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Recovery of K by NH$_4$HSO$_4$ low-temperature roasting from brown corundum Fly Ash

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**Abstract**

Brown corundum dust ash (BCFA) is an industrial solid waste from the brown corundum production process. The alkali metal is a key factor limiting its comprehensive use. Currently, BCFA is mainly stockpiled and occupies a large amount of land. Its fine particles are easy to cause air pollution. The addition of NH$_4$HSO$_4$ allows for the effective extraction of K from BCFA and the efficient use of BCFA. Under optimum conditions: NH$_4$HSO$_4$ to BCFA mass ratio of 1.2:1, the roasting temperature of 240 °C, roasting time of 2 h, water leaching time of 90 min, water leaching temperature of 65 °C, water leaching liquid to solid ratio of 3:1, the leaching rate of K from BCFA reached 97%. The leachate was crystallised by evaporation to obtain K, N compound fertiliser for agricultural use. The leaching residue is mainly Al and Si, which can be used for the preparation of refractory materials, aluminium and silicon molecular sieves, construction materials and other raw materials.

1. **Introduction**

Potassium is an essential element for crop growth and affects crop yield. China is a agricultural country with a high demand for potassium. Fifty per cent of the total potassium used in agriculture in China needs to be imported [1, 2]. Currently, potassium resources are mainly derived from water-soluble potassium. Water-soluble potassium resources are distributed, and only a few countries are rich in reserves. Water-soluble potassium resources in China are scarce and distributed in remote areas. The reserves of insoluble potassium in China are large [3, 4]. The main primary minerals containing potassium are mica and potassium feldspar, with a K$_2$O mass fraction of about 7%–12%. BCFA, an industrial solid waste collected during the production of brown corundum, has a potassium mass fraction of up to 16.9%. At present, the theoretical annual output of BCFA is 500,000 tons [5]. BCFA is stored on the ground using heap storage, which is prone to environmental problems such as air and soil pollution due to its fine particles. According to current literature, potassium extraction methods include high-temperature reaction methods [6–8]. Inorganic acid decomposition method [9, 10], microbial decomposition method [11–14], hydrothermal method [15–17].

Yuan [18] et al used CaCl$_2$ as an additive to extract potassium from potassium feldspar. Under high temperature, CaCl$_2$ reacts with KAlSi$_3$O$_8$ to form CaAl$_2$Si$_2$O$_8$, SiO$_2$ and KCl to extract potassium from potassium feldspar. The results showed that the optimum conditions for the extraction of potassium were roasting temperature of 900 °C and CaCl$_2$ to ore mass ratio of 1.15:1. The roasting temperature exceeded 900 °C and KCl volatilized, leading to a decrease in the potassium extraction rate. Kuai [19] et al extract lithium and potassium from lepidolite through the calcination process with the additive of K$_2$CO$_3$. Maximum extraction of lithium (95.52%) and potassium (95.70%) was obtained from the soluble silicates at the optimum leaching conditions. (850 °C calcined product leached at 100 °C for 1 h using a liquid to solid ratio of 5:1). At 850 °C, K$_2$CO$_3$ can convert lepidolite to soluble K$_2$SiO$_3$ and Li$_2$SiO$_3$, and thus leach potassium and lithium. Schimicoscki [20] et al used sulfuric acid to recover potassium from Brazilian glauconitic siltstone. Leaching of...
potassium was found to be related to acid concentration. Wang et al. used the low-temperature molten salt method to extract potassium from potassium feldspar. Under the optimum conditions, the mass ratio of NaNO3/K-feldspar 1:1, NaOH/K-feldspar 1.4:1, H2O/K-feldspar 0.5:1, particle size under 61 μm (240 mesh), reaction temperature of 200 °C, and reaction time of 6 h, the extraction rate of potassium can reach 96.25%.

In summary, it is of general research significance to extract potassium from BCFA. On the one hand, it can achieve environmental protection and green sustainable development, on the other hand, avoid the waste of resources. In this study, NH4HSO4 was mixed with BCFA followed by roasting and water leaching to extract potassium from BCFA. The leaching residue can be used for refractory materials and the preparation of aluminum-silica molecular sieves. This approach avoids the waste of BCFA’s valuable components and achieves green sustainable development.

2. Experiment

2.1. Materials and experimental method
Experimental materials are obtained from A brown corundum production plant in Guizhou, China. The main components of BCFA are shown in table 1. The water used for the experiments was distilled water. NH4HSO4 is analytically pure and was produced from Aladdin Co.

