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# Extraction of potassium from K-feldspar *via* the CaCl$_2$ calcination route☆

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## ARTICLE INFO

## ABSTRACT

The extraction of potassium from K-feldspar *via* a calcium chloride calcination route was studied with a focus on the effects of the calcination atmosphere, calcination temperature and time, mass ratio of CaCl$_2$ to K-feldspar ore and particle size of the K-feldspar ore. The results demonstrated that a competing high-temperature hydrolysis reaction of calcium chloride with moisture in a damp atmosphere occurred concurrently with the conversion reaction of K-feldspar with CaCl$_2$, thus reducing the amount of potassium extracted. The conversion reaction started at approximately 600 °C and accelerated with increasing temperature. When the temperature rose above 900 °C, the extraction of potassium gradually decreased due to the volatilization of the product, KCl. As much as approximately 41% of the potassium was volatilized in 40 min at 1100 °C. The mass ratio of CaCl$_2$/ K-feldspar ore significantly affected the extraction. At a mass ratio of 1.15 and 900 °C, the potassium extraction reached 91% in 40 min, while the extraction was reduced to only 22% at the theoretical mass ratio of 0.2. Optimal process conditions are as follows: ore particle size of 50–75 μm, tablet forming pressure of 3 MPa, dry nitrogen atmosphere, mass ratio of CaCl$_2$/ore 1.15:1, calcination temperature of 900 °C, and calcination time of 40 min. The XRD analysis revealed that a complex phase transition of the product SiO$_2$ was also accompanied by the conversion reaction of K-feldspar/CaCl$_2$. The SiO$_2$ product formed at the initial stage was in the quartz phase at 900 °C and was gradually transformed into cristobalite after 30 min.
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## 1. Introduction

Potassium is one of the three most important nutritional elements for crop growth. The crop yield has been reported to be increased by 20% to 30% when potash fertilizers are applied to the potassium-deficient soils [1]. The water-soluble potassium resources in China, however, are very scarce and account for only 2.20% (approximately $2.1 \times 10^8$ t K$_2$O) of the total potash resources all over the world [2–4]. At present, approximately 50% of the total potassium fertilizer demand for agriculture in China depends on imports [5–7]. However, the water-insoluble K-feldspar resources in China are extremely abundant, exceeding $200 \times 10^8$ t K$_2$O [8]. A similar situation also exists in many other countries and regions [9–11]. Therefore, the conversion of K-feldspar into water-soluble potassium fertilizers at a low cost and high efficiency is very important [12,13].

The existing methods for extracting potassium from K-feldspar can be divided into two categories: the wet and dry processes. The wet processes include the hydrofluoric acid method [14,15], the hydrofluoric acid–sulfuric acid method [16–20], the hydrofluoric acid–hydrochloric acid method [21], and the fluosilicate method [22,23]. Although these wet processes have the advantage of a high potassium extraction ratio at low reaction temperatures, great quantities of the acidic waste gases, waste liquids and waste residues are discharged, resulting in serious environmental problems.

The dry processes refer mainly to the calcination of K-feldspar with various sodium- and calcium-containing additives, including sodium carbonate, sodium sulfate, sodium chloride, calcium carbonate, gypsum and calcium chloride, at higher temperatures to convert K-feldspar to water-soluble potassium salts, followed by water dissolution for the extraction of potassium. With mixed gypsum and calcium carbonate as additives, Bakr *et al.* [24] obtained a maximum potassium extraction of 80% at 1000 °C, while Wang *et al.* [26,27] achieved an 84%–90% K-feldspar decomposition at 950–1050 °C. Upon the addition of a third additive, sodium sulfate, the conversion temperature could be further reduced to 900 °C. Using mixed calcium chloride and calcium carbonate as additives, a potassium extraction of 85% could be reached at 800–850 °C [25]. Zhao *et al.* [28] employed a first calcination with calcium carbonate and sodium carbonate as additives at 1280–1330 °C, and then the NaOH dissolution route and the extraction of potassium reached 70%. Ma *et al.* [29] examined the sodium carbonate decomposition of K-feldspar with a maximum potassium extraction of 97.1% at

880 °C. Han *et al.* [30,31] investigated the $CaCl_2$ and NaCl decomposition of K-feldspar, and the potassium extraction achieved 90%–99% at 960 °C.

Clearly, among the various calcination additives mentioned above, the addition of chloride salts could considerably reduce the calcination temperature and hence is a more promising approach. Because of the difficulty of separating potassium chloride from sodium chloride, using only calcium chloride may be a better alternative. However, there have been few reports of the K-feldspar/calcium chloride calcination reaction. Peng *et al.* [32] considered the reaction to be a reversible liquid–solid reaction and experimentally determined the conversion ratio of K-feldspar under different reaction conditions. Han *et al.* [33] regarded the high temperature reaction as a cation exchange reaction between potassium ions in the silica-alumina-oxygen network structure of K-feldspar and calcium ions in the calcium chloride melt. Recently, Xie *et al.* [34] and Ye *et al.* [35] proposed a novel approach for the simultaneous extraction of potassium *via* the calcination of K-feldspar with $CaCl_2$ and aqueous carbonation of the potassium-extracted residue for $CO_2$ sequestration with the aim of reducing costs of both the potassium extraction and the $CO_2$ mineralization. However, until now, the process and mechanism of extracting potassium have not been well understood.

In the present study, the calcination reaction of K-feldspar with calcium chloride was systematically investigated by using various characterization techniques focusing on the effects of the calcination atmosphere, the calcination temperature and time, the particle size of the K-feldspar ore, and the mass ratio of $CaCl_2$/K-feldspar ore for the potassium extraction and the phase transition. The mechanism was discussed.

## 2. Experimental

### 2.1. Materials

The K-feldspar ore used in the experiments was mined in Baoxing, Sichuan Province, China. The ore was crushed, ground and dried at 120 °C for 2 h. The main minerals analyzed by X-ray diffraction (XRD) were microcline and quartz. To analyze the trace phase, the raw K-feldspar ore was identified with PLM (Polarized Light Microscopy) by observing the different interference colors under perpendicularly polarized light. As shown in Fig. 1, K-feldspar was observed to be gray with a granular texture under the polarizing microscope. The major component of the K-feldspar was colorless under plane polarized light. The minor component that was white under the polarizing microscope and transparent under plane polarized light was unevenly distributed quartz, and the trace components were mica, calcite, sphene and hematite, which were colorful, brown, green and tawny under the polarizing microscope, respectively.

The chemical composition of K-feldspar is listed in Table 1. The chemical composition, except $K_2O$, was measured by X-ray fluorescence spectrometry (XRF).

### 2.2. Calcination experiments

The K-feldspar ore powder sample with certain particle sizes was mixed uniformly with anhydrous calcium chloride powder according to the specific mass ratios in an agate mortar. The mixture was shaped into tablets with a diameter and thickness, respectively, of 10 mm and 5–7 mm using a tablet machine (HW-01, Tianjin, China) under 3 MPa pressure and was then dried in a muffle furnace at 300 °C for 1 h to remove the water adsorbed during the mixing. Three tablets (approximately 4 g) placed in a porcelain boat were weighed accurately and calcined in a tube furnace at preset temperatures in a dry or damp nitrogen atmosphere at gas flow of $3 \times 10^{-4} \, m^3 \cdot min^{-1}$ for certain periods of time. The calcined slag thus obtained was withdrawn, cooled naturally to room temperature in a desiccator, pulverized and then leached. The

dissolution was conducted in deionized water with the mass ratio of liquid to solid of 50:1 at 70 °C for 30 min to extract potassium, then the slurry was filtered (the process is shown in Fig. 2).

The contents of potassium and chlorine in the resulting filtrates were measured. The extraction ratio of potassium and the thermal hydrolysis ratio of calcium chloride were calculated. The calcined slag and leach residue were characterized by XRD and SEM.

### 2.3. Analysis and characterization

The content of potassium in the filtrate was measured by the potassium tetraphenylborate gravimetric method. To measure the content of potassium in the K-feldspar ore or leach residue, the solid samples were first digested. Approximately 0.5 g of K-feldspar ore or leach residue was mixed with 4 g of NaOH and 1 g of $Na_2O_2$ in a nickel crucible, was smelted in a muffle furnace at 750 °C for 10 min, and was then dissolved in a mixed solution of 30 ml of dilute sulfuric acid with a volume ratio of 98 wt.% sulfuric acid to deionized water 1:1 and 50 ml of dilute hydrochloric acid with a volume ratio of 31 wt% hydrochloric acid to deionized water 1:1. The content of potassium in the leach liquor was also measured by the potassium tetraphenylborate gravimetric method.

The content of chloride in the filtrate was determined by the silver chloride gravimetric method.

The XRD analyses of the calcined slag and leach residue were performed using a Philips X'pert PRO diffractometer employing graphite-filtered Cu $K_\alpha$ radiation ($\lambda = 0.15406$ nm) with an accelerating voltage of 40 kV and tube current of 30 mA. Data points were acquired by step scanning with a ratio of $12(°) \cdot min^{-1}$ from $2\theta = 10°$ to $2\theta = 80°$.

The surface morphology of the raw K-feldspar ore and the calcined slag was observed using a Hitachi S-4800 scanning electron microscope (SEM) at an accelerating voltage of 5 kV. The relative elemental abundance of the K-feldspar ore and the calcined slag was analyzed with an energy-dispersive X-ray spectrometer (EDS, Oxford IE 250).

## 3. Results and Discussion

The extraction of potassium from K-feldspar by calcium chloride calcination is a heterogeneous reaction. Generally, the factors affecting the extraction involved mainly the calcination temperature, reaction time, mass ratio of the $CaCl_2$/K-feldspar ore and particle size of the K-feldspar ore. However, a preliminary experiment indicated that the existence of moisture in the calcination atmosphere also remarkably influenced the extraction. Therefore, the effect of water vapor was first examined.

### 3.1. Effect of moisture in the calcination atmosphere

A comparison test was conducted in dry and damp nitrogen atmospheres at 900 °C, with a mass ratio of $CaCl_2$/K-feldspar ore of 0.4 and a particle size of the K-feldspar ore of 75 to 150 μm. The damp nitrogen atmosphere, which simulated damp air with a relative humidity of 75% at 25 °C, was prepared by the addition of a certain amount of deionized water to dry $N_2$ gas in a custom-designed damp nitrogen atmosphere device, which was heated for evaporation to obtain a mixture of gas with 18.5 g of moisture vapor per $m^3$ dry nitrogen and was introduced into the tube furnace at gas flow of $3 \times 10^{-4} \, m^3 \cdot min^{-1}$. The extraction of potassium at different reaction times was measured and is shown in Fig. 3.

As Fig. 3 shows, the extraction of potassium in the damp $N_2$ atmosphere was approximately 5% lower than the extraction in a dry $N_2$ atmosphere when the calcination time exceeded 40 min. To explain this phenomenon, the chloride content remaining in the calcined slag was measured. The residual chloride content was found to be almost unchanged with the increasing reaction time when the calcination was in a dry $N_2$ atmosphere, while the chloride content under the