

Conditions and mechanism for extracting potassium from muscovite in potassium-bearing shale by the barium ion-exchange method



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ABSTRACT

By a cation-exchange method, potassium was extracted from muscovite using hydrochloric acid as a motivator and barium ion as a potassium-exchange agent. The influences of various extracting conditions, such as initial barium concentration, reaction temperature, and reaction time, on cationic exchange were investigated at a constant pH value. Mineral phases of the treated samples were also investigated by X-ray diffraction and a significant inflective change of the interlayer spacing was detected. In addition, the significant inflective changes of stretching bonds of hydroxyl and silicon-oxygen were also discovered by Fourier transform infrared spectroscopy analysis. 'Vacancy effect' and 'Radius effect' were proposed as two representative extraction mechanisms to interpret the synchronous inflective changes of the interlayer spacing and the stretching bonds of hydroxyl and silicon-oxygen.

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1. Introduction

As we know, K^+ between muscovite layers compensates for the positive charge absence caused by substitution of Al for Si in silicon-oxygen tetrahedra. The electronegative interlayer environment results in a strong binding on K^+ (Juo and White, 1969). In addition, because of its dioctahedral structure, muscovite is resistant to K extraction (Dreher and Niederbudde, 1994). Ammonium and magnesium ions could extract a very limited amount of potassium without the help of hydrogen ion in muscovite (Rich and Black, 1964), because of ion selectivity. Cesium (about 25% larger than K in crystallographic ionic radius) and barium (similar in size to K, but divalent) had been used to study the ion selectivity in relation to clay mineral structure (Sawhney, 1970; Ross and Kodama, 1970). It had been proved that barium was capable of replacing a limited amount of interlayer K in muscovite mica (the reaction time was prolonged to a few days). But, the exchange feature and mechanism of Ba exchange for K is not obvious yet.

In our preliminary experiments, we found that, to get the same K^+ extraction rate, the reaction time could be condensed to a few hours on the motivation of hydrochloric acid, compared to a neutral environment. In this work, the effect of reactive temperature and initial concentration of $BaCl_2 \cdot 2H_2O$ on K extraction from muscovite in potassium-

bearing shale on a constant pH value was mainly introduced and a sort of mechanism was also proposed.

2. Material and methods

The potassium-bearing shale was obtained from Yichang, China. The chemical compositions were confirmed by X-ray fluorescence spectroscopy (XRF, S4 Pioneer, made by Bruker AXS Co., Ltd, Germany) with a standardless quantitative analysis method and chemical analyses. The mineral phase composition was determined by polarizing microscope and X-ray powder diffraction (XRD) analyses.

The experimental variables (Table 1) were reaction time (t), initial $BaCl_2 \cdot 2H_2O$ concentration ($[Ba]_i$), and reactive temperature (T).

The experiments were conducted in ambient air. Firstly, 0.2 g of potassium-bearing powder and a calculated amount (shown in Table 1) of $BaCl_2 \cdot 2H_2O$ (analytical pure) were in turn introduced into 20 ml 0.5 M hydrochloric acid in a sealed beaker. Subsequently, the beaker was placed in a thermostatic water bath with fixed constant temperature and stirring. After reaction for a certain time period, solid particles were collected by filtration with a medium speed qualitative filter paper, then washed three times with distilled water, and dried for 12 h at 90 °C. All the washing solutions were mixed with the filtered solution, and then the mixed solution was diluted to 100 ml to determine the K content by flame spectroscopy (FP-640, made by INESE, linear error of K: ≤ 0.005 mmol/L). Every experiment was conducted three times, and three experimental values were averaged as experiment results. The crystal phases of collected solid product were determined by

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Table 1
Experimental variables.

Reaction time (<i>t</i>) (h)	1	2	3	4						
Code number (first)	1	2	3	4						
Reactive temperature (<i>T</i>) (°C)	30	45	60	80						
Code number (second)	1	2	3	4						
Initial concentration of BaCl ₂ ·2H ₂ O [Ba] _i [M]	0.00	0.10	0.25	0.50	0.75	1.00	1.25	1.50	1.75	
Code number (third)	0	1	2	3	4	5	6	7	8	

Note: The sample number was set with three numbers, for instance No. 1-1-0 (*t* = 1 h, *T* = 30 °C, [Ba]_i = 0.00 mol/L) or No. 3-3-2 (*t* = 3 h, *T* = 60 °C, [Ba]_i = 0.25 mol/L).

X-ray diffractometry (XD-5). The diffraction patterns were measured in a 2θ range of 5–50° and at an increment of 0.01534° using (Cu-K_α) radiation from a tube operating at 40 kV and 30 mA. The change of chemical bonds was examined by Fourier transform infrared spectroscopy of powder mounted on a KBr disk (Nicolet Impact 420, America, resolution 0.125 cm⁻¹).

3. Results

3.1. Chemical composition and mineral composition analyses

XRF result (Table 2) revealed that the potassium content of the potassium-bearing shale was 3.94 wt.% as K₂O, and a little sodium (0.08 wt.%) was contained. The sodium extraction therefore was neglected.

Mineral composition (Table 3) derived from XRD (Fig. 1) and polarizing microscope demonstrated that muscovite content was 42.50 wt.%. The other minerals barely contained potassium in theory.

