Extraction of Potassium from Biotite by \( \text{Ca}^{2+}/\text{K}^+ \) Ion Exchange and the Structural Transformation

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ABSTRACT

In order to alleviate the contradiction between supply and demand of potassium resources in China, we extracted potassium from biotite by \( \text{Ca}^{2+}/\text{K}^+ \) ion exchange. Soluble potassium salts were obtained from the filtrate by hydrothermal reaction of biotite with oxidant, ion exchanger and other reagents at 80 °C. The extraction rate of potassium and the structure change of biotite during the process of potassium exchange were determined by atomic absorption spectrophotometer and X-ray diffraction. The results showed that the layered silicate structure of biotite after ion exchange had not been destroyed, the base-plane spacing has expanded from 1.012 nm to 1.4288 nm, and most of the interlayer potassium ions have been extracted after 24 hours. The potassium extraction rate is 89%.

INTRODUCTION

Potassium is one of the two scarcest non-metallic minerals in China. There are three kinds of potassium resources: soluble solid-state potassium salts, soluble liquid salt lake brine or seawater, and insoluble potassium-bearing minerals[1]. At present, the third kind of insoluble potassium minerals is still in the development stage. The main methods of extracting potassium concentrate on the premise of destroying the structure of mica, and this method is one-off, which is not conducive to the comprehensive utilization of resources[2]. In fact, mica has important applications in petroleum cracking and polymer modification because of its good lamellar structure, good thermal stability and acid-base resistance. Therefore, it is necessary to propose

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a new method with high efficiency and low energy consumption without destroying the good lamellar structure of mica.

After many years of study on biotite, a potassium-bearing mineral in the associated potassium-bearing shale of collophaneite[3-5], biotite was oxidized under hydrothermal conditions to increase the valence of Fe$^{2+}$ in biotite octahedron and reduce the electronegativity of biotite tetrahedron lamellae, thus making potassium ions more easily displaced by Ca$^{2+}$.

**EXPERIMENTS**

On the analytical balance, 1.0 g biotite powder was weighed, placed in a 250 ml glass cone bottle, and slowly poured into a 200 ml saturated calcium nitrate solution. Then dilute hydrochloric acid of 0.5 mol/L made in the laboratory was added to the solution dropwise, adjusted to pH 6, sealed and placed in a constant temperature water bath pot, stirred, removed the cone bottle every 1 h, and collected. After the reaction, the samples were repeatedly tested until the reaction time was 24 h, and the calcified biotite samples were collected.

**RESULTS AND DISCUSSION**

![Figure 1. Potassium release rate versus reaction time.](image1.png)

![Figure 2. XRD patterns of products obtained at different reaction time.](image2.png)
As can be seen from Figure 1, potassium extraction by ion exchange method shows an obvious upward trend with time. The curve of the relationship between potassium removal rate and reaction time is similar to “S” curve, and the reaction time of the inflection point of “S” curve is about 12.5 hours. Within the reaction time of 0 h-12.5 h, the rate of potassium removal increased slowly with the extension of reaction time, and the rate of potassium removal was 0-55%. During this period, the potassium removal occurred at the edge of biotite, which was the initial stage of potassium removal. The main power of potassium removal was the difference of Ca2+ concentration between biotite lattice and aqueous solution. During the period of 12.5 h-17.5 h, the curve increased rapidly and the K+ removal rate was 55%-83%. During this period, the K+ removal area gradually approached to the center of biotite lamellae from the edge, which was the middle stage of K+ removal. At this time, when one Ca2+ replaced two K+, one defect vacancy would occur. Point defect vacancies can provide vacancy space for Ca2+ to enter biotite layer continuously, thus accelerating the exchange of calcium and potassium. During the period of 17.5 h-24 h, with the extension of reaction time, the rising trend slowed down again, and finally approached a straight line. The potassium removal rate was 83% -89%. This period was the end of potassium removal, and gradually reached the limit of Ca2+ exchange K+. The biotite was transformed into Ca-biotite of vermiculite type.

As can be seen from Figure 2, the protobiotite (001)(d =1.012 nm) peak in calcified biotite sample almost disappeared, and a new (001)* characteristic peak appeared, d =1.4288 nm. In comparison, the interlayer spacing is about 0.4 nm, because Ca2+ substituted for K+ exists in the form of large radius hydrated calcium ions between mica layers, and the encapsulated water molecules slightly prop up the hydromica layer, which is consistent with the phenomenon observed by Yu[6].

CONCLUSIONS

Soluble potassium ions were extracted from potassium-bearing biotite associated with potassium-bearing shale by ion-exchange method. The “coulomb effect” and “vacancy effect” were used to make Ca2+/K+ exchange possible, and 89% K+ was extracted within 24 hours.

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