Experimental Kinetic Analysis of Potassium Extraction from Ultrapotassic Syenite Using NaCl–CaCl₂ Salt Mixture

Pegah Haseli,* Peter Majewski, Farid Christo, Mark Raven, Steve Klose, and Frank Bruno

ABSTRACT: This kinetic experimental analysis reports on the application of a eutectic NaCl–CaCl₂ salt system for the extraction of potassium from ultrapotassic microsyenite. The reaction parameters, time, temperature, salt composition, and salt to ore ratio, were systematically analyzed. It was found that a salt mixture increases the potassium cation extraction in comparison with using either pure NaCl or pure CaCl₂. It was also found that adding CaCl₂ into pure NaCl has a considerably stronger effect on increasing the potassium recovery than adding NaCl to pure CaCl₂. The salt as a melting agent offers a reduction in the reaction temperature due to its lower melting temperature when compared to pure salts (NaCl or CaCl₂). Approximately 70% of K⁺ in the deposit was extracted at 650 °C. Different characteristic methods have been used to understand the reaction mechanism of the salt mixture and ore, as well as to qualify and quantify the end product mineral phases.

1. INTRODUCTION

Production of potassium fertilizer (potash) from ultrapotassic syenites as a potential alternative to limited soluble salt deposits¹ is receiving growing attention due to their potential to reduce the cost of potash, improve agriculture sustainability, and mitigate complex mining operations.²–⁵ Potassium feldspar (K-feldspar), which occurs in ultrapotassic syenite in high concentration (~85 wt % corresponding to ~14.3 wt % K₂O),⁶ is the most abundant K-bearing mineral. However, its low solubility of K⁺ in water solution remains a major challenge associated with the processing of K-feldspar. This consequently has led to the development of different methods including acid leaching, hydrothermal alkali decomposition,⁷–¹⁸ and thermal decomposition¹⁷,¹⁸–²⁸ for improving K⁺ exchange and converting an insoluble potassium resource into a soluble form.

Among the thermal decomposition methods,³,⁷,¹⁸–²⁸ several potential chloride sulfate, and carbonate molten salt candidates have been verified to convert a nonsoluble K⁺ presented in K-bearing ore into a salt solution form based on the roast–leach process. In the process, molten salt agents break the bond of K⁺ in the ore at the desired temperature and then the post product (typically called the roasted salt–ore mixture) is leached mainly by deionized water to separate the molten salt mixture containing KCl and the untreated molten salt agent from the residual ore. Among different molten salt candidates, molten chloride salts such as CaCl₂,¹⁹,²⁵,²⁶,²⁷ NaCl,²⁹–⁳¹ have been identified as promising melting agents owing to their ability to thermally decompose the K-bearing ore at a lower temperature range between 800 and 900 °C, compared with temperatures above 1200 °C when using sulfate and carbonate melting agents.

Despite the above advantages, the use of only NaCl and CaCl₂ as a melting agent for the decomposition of K-feldspar is limited by some challenges. It has been reported²⁹ for NaCl that a high salt to ore mass ratio of about 5 is required to achieve more than 80% potassium recovery from K-feldspar, which can lead to intensive energy for its thermal activation. In comparison, the use of CaCl₂ requires a much lower salt to ore ratio of about 1 but the salt itself is more expensive and more hygroscopic than NaCl, which can increase the energy required for the drying process for industrial application. Moreover, for the use of CaCl₂, recovering the salt from the KCl–CaCl₂–H₂O system obtained from water leaching would also be energy-intensive due to the high solubility of CaCl₂–4H₂O in this system.³² In terms of the operating temperature of the roast–leach method for these melting agents, a temperature of above 850 °C has been reported for the desired potassium recovery from the ore.²⁹ This makes the roast–leach method an energy-intensive process. Nevertheless, the binary eutectic NaCl–CaCl₂ salt system has a much lower eutectic melting point of ~506 °C at 68 wt % CaCl₂–32 wt % NaCl in...
comparison with a melting temperature of 772 and 801 °C for pure CaCl₂ and NaCl, respectively. Therefore, the NaCl–CaCl₂ mixture is a potential melting agent candidate to decompose K-bearing ore while reducing the roasting temperature. This offers the potential to mitigate the energy required for the activation of the ore and possibly the heat losses. Nevertheless, it can also potentially reduce the reaction rates because the rate of reactions significantly depends on temperature. This implies that the scalability and engineering perspective of this technology requires further technical evaluation, while the experimental investigation in the current study is necessary to implement any further assessments. Therefore, the current study aims to understand and systematically investigate the potential application of the use of a eutectic NaCl–CaCl₂ system to convert a nonsoluble K⁺ presented in ultrapotassic syenite into a salt solution form based on the previously proposed roast–leach method. The reaction parameters, time, temperature, and salt to ore ratio, have been systematically investigated at the eutectic composition, 68 wt % CaCl₂–32 wt % NaCl. Furthermore, the effect of different salt compositions of the NaCl–CaCl₂ mixture has also been assessed on thermal decomposition of the ore at different operating temperatures based on the previously developed binary eutectic NaCl–CaCl₂ phase diagram. Another objective is to explore the principal reaction of the deposit with a salt mixture of NaCl and CaCl₂ using quantitative X-ray diffraction (XQRD) and scanning electron microscopy/energy-dispersive X-ray spectroscopy (SEM-EDS).