The reactants were mixed with BCFA to NH4HSO4 mass ratios of 0–1.2. The mixed samples are roasted in a muffle furnace (Model 8401–1) and the roasting temperature range is 160 °C~320 °C. The roasted clinker and distilled water were subjected to water leaching experiments at a liquid to solid ratio of 1:1 to 5:1. After the water leaching experiment, the leachate was separated by filtration using a filter extractor (SHB-III A). The leach residue was washed three times with distilled water and dried in an oven at 100 °C for 12 h. ICP was used to analyse the composition of the leach residue and leach solution.

2.2. Calculation of leaching rates of K and Al
The extraction rate of potassium (%) was estimated using the following equation:

$$\eta = \frac{m_1 w_1 - m_2 w_2}{m_1 w_1} \times 100\%$$

Where $m_1$ is the weight of the original BCFA. $w_1$ is the mass fraction of K2O or Al2O3 in the original BCFA. Where $m_2$ is the weight of the Leaching residues. Where $w_2$ is the mass fraction of K2O or Al2O3 in the leaching residue.
2.3. Experimental analysis instruments
Analysis of K$_2$O and Al$_2$O$_3$ content in leach residue and solutions by ICP-OES (Agilent 5110, American). The material phase is characterised by XRD (BrukerAXS D8 Advance, Germany). The surface morphologies of the samples were characterized by SEM (ZEISS Gemini 300, Germany). The elemental constitution of the different samples was analyzed by energy-dispersive x-ray spectroscopy (EDS: Smartedx, Germany). The chemical composition detected by ARL Perform $'X$ wavelength dispersive fluorescence spectrometer (XRF: ARL Perform $'X$, Switzerland).

3. Result and discussion
3.1. Analysis of the BCFA
The chemical composition of the BCFA used in this work is listed in table 1, which revealed 43.29wt% SiO$_2$ and 18.62 wt% Al$_2$O$_3$ and 16.90 wt% K$_2$O. Figure 1 shows the BCFA phase analysis by XRD. The major phases in BCFA are K$_2$SO$_4$, quartz and $\alpha$-Al$_2$O$_3$. SEM images and EDS images of the BCFA are shown in figure 2. The BCFA consists of spherical particles of varying sizes, and small quantities of lumpy agglomerates. It is clear from figure 2 that there is adherence to the surface of the sphere. The spheres contain mainly Al, Si and K.
3. BCFA treated under different conditions

BCFA was subjected to two treatments to examine the leaching rate of K2O without additives, namely:

1. water leaching, and
2. roasting followed by water leaching, as shown in table 2.

Table 2. BCFA, BCFA(a)(Under the conditions of water leaching temperature 95 °C, leaching time 120 min, the liquid-solid ratio of 4: 1), BCFA(b)(Calcined at 240 °C for 120 min. Under the conditions of water leaching temperature 95 °C, leaching time 120 min, the liquid-solid ratio of 4: 1).

|         | SiO₂  | Al₂O₃ | K₂O  | K₂O leaching rate % |
|---------|-------|-------|------|---------------------|
| BCFA    | 43.29 | 18.62 | 16.90| —                   |
| BCFA (a)| 47.28 | 20.41 | 10.78| 36.10               |
| BCFA (b)| 48.23 | 21.23 | 9.94 | 41.20               |

Figure 3. SEM images of BCFA (g) and washing residue (e), (f).

Figure 4. Effect of roasting temperature on K₂O and Al₂O₃ leaching rate.
As can be seen from table 2, only 36.10% of K2O could be leached using water washing. BCFA was roasted at 240 °C followed by water leaching and the leaching rate of K2O was only 41.2%, although there was a slight increase in the leaching rate. The increased SiO2 and Al2O3 content in the leach residue are mainly due to the leaching of K2O, while SiO2 and Al2O3 are insoluble in water. SEM images of the water washing residue are shown in figure 3. Figure 3 shows after the BCFA has been washed with water, the adhesion on the surface of the spheres is significantly reduced.

3.3. Effect of roasting temperature
To further enhance the leaching rate of K2O. A mixture of NH4HSO4 and BCFA was used for roasting and water leaching. The effect of roasting temperature on leaching rate is shown in figure 4 under the condition of NH4HSO4 to BCFA mass ratio of 1.2:1, roasting time of 120 min, liquid to solid ratio of 4:1, leaching temperature of 95 °C and water leaching time of 120 min.