An energy dispersive spectrometer (Fig. 2) represented K content (K₂O) in muscovite mineral at 9.21% (this was an average value of three points). This was in agreement with the potassium content in shale, which meant that almost all the K existed in muscovite mineral.

3.2. Effect of reaction temperature (*T*) on the K⁺ extraction efficacy

The effect of reaction time on the K⁺ extraction efficacy was investigated at different initial concentrations of BaCl₂. It was found that the percentage of K⁺ extracted increased with increasing initial concentration of BaCl₂ at each of the four reaction temperatures (Fig. 3). However, at each of three different initial BaCl₂ concentrations, the K⁺ extraction efficacy was maximum at 45 °C and was less at the two higher extraction temperatures.

3.3. Effect of reactive time (*t*) and initial concentration of BaCl₂·2H₂O on the efficacy of K⁺ extraction

Fig. 4 shows that K extraction always increased as [Ba]_i rose for a given reaction time (*t*). The K extraction had a slight increase when the reaction time (*t*) reached 4h as well as after [Ba]_i reached 1.50 M. In addition, not linear but polynomial regression was required to describe the relationship between the extent of K extraction and initial

Table 2
Chemical composition of potassium-bearing shale (wt.%).

SiO ₂	Al ₂ O ₃	CO ₂	Fe ₂ O ₃	MgO	K ₂ O	CaO	V ₂ O ₅	BaO	Other
48.00	16.60	12.60	7.23	4.96	3.94	2.69	1.51	0.66	1.81

Table 3
Mineral composition percentage of potassium-bearing shale (wt.%).

Clinocllore	Dolomite	Plagioclase	Muscovite	Quartz	Other
11.68	7.67	3.66	42.50	32.11	2.38

barium concentration. The rise of K extraction was quickest from start of reaction until [Ba]_i = 0.25 M, then slowed and picked up with every 0.5 M interval in [Ba]_i. And initial BaCl₂·2H₂O concentration of 0.25 M, 0.75 M, and 1.25 M were therefore values of rate of changes dividing the curves into four regions (I, II, III, and IV) (Fig. 5a, b, c, and d).

The changes in rate (of increase of K concentration with increasing initial Ba concentration) were more clearly evident for the longer reaction times (*t*). The average slopes of the four regions in a, b, c, and d are shown in Table 4.

3.4. X-ray diffraction analyses

The residual solids from the experiments in optimal reaction time (*t* = 3 h) and reaction temperature (*T* = 45 °C) were examined by XRD.

The XRD patterns (Fig. 6a) presented the remarkable muscovite (002) diffraction peak, which meant muscovite structure had been retained. Furthermore, the plot, Fig. 6b, of *d*₀₀₂ vs. [Ba]_i showed three extrema (0.25 M, 0.75 M, and 1.25 M) where the prevailing trend in basal spacing variation appeared to reverse course. The resulting four regions of *d*₀₀₂ were the same as for the segmental changes of curve slope of K extraction with [Ba]_i (Fig. 5).

3.5. Fourier transform infrared spectroscopy analyses

The vertical Si(Al^{IV})-O stretching band (Fig. 7a) was seen at ± 1080 cm⁻¹ (Lu et al., 1988).

The absorptive band at ± 3600 cm⁻¹ (Fig. 8a) was assigned to hydroxyl bond stretching (Besson and Drits, 1997; Farmer, 1968).

The general trends of $\nu_{(\text{Si}(\text{Al}^{\text{IV}})-\text{O})}$ (Fig. 7b) and $\nu_{(\text{O}-\text{H})}$ (Fig. 8b) with [Ba] were inverse: the decreasing parts of $\nu_{(\text{Si}(\text{Al}^{\text{IV}})-\text{O})}$ corresponded to the increasing parts of $\nu_{(\text{O}-\text{H})}$. Additionally, after 0.25 M of [Ba]_i, the prevailing trends appeared to reverse course synchronically with

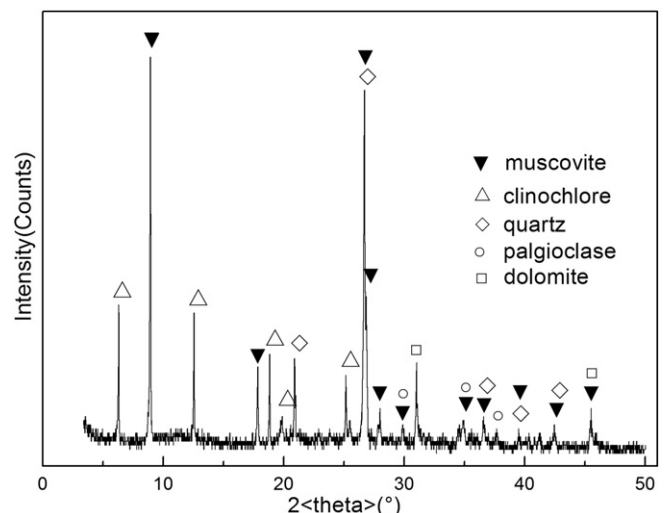


Fig. 1. XRD pattern of potassium-bearing shale.

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