), the resulting lithium concentrations were relatively lower (69–89 mg/L), which may be undesirable for downstream processing [12]. As a result, the compositions of the leach solutions for the 8% solids tests are not included here.

Due to the swelling properties and viscous nature of the clay, the solids content during direct acid leaching was limited to 12%. This restricted the lithium concentration in solution (maximum of 129 mg/L) and made handling and filtration difficult. Roasting at high temperature altered the clay's swelling behaviour, allowing operation at a higher solids content during leaching; consequently, higher lithium concentrations (up to 350 mg/L) could be achieved using the roast-leach process.

For the roast-leach process, aluminium, iron, and magnesium concentrations remained below 5 mg/L (Table 3), consistent with the behaviour observed in the screening tests (Section 3.1). In comparison, during direct acid leaching, significant co-dissolution of these metals was observed. Due to the alkaline nature of the leach solution from the roast-leach process, neutralisation is not required during downstream processing.

The absence of acid in the roast-leach system shifts the primary reagent management challenge to the use and recovery of sulphate salts. The recovery of sodium sulphate from downstream process streams, for example via evaporation and crystallisation, is identified as a potential process integration option for future work, enabling recycling of the recovered salt to the roasting step.

Table 3. Comparison of roast-leach and direct acid leach processes.

Parameter	Roast-Leach ¹		Sulphuric Acid Leach	Oxalic Acid Leach
% Solids	30	46	12	12
Acid conc. (M)	-	-	2	1.5
Temperature (°C)	60	60	60	60
Leaching time (h)	2	2	6	6
% Li dissolution	86.3%	79.5%	93%	68%
Final pH	10.5	10.8	0.5	1.2
Li (mg/L)	191	351	129	108
Al (mg/L)	<5	<5	1480	1713
Ca (mg/L)	676	644	641	68
Fe (mg/L)	<5	<5	1760	2120
K (mg/L)	4240	7900	1100	1100
Mg (mg/L)	<5	<5	17,800	1850
Na (mg/L)	22,200	38,600	3000	2440

¹ Roasting conducted at 850 °C for 1.5 h using a clay:total salt ratio of 2:1 and Na₂SO₄:CaSO₄ ratio of 1:2.

4. Conclusions

Screening tests were conducted to investigate the effect of roasting additive composition on lithium dissolution during subsequent water leaching. The binary sulphate salt system consisting of sodium sulphate and calcium sulphate yielded the highest lithium dissolution and was selected for optimisation tests. Lithium dissolution was found to increase with roasting temperature (650–1100 °C), while increasing roasting duration (0.5–2.5 h) had no significant effect.

The intermediate clay:total salt ratio of 2:1 and the lowest Na₂SO₄:CaSO₄ ratio of 1:2 yielded the highest lithium extraction. Roasting with these ratios at 850 °C for 1.5 h, followed by leaching at 30% solids and 60 °C, resulted in 86.3% lithium dissolution after 2 h. The study has therefore illustrated the technical feasibility of utilising this processing route for lithium recovery from low-grade smectite-rich clay deposits.

The roast-leach process offers several advantages over direct acid leaching for this application:

- The roast-leach process results in minimal co-dissolution of aluminium, iron, and magnesium (<5 mg/L), reducing the complexity of downstream solution purification.
- Roasting alters the clay's swelling behaviour, enabling leaching at higher solids content, which yields higher lithium concentrations in the leach solution (up to 350 mg/L).
- The alkaline nature of the leach solution from the roast-leach process eliminates the need for neutralisation during downstream processing, thereby reducing chemical consumption.

A key limitation of the study is the high salt consumption during roasting. Future work should focus on optimising the reagent mixture to minimise chemical consumption and to prioritise the use of recoverable and recyclable reagents, such as sodium sulphate. Process integration opportunities for salt recovery and recycling warrant further investigation.

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Abbreviations

The following abbreviations are used in this manuscript:

DSC	Differential scanning calorimetry
GC-MS	Gas chromatography–mass spectrometry
ICP-OES	Inductively coupled plasma–optical emission spectroscopy
PLS	Pregnant leach solution
TGA	Thermogravimetric analysis
XRD	X-ray diffraction
XRF	X-ray fluorescence

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