



## Effects of BaCl<sub>2</sub> on K-feldspar flotation using dodecyl amine chloride under natural pH

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Received 9 September 2017; accepted 15 March 2018

**Abstract:** The effects of BaCl<sub>2</sub> on the flotation of K-feldspar using dodecyl amine chloride as the collector under natural pH were investigated by flotation tests, absorption measurements, Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS). The results indicated that lower BaCl<sub>2</sub> concentration can increase the floatability of K-feldspar, whereas higher BaCl<sub>2</sub> concentration can significantly inhibit the flotation of K-feldspar. Peaks at 3548.18, 3475.56 and 3414.35 cm<sup>-1</sup> in the FTIR spectra of K-feldspar adsorbed by dodecyl amine chloride revealed three forms of —OH. XPS analyses of K-feldspar adsorbed by Ba<sup>2+</sup> showed that the concentration of K atom was reduced by nearly twice as those of Si, Al, and O. The activation of BaCl<sub>2</sub> at a low concentration was mainly caused by Ba<sup>2+</sup> in the form of the ion exchange between K<sup>+</sup> and Ba<sup>2+</sup>. The inhibitory action of BaCl<sub>2</sub> at a high concentration is mainly attributed to the physical absorption of Ba<sup>2+</sup> on the surface of K-feldspar and the fact that a high concentration of Cl<sup>-</sup> causes the chemical equilibrium of dodecyl amine chloride to be changed, and the dodecyl amine chloride in the form of RNH<sub>2</sub>H<sup>+</sup> is reduced.

**Key words:** K-feldspar; BaCl<sub>2</sub>; dodecyl amine chloride; activation; flotation

## 1 Introduction

K-feldspar is a type of feldspar mineral with a main chemical composition of K<sub>2</sub>O, SiO<sub>2</sub>, and Al<sub>2</sub>O<sub>3</sub>. A significant amount of K-feldspar is used in the glass and ceramics industries [1]. The quality of K-feldspar is mainly determined by the colored impurities, the quartz, and the ratio of K<sub>2</sub>O/Na<sub>2</sub>O (percentage composition) [2]. Flotation is the most commonly used method for feldspar separation. It is also the only means to increase the ratio of K<sub>2</sub>O/Na<sub>2</sub>O.

Numerous studies were focused on the effects and interaction mechanism of various ions on the flotation of minerals [3–5]. Metallic ions such as Fe<sup>3+</sup> and Ca<sup>2+</sup> effectively activate the flotation of spodumene and beryl. FTIR analysis suggested that the activation mechanism of Fe<sup>3+</sup> involves the chemical absorption of the collector onto the surface of Fe<sup>3+</sup>-activated mineral. Fe<sup>3+</sup> can be activated in the flotation of spodumene, albite, and

quartz [6]. The adsorption of Fe<sup>3+</sup> onto the surface of spodumene, albite, and quartz can unexpectedly increase the amount of sodium oleate collector, and Fe<sup>3+</sup> can switch the surface of these minerals from polar to non-polar [7,8]. The effect of Pb<sup>2+</sup> ions on the flotation of ilmenite was researched, the pH had an influence on the form of Pb<sup>2+</sup> and the adsorption of Pb<sup>2+</sup> influenced the zeta potential and the number of activated sites on the mineral surface [9].

Activator is a general term for flotation reagents, which can be classified as organic or inorganic [10–12]. The inorganic reagent BaCl<sub>2</sub> was used in the present research. Ions with similar atomic radii, such as Ba, Rb, and Cs, can be used to depress the flotation of K-feldspar [13]. The adsorption and ion exchange of bivalent ions on the surface of feldspar were complex, and the selective separation of albite from microcline was achieved by micro-flotation with CaCl<sub>2</sub> and BaCl<sub>2</sub> as the regulators and amine (G-TAP) as the collector [14].

FTIR studies on the effects of Ca<sup>2+</sup> and Mg<sup>2+</sup> on the

flotation of spodumene showed that the surface change of spodumene through the absorption of hydroxyl complexes and precipitates promotes oleate complex formation, collector adsorption and mineral flotation [15]. Clay minerals have been studied using FTIR spectroscopy, suggesting that this method can be used to obtain fundamental information on the chemical composition, surface properties, and structural changes of minerals and their effects. The adsorption of organo-cations