2. EXPERIMENTAL ANALYSIS

2.1. Materials. A critical evaluation of ultrapotassic syenite deposit mined in Western Australia has been described in detail in an earlier work of Haseli et al. The particle size used in the previous study was a mean diameter of ~150 μm. The deposit contained mainly K₂O (10.5 wt %), Fe₂O₃ (14.42 wt %), SiO₂ (53.53 wt %), and Al₂O₃ (15.80 wt %). XRD analysis from a previous work showed that the mineral compositions were K-feldspar (64.8 wt %), quartz (8 wt %), hematite (13 wt %), and clay/phyllosilicate minerals (14.2 wt %), including kaolinite and muscovite. Sodium chloride and calcium chloride dihydrate were supplied by ACE Chemical (Australia) and were of technical grade with a purity of 99.4 and 99.0%, respectively. The major impurities in sodium chloride are magnesia (max 0.05%), calcium (max 0.1%), and sulfate (max 0.25%). The major impurities in calcium chloride dihydrate are free alkali (max 0.25%), magnesium and alkal salts (max. 0.05%), and the heavy metal Pb (0.002%).

2.2. Salt Sample Preparation. In this study, the salt mixture with the eutectic composition of 68 wt % CaCl₂–32 wt % NaCl was used to assess the effect of different operating conditions, temperature, time, and salt to ore ratio. For the assessment of the salt mixture ratios on the decomposition of the ore, different mole compositions of CaCl₂, 0.12, 0.31, 0.53, 0.75, and 0.96, were investigated. For the salt mixture preparation, calcium chloride dihydrate (CaCl₂·2H₂O) were dried out in the quartz tube furnace under an argon atmosphere at 250 °C for 72 h to obtain anhydrous CaCl₂. For sodium chloride, the salt was dried in a furnace at 120 °C for 24 h. Thermogravimetric (TG) analysis of the dried calcium chloride and sodium chloride showed no weight loss. The sample handling was performed in a glove box under a nitrogen atmosphere. The dried salts were then mixed in a mortar and pestle at the desired weight ratio and placed in quartz crucibles with lids. The samples were then heated in an electric furnace up to 800 °C, where the salt mixture was molten for 4–5 h to obtain a homogenous mixture. Then, the salt was left to cool to room temperature. The samples were then ground into a powder and kept in a drying oven for further use.

2.3. Molten Salt Potassium Recovery Process. In this study, molten salt potassium recovery from the ore is based on the roast–leach method whereby the ore is thermally activated by the molten salt NaCl–CaCl₂ mixture and then leached by deionized water for the production of KCl in the solution form. In this process, the prepared salt mixture was mixed with the ore in a mortar and pestle at the desired weight ratio and then placed in quartz crucibles. The salt and ore mixtures were then placed back in the furnace and heated to 450 °C for 2 h in air to ensure complete removal of residual moisture that could have been absorbed during sample handling. The salt and ore mixture was then placed into the muffle furnace under atmospheric air for sufficient time to ensure that the reaction occurs at temperatures between 550 and 900 °C. The roasted samples were air-quenched in a desiccator and ground using a hand mortar and pestle, followed by water leaching. The leaching of the powder roasted sample was done using deionized water (pH 7) at a powder-to-water mass ratio of 1:10. The solid–liquid mixture was heated at 90 °C in a beaker for 1 h using a heated magnetic stirrer plate, and then the leaching solution, which contains the extracted KCl and the unreacted NaCl and CaCl₂, was separated from the residual ore (referred to as the roast–leach sample) by filtration. The roast–leach sample was dried out in the oven at 120 °C for 24 h for further analysis. The dried sample was characterized using X-ray fluorescence (XRF), quantitative X-ray diffraction (XQRD), and SEM-EDS.

The potassium recovery ratio, η, is defined as per eq 1

$$\eta = 1 - \frac{R_1}{R_3}$$  \hspace{1cm} (1)

where $R_1$ and $R_3$ represent the percentage of K in the roast–leach residue and in the bulk potassium feldspar sample, respectively, which were determined from XRF analysis.

2.4. Sample Preparation and Characterization Methods. 2.4.1. X-ray Fluorescence (XRF) by the Fusion Bead Method for Ores. The elemental contents of K-feldspar and roast–leach residue samples were determined by XRF (Panalytical Axios Advanced). The method involves fusing a subsample of the prepared pulp (85% passing 75 μm) with a lithium borate flux heated to 1000 °C and casting into a 40 mm diameter glass disc prior to introduction to the XRF instrument for analysis. Corrections were made for interelement and matrix effects to achieve results of the highest quality. Loss on ignition (LOI) was determined in fully programmable thermogravimetric systems in which temperature ramp rates, hold times, and the atmosphere were fully controllable. LOI is reported at 1000 °C.

2.4.2. X-ray Diffraction (XRD). Approximately 1.5 g of subsamples of the roast–leach samples were wet-ground for 10 min in a McCrone micronizing mill with ~10 mL of ethanol according to the earlier work of O’Connor and Chang. This method minimizes mechanical stresses, and hence avoids the formation of amorphous phases. The resulting slurries were oven-dried at 60 °C, then thoroughly mixed in an agate mortar and pestle before being lightly pressed into stainless steel.
sample holders for X-ray diffraction analysis. XRD patterns were recorded with a PANalytical X’Pert Pro Multipurpose Diffractometer using Fe-filtered Co Kα radiation, auto divergence slit, 2° antiscatter slit, and fast X’Celerator Si strip detector. The diffraction patterns were recorded in steps of 0.016° 2θ with a 0.4 s counting time/step and logged to data files for analysis. Quantitative analysis was performed on the XRD data using the commercial package TOPAS V5 from Bruker AXS. For determination of the amorphous phase, the internal standard method was used. This method is one of the most common approaches, which was studied in the earlier work of Madson et al. Amorphous content was determined by difference using 50% by weight of Baikowski 1 μm corundum added as an internal standard.

2.4.3. Scanning Electron Microscopy/Energy-Dispersive X-Ray Spectroscopy (SEM/EDS). Subsamples were taken of the roast–leach residues and graphite added to aid in the separation of the individual particles. The sample/graphite mixture was mounted in an epoxy resin (contains Cl) to form a block. The block was ground, wet-polished, and coated with 98% mixture was mounted in an epoxy resin (contains Cl) to form a separation of the individual particles. The sample/graphite (SE) detector and a backscatter electron (BSE) detector. The data is normalized to 100%.

Quantitative analysis was calculated using standardless ZAF correction provided images are BSE (backscatter electron) images. The experimental results are used to provide an insight into the rate of reaction between the liquid salt cation and the ore is increased with an increase in the reaction temperature. The principal reaction of the ore with the salt mixture are also investigated.

3. RESULTS AND DISCUSSION

The experimental results are used to provide an insight into the effect of various parameters, such as reaction time, temperature, and salt to ore ratio, on thermal decomposition of the ore using a salt mixture of NaCl and CaCl₂ at a eutectic composition of 68 wt % CaCl₂−32 wt % NaCl. In addition, the effect of different salt mixture compositions from sodium to calcium-rich compositions has also been assessed. The crystalline structure of the roast–leach samples and the principal reaction of the ore with the salt mixture are also investigated.

3.1. Reaction Time. Figure 1 presents the dependence of potassium extraction on salt to ore ratio using the eutectic binary salt 32 NaCl to 68 CaCl₂ (wt %) at a reaction temperature of 650 °C. Fitting of the dotted line was obtained using the least-squares method. The thermal decomposition of the ore was also assessed at salt to ore mass ratios of 1:1, 2:1, and 3:1. The results show that the increase in the reaction time and salt to ore ratio significantly increased potassium extraction (i.e., 20–77%) when the salt to ore ratio was increased from 1:1 to 3:1 and after 9 h reaction time. For all salt to ore ratios, the potassium extraction increased notably in the first 6 h, then slowed down and seemed to asymptotically plateau.

Potassium extraction (η) is shown to be strongly affected by an increase in the salt to ore ratio (Figure 1). For example, η = 40% at t = 6 h for a salt/ore ratio = 1:1, but for the salt/ore ratio = 3:1, it reached 74% for the same operating conditions. This is mainly because an increase in the reaction time, combined with a higher salt to ore ratio, reduces the diffusion distance between Na⁺ and Ca²⁺ cations in the molten salt and K⁺ in the ore, which accordingly improves potassium recovery.

3.2. Mass Ratio of Salt to Ore and Reaction Temperature. Figure 2 presents the dependence of potassium extraction on the salt to ore mass ratios and reaction time for different values of temperature where the salt mixture is in a liquid phase at the eutectic composition (32 wt % NaCl and 68 wt % CaCl₂). As shown, potassium extraction strongly increases with an increase in the reaction temperature. The rate of reaction between the liquid salt cation and the ore is extremely low at 550 °C; almost no potassium extraction is obtained at this temperature regardless of the changes in the salt to ore ratio and the reaction time even after 6 h. In contrast, potassium recovery of approximately 90% has been achieved when the temperature is increased to 850 °C. However, the effect of the salt to ore ratio, which is varied between 1:1 and 3:1, on potassium recovery at 850 °C is found to be insignificant (Figure 2a). This is attributed to the almost fully extracted K⁺. A similar trend is identified for varying the reaction time, showing K⁺ extraction to be insensitive to reaction time above 3 h (Figure 2b).

On the other hand, at reaction temperatures of 650 and 750 °C, potassium extraction is strongly influenced by changing both the salt to ore ratio and the reaction time. For example, at a temperature of 750 °C, the potassium recovery after 3 h increased notably from 65 to 80% by changing the salt to ore ratio from 1:1 to 2:1. Similarly, potassium extraction is increased notably from 52 to 75% (Figure 2b) with an increase in the time from 1 to 6 h for salt/ore = 3:1 (mass ratio).

3.3. Salt Compositions. Figure 3 presents the dependence of potassium extraction on the salt mixture composition for a range of temperatures and salt/ore = 1:1 (mass ratio). The salt compositions selected for this study are obtained from the phase diagram developed (Figure 3b). The different phases of salt mixtures including liquid and solid–liquid phases, depending on the composition and temperature, were analyzed in the current investigation. The phase state of salt mixtures including liquid and solid phases, together with a liquid state. For a temperature of 750 °C, the compositions corresponding to a liquidus line (Figure 3b) were also assessed together with a liquid state. For a temperature of 650 °C, the compositions in the equilibrium region where the salt mixture is in both solid and liquid phases were also analyzed in addition to the compositions related to the liquidus line. The results were compared with a pure salt of NaCl and CaCl₂.

![Figure 1](https://dx.doi.org/10.1021/acsomega.0c00549)

**Figure 1.** Effect of reaction time on the potassium extraction using a eutectic molten salt mixture of NaCl 32 (wt %) and CaCl₂ 68 (wt %) for salt to ore mass ratios of 1:1, 2:1, and 3:1 (1r, 2r, and 3r) at T = 650 °C and for ore PSD = 150 μm. Fitting of the dotted line was obtained using the least-squares method.
studied in a previous work. It is worth noting that the eutectic temperature, $503^\circ C$, was not analyzed as the results of the temperature effect on potassium extraction at the eutectic composition, Figure 2a,b, show that a temperature of $550^\circ C$ is not high enough to be able to thermally activate the ore for extraction of K$_2$O. Therefore, there is no point in assessing a temperature lower than $550^\circ C$. For a temperature of $650^\circ C$, as expected, almost no potassium recovery has been achieved using a pure single salt, either NaCl or CaCl$_2$, due to the solid–solid reaction between the solid salt cation and the ore. In addition, using a salt mixture with equilibrium compositions of 12 and 96 mol % CaCl$_2$ was also unable to break the bond between K$^+$ and the Si–Al–O structure. This is in part because of the partial solid–solid reaction between the cation salt and the ore and also because of the low reaction temperature of $650^\circ C$. However, for compositions of 31 and 75 mol % CaCl$_2$ at a liquidus temperature of $650^\circ C$, a potassium extraction of 23 and 30%, respectively, has been achieved. This indicates that the use of liquid salt improves the extraction of K$^+$ due to the faster diffusion of Na$^+$ and Ca$^{2+}$ cations present in the molten salt into the ore. However, for a temperature of $650^\circ C$, the potassium extraction increases significantly by increasing the reaction temperature (>3 h) and increasing the salt to ore mass ratio (>1:1), as discussed in the previous Section 3.1.

In a previous study, potassium extraction of ~20 and 54% using pure salts NaCl and CaCl$_2$ was achieved at a reaction temperature of $750^\circ C$. Although the pure salts are in the solid phases at this temperature, due to the formation of a small amount of KCl, the melting temperature of CaCl$_2$–KCl and NaCl–KCl reduces causing the reaction to proceed in the solid–liquid rather than solid–solid state at a faster rate. In the present study, adding 20 wt % (12 mol %) CaCl$_2$ to the NaCl salt has led to a significant increase in potassium extraction from 20% to almost 60% at $750^\circ C$. On the other hand, adding NaCl into the pure CaCl$_2$ salt has marginally improved the potassium extraction. Figure 3 shows clearly that a further increase in the concentration of CaCl$_2$ (>12 mol %) slightly enhances the potassium extraction to 65% at the eutectic composition.

Figure 2. Influence of salt to ore ratio (a) and reaction time (b) on potassium extraction for a range of reaction temperatures at $t = 3$ h (a) and salt/ore = 1:1 (b) for the salt composition of 32 wt % NaCl and 68 wt % CaCl$_2$. Fitting of the dotted line was obtained using the least-squares method.

Figure 3. (a) Effect of salt composition on potassium extraction for a range of temperatures and salt/ore = 1:1 and (b) salt compositions (red stars) studied for the extraction of potassium from the ore in this work identified in the blue boundary on the previously developed NaCl–CaCl$_2$ system. (b) is adapted from Mediaas et al. with their provided references.

Figure 4. (a) X-ray diffraction pattern and (b) quantitative XRD analysis of the roast–leach samples over the various salt to ore mass ratios of (i) 1:1, (ii) 2:1, and (iii) 3:1 using a salt mixture of 32 wt % NaCl–68 wt % CaCl$_2$ at $T = 650^\circ C$ and $t = 3$ h.
A similar trend was also observed for a reaction temperature of 900 °C. That is, $\eta$ increases initially from 70% using pure NaCl to a maximum of 85% at 12 mol % CaCl$_2$ and then remains almost constant irrespective of the CaCl$_2$ composition up to 45 mol %, but then it drops slightly to 82% at higher CaCl$_2$ concentration ratios. A 12 mol % CaCl$_2$ (mixed with 88% NaCl), rather than pure CaCl$_2$, not only provided the highest potassium recovery but also minimized the use of CaCl$_2$, and consequently, in industrial use, it translates into a reduction in energy cost related to the drying process of the hydroscopic CaCl$_2$ salt. In addition, the energy required to recover CaCl$_2$ from aqueous solution after water leaching for recycling is potentially minimized.

### 3.4. Evaluation of XRD Analysis

The effects of salt to ore mass ratio at 650 °C and temperature between 650 and 850 °C on the crystalline structure of the roast–leach samples after 3 h are shown in Figures 4a and 5a, respectively, for the eutectic salt mixture (32 wt % NaCl–68 wt % CaCl$_2$). The reason for the use of this eutectic composition is that the assessment of the salt composition discussed earlier (Section 3.3) confirms that this composition can be considered as an optimum salt mixture at 650 °C. Figures 4b and 5b present the mineral product compositions quantified based on the Rietveld refinement method using TOPAS. The XRD patterns show that with an increase in the salt to ore ratio from 1:1 to 3:1 at 650 °C, the diffraction peak of microcline/orthoclase becomes weaker owing to its conversion to plagioclase. Figure 4b shows that the microcline/orthoclase decreases from 44% at salt/ore = 1:1 to 27% at salt/ore = 3:1, while plagioclase compositions increase from 20 to 36%.

The increase of the reaction temperature from 650 to 850 °C (Figure 5a,b) significantly affected the decomposition of K-feldspar, more than the effect of increasing the salt to ore ratio at 650 °C. That is, the intensity of K-feldspar (microcline/orthoclase) is significantly reduced between 650 and 750 °C and disappears at 850 °C, while that of plagioclase notably increases.

Kaolinite and mica content in the original ore has been reported at 5.9 and 8.1 wt %, respectively, in the previous work. Kaolinite has not been detected by XRD analysis in the current study (Figure 4b) and the mica content significantly reduces from 8 to 4 wt % at 650 °C using salt/ore = 1 (Figure 4b). On the other hand, the composition of amorphous phases is determined to be 10 wt % at 650 °C and salt/ore = 1. Therefore, the lack of kaolinite and reduction in mica content could be associated with a dihydroxylation reaction causing the formation of disordered and noncrystalline structures or amorphous phases. The identification of the amorphous phase in the current XRD analysis shows that this conclusion should be plausible. The further reduction in the mica from 4 wt % using salt/ore = 1 to 1.5 wt % using salt/ore = 3 could be associated with the reaction of the nonamorphous mica phase with the molten salt mixture due to the use of the excess molten salt mixture. Assuming K$_2$O in the feldspar and mica is $\sim$16.5 and 9.87 wt %, respectively, it can be estimated that $\sim$6% of the total K$_2$O extracted is originated from mica by increasing the salt to ore ratio from 1 to 3 at 650 °C. There is a similar trend for the mica and kaolinite content when increasing the temperature from 650 to 850 °C given in Figure 5b. Both XRD peaks and product compositions of quartz and hematite, which are the main ore impurities, remain constant and have the same values as those present in the original ore. This implies that these impurities do not undergo a reaction between the salt mixture and the ore.

To further assess the end product of the salt mixture followed by water leaching (deionized water), both XRD and inductively coupled plasma-optical emission spectrometry (ICP-OES) analysis were performed. Figure 6 shows the XRD pattern of the crystallized salt mixture of the leaching solution. The salt mixture at the eutectic composition reacted with the ore at $T = 750$ °C, salt/ore = 1:1 (mass ratio), and $t = 3$ h. Considering the stoichiometric of the chloride salts, the mass fraction of K, Ca, and Na at 6.78, 25.90, and 9.69 wt %, respectively. Concerning the stoichiometric of the chloride salts, the mass fraction (wt %) of KCl, CaCl$_2$, and NaCl were estimated at 16, 61, and 23, respectively.

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**Figure 5.** (a) X-ray diffraction pattern and (b) quantitative XRD analysis of the roast–leach samples over the various temperature ranges using a salt mixture of 32 wt % NaCl–68 wt % CaCl$_2$ at salt/ore = 1 (mass ratio) and $t = 3$ h.

**Figure 6.** X-ray diffraction pattern of the crystallized salt solution obtained after the water leaching process with the use of initial salt mixture of 32 wt % NaCl–68 wt % CaCl$_2$ and the roasting operating conditions: salt/ore = 1:1 (mass ratio), $T = 750$ °C, and $t = 3$ h.
3.5. Understanding the Principle Reaction between the Salt Mixture and the Ultrapotassic Syenite. Figures 7 and 8 present the SEM-EDS mapping of thermal decomposition of the ore with the salt mixture (65 wt % NaCl−35 wt % CaCl₂) at 950 °C within 30 min and 1 h reaction time, respectively. Tables S1 and S2 also summarize the EDS X-ray analysis on the polished section of the roast−leach samples. Mineral phases, given in Tables S1 and S2, are identified based on their stoichiometric ratio, EDS X-ray spectrum, and also information obtained from XRD analysis. Both Figures 7 and 8 confirm that the reaction between the ore and the salt mixtures takes place. Sodium cation (Na⁺) identified by the blue color on the EDS map is distributed all over the residual ore. This is mainly because sodium cations of NaCl diffuse into the K-feldspar and replace the K⁺. That is, the ore reaction with Na⁺ is a diffusion-controlled process. This finding is also in agreement with the earlier work of Neusser et al. However, Ca²⁺, which is identified by the green color on the EDS map, follows the cracks or grain boundaries and is also around impurities of the ore, e.g., hematite and quartz. EDS analysis of the roast−leach samples, given in Tables S1 and S2, shows that the main end products are alkali feldspar (AF) and plagioclase feldspar (PF). The plausible AF and PF compositions are highlighted in the developed ternary feldspar; Figure 9.41

Figure 7. SEM-EDS image on the roast−leach ore residues obtained from thermal decomposition of the ore with the salt mixture of 65 wt % NaCl−35 wt % CaCl₂ at 950 °C and 30 min reaction.
possible compositions of PF were estimated to be between 10 and 50% Ca-feldspar. It should be noted that quartz should be another product due to the reaction between K-feldspar and CaCl₂; however, it is not possible to distinguish quartz generated by the reaction from the quartz that is already a mineral in the ore. EDS results confirm that possibly other mineral phases exist in the ore, including Fe and Ti phases, quartz, apatite, and mica. The EDS results also confirm that the reaction does not proceed completely within 1 h reaction time due to the presence of alkali feldspar rich in K-feldspar, spectra 5 and 6 in Table S2. It is worth noting that a thin green layer (clintonite), spectra 11 and 12 in Figure 7, that surrounded the mica (phlogopite) is most likely formed due to the reaction between phlogopite and CaCl₂.

4. CONCLUSIONS

The application of the NaCl–CaCl₂ system for the production of potash from ultrapotassic syenite has been assessed experimentally. Different operating parameters including reaction temperature, time, salt composition, and salt to ore ratio have been systematically evaluated. It was found that potassium extraction of approximately 90% can be achieved when using a NaCl–CaCl₂ system at eutectic composition with a salt to ore ratio of 1:1, a reaction temperature of 850 °C, and a minimum reaction time of 3 h. Several analytical techniques, XRF, QXRD, and SEM-EDS, were used to understand the principal reaction between the salt mixture and the ore and also to qualify and quantify the end products. Quantitative XRD analysis confirms the existence of amorphous phases in the quenched roast–leach samples. This is partly due to dehydroxylation of mica and kaolinite.
from the original ore that forms noncrystalline structures at high temperatures (i.e., >500 °C).

Both QXRD and SEM-EDS analyses confirm that the reaction between the salt mixture and the ore takes place over the temperature range between 650 and 900 °C and that the main residual ore products are alkali feldspar and/or plagioclase. It is also found that there is a possibility of the reaction between clay mineral (mica) presented in the ore and the molten salt mixture for extraction of K⁺. The end salt solution mixture obtained from the water leaching process is found to be a quaternary system of KCl solution mixture obtained from the water leaching process is obtained. Ca²⁺ follows cracks, grain boundaries, and reaction mechanism in which Na⁺ is a diffusion-controlled process, while Ca²⁺ follows cracks, grain boundaries, and around imurities. The results also showed that using a eutectic NaCl–CaCl₂ mixture offers the following advantages in comparison with pure NaCl or pure CaCl₂ for thermal decomposition of K-feldspar:

- Lowering the temperature to 650 °C and achieving potassium recovery of more than 70% at t = 6 h and salt/ore = 3:1 (mass ratio). The distinctive feature of 650 °C is to mitigate the effect of salt corrosion in comparison with T > 850 °C required for single NaCl and CaCl₂ molten salts. In addition, a reduction in the reaction temperature potentially lowers the energy required for the system. However, lowering the temperature in this study is associated with the use of a higher salt to ore ratio by approximately three times. This might add to the cost of material handling, heat recovery, latent heat, and plant size. Therefore, further process simulation and technoeconomic analysis are required to precisely evaluate the potential benefits and limitations of this method.

- The NaCl–CaCl₂ salt mixture increases potassium recovery in comparison to using a pure NaCl or pure CaCl₂. The addition of CaCl₂ into pure NaCl has a considerably stronger effect on increasing the potassium recovery than the addition of NaCl into pure CaCl₂. Therefore, a reduction in the use of CaCl₂ has the added benefits of reducing material costs, lowering the energy cost associated with the drying process of CaCl₂ in industrial applications, and also reducing the energy required for separating CaCl₂ from aqueous solution for recycling. The optimized salt mixture composition is 20 wt % CaCl₂–80 wt % NaCl, which yielded a maximum potassium recovery of ~65 and 90% at 750 and 900 °C, respectively, for t = 3 h and salt/ore ratio of 1:1.

A technoeconomic assessment that covers the potential energy reduction and scalability of this approach for industrial applications forms a part of the next stage of this work.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c00549.

EDS analysis of the polished section of the roast–leach residues at different reaction times using the salt mixture of 65 wt % NaCl–35 wt % CaCl₂, ore/salt = 1, and T = 950 °C (PDF)

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**Notes**

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