Figure 4 shows that the leaching rate of K2O and Al2O3 increases with the increase in roasting temperature. When the roasting temperature was 160 °C, the leaching rate of K2O was 88%. As the roasting temperature went up, K2O leaching increased to 240 °C, and the leaching rate of K2O reached 97%. The leaching rate of K2O remained almost the same when the roasting temperature was increased. So 240 °C was chosen as the optimum roasting temperature. The increase in K2O leaching rate is mainly due to the reaction between NH4HSO4 and BCFA, which destroys the BCFA structure, thus releasing the encapsulated K2O. The main reactions of BCFA with NH4HSO4 are as follows (1–1,1–2):

![Figure 5. Effect of NH4HSO4 to BCFA mass ratio on K2O and Al2O3 leaching rate.](image)

![Figure 6. Effect of roasting time on K2O and Al2O3 leaching rate.](image)
3.4. Effect of NH₄HSO₄ addition

The effect of mass ratio of NH₄HSO₄ to BCFA on leaching rate is shown in figure 5 under the condition of roasting temperature of 240 °C, roasting time of 120 min, liquid to solid ratio of 4:1, leaching temperature of 95 °C and water leaching time of 120 min.

Figure 5 shows that when the mass ratio of NH₄HSO₄ to BCFA is 0, the leaching rate of K₂O is 40% and the leaching rate of Al₂O₃ is 0. At this time, the leached K is attached to the surface of the sample. When the mass ratio of NH₄HSO₄ to BCFA was 0.3, BCFA reacted with NH₄HSO₄ and the structure was destroyed, the leaching rate of K₂O was 61% and the leaching rate of Al₂O₃ was 7%. As the mass ratio of NH₄HSO₄ to BCFA increased, the leaching rates of K₂O and Al₂O₃ also increased. At a mass ratio of NH₄HSO₄ to BCFA of 1.2, the leaching rate of K₂O reached over 97% and the leaching rate of Al₂O₃ reached 25%.

3.5. Effect of roasting time on leaching rate

The effect of roasting time on leaching rate is shown in figure 6 under the condition of NH₄HSO₄ to BCFA mass ratio of 1.2:1, roasting temperature 240 °C, liquid to solid ratio of 4:1, leaching temperature of 95 °C and water leaching time of 120 min.

Figure 6 shows that the increase in roasting time favours the reaction of BCFA with NH₄HSO₄ and the leaching of K₂O. When the roasting time was 30 min, the leaching rate of K₂O was 82%. With the extension of
roasting time, when the roasting time was 120 min, the leaching rate of K₂O reached more than 97%, and at this time, the leaching rate of K₂O remained the same when the roasting time was continued to be extended. So the optimal roasting time is 120 min.

3.6. Effect of leaching time
The effect of leaching time on leaching rate is shown in figure 7 under the condition of NH₄HSO₄ to BCFA mass ratio of 1.2:1, roasting temperature 240 °C, roasting time 120 min, liquid to solid ratio of 4:1, and leaching temperature of 95 °C.

Figure 7 shows that the appropriate extension of the water leaching time is beneficial to the leaching rate of K₂O. At the leaching time of 60 min, the leaching rate of K₂O reached more than 97%. And at this time, the
leaching rate of K$_2$O remained the same when the leaching time was continued to be extended. Therefore, 60 min was chosen as the optimal water leaching time.

### 3.7. Effect of leaching liquid-solid

The effect of leaching liquid-solid on leaching rate is shown in figure 8 under the condition of NH$_4$HSO$_4$ to BCFA mass ratio of 1.2:1, roasting temperature 240 °C, roasting time 120 min, leaching time of 60 min, and leaching temperature of 95 °C.

#### Table 3. K$_2$O mass fraction in leach residue and K$_2$O, Al$_2$O$_3$ leaching rate.

|   | K$_2$O (%) | K$_2$O leaching rate (%) | Al$_2$O$_3$ leaching rate (%) |
|---|------------|--------------------------|-------------------------------|
| 1 | 0.53       | 97.32                    | 18.7                          |
| 2 | 0.49       | 97.94                    | 18.8                          |
| 3 | 0.52       | 97.54                    | 18.7                          |

#### Table 4. The chemical composition of the leaching residue (wt%).

| SiO$_2$ | Al$_2$O$_3$ | K$_2$O | Na$_2$O | ZnO | Fe$_2$O$_3$ | SO$_3$ | LOI  |
|-------|-------------|-------|--------|-----|-------------|--------|------|
| 68.33 | 17.68       | 0.52  | 0.2    | 0.01| 0.5         | 0.2    | 12.56|

The leaching rate of K$_2$O remained the same when the leaching time was continued to be extended. Therefore, 60 min was chosen as the optimal water leaching time.
Figure 8 shows that the leaching rate of K$_2$O was 87% when the liquid-to-solid ratio was at 1:1. As the liquid-solid ratio increased, the leaching rate of K$_2$O also increased. When the leaching liquid-solid ratio was 3:1, the leaching rate of K$_2$O reached 97%. The leaching rate of K$_2$O remained the same when the liquid-solid ratio continued to increase. The high liquid-solid ratio also increases the energy consumption for subsequent solution evaporation.

3.8. Effect of leaching temperature
The effect of leaching temperature on leaching rate is shown in figure 9 under the condition of NH$_4$HSO$_4$ to BCFA mass ratio of 1.2:1, roasting temperature 240 $^\circ$C, roasting time 120 min, leaching time of 60 min, and liquid to solid ratio of 3:1.

Figure 9 shows that the leaching rate of K$_2$O and Al$_2$O$_3$ increases with the increase of water leaching temperature. The leaching rate of K$_2$O was 88% when the water leaching temperature was 35 $^\circ$C. At the water leaching temperature of 65 $^\circ$C, K$_2$O reached more than 97% at this time, and the leaching rate of K$_2$O remained the same when the water leaching temperature continued to be raised, and the leaching of Al$_2$O$_3$ continued to increase. 65 $^\circ$C was chosen as the optimal leaching temperature.

To verify the reproducibility of the experimental conditions, three experiments results are shown in table 3 under the condition of NH$_4$HSO$_4$ to BCFA mass ratio of 1.2:1, roasting temperature 240 $^\circ$C, roasting time 120 min, leaching time of 60 min, liquid to solid ratio of 3:1 and leaching temperature 65 $^\circ$C.

The leaching residue composition is shown in table 4.
Table 4 shows that the K₂O content in the leaching residue is only 0.5%. The leaching residue is mainly SiO₂ and Al₂O₃, and the leaching residue can be used as raw material for refractory materials [22] aluminium-silicon molecular sieve [23] and high purity silica [24].

3.9. Leaching residue SEM images and XRD
Figure 10 XRD pattern shows that the main phases of the leached residue are quartz and corundum. The SEM of the leached residue shows that the surface attachment of the leached residue has disappeared and there are obvious etching marks on the block sample.

3.10. EDS images of leaching residue
Figure 11 EDS images show leaching residues mainly Al and Si. The spherical sample is mainly composed of Al, Si, and O. A small amount of potassium is diffusely distributed in the leach residue.

3.11. Handling of leaching solutions
The pH of the solution is adjusted to 4 using ammonia, at which point the metal ions in the solution precipitate out in the form of a precipitate. The solution is filtered and crystallized by evaporation to obtain white crystals as shown in figure 12.

Figure 12 XRD pattern shows that the white crystals are mainly K₂SO₄ with N, K complex sulfate. It can be used as compound fertilizer for agricultural production. From the EDS images in figure 13, it can be seen that the white crystals are mainly composed of three elements, K, S and O.

4. Conclusions
The potassium in BCFA consists of surface attachment and internal encapsulation. The addition of NH₄HSO₄ can open the wrapping structure of BCFA and leach out most of the potassium. Under the optimal conditions: NH₄HSO₄ to BCFA mass ratio of 1.2, roasting temperature of 240 °C, roasting time of 120 min, water leaching temperature of 65 °C, water leaching time of 60 min, water leaching liquid-solid ratio of 3:1. The leaching rate of K₂O can reach more than 97%. Meanwhile, the leaching rate of aluminium is only 25%, and most of the aluminium is still retained in the leaching residue. The leached residue can be used for refractory materials, aluminium-silicon molecular sieve, and the preparation of silica. The leaching solution is purified and the solution is evaporated and crystallized to obtain K, N compound fertilizer. This method can realize the harmless treatment of BCFA and can avoid the waste of valuable components in BCFA.

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Data availability statement
All data that support the findings of this study are included within the article (and any supplementary files).

Compliance with ethical standards
Conflict of Interest The authors declare that they have no conflict of interest.

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**Ethics declarations**

**Competing interests**

The authors declare no competing interests.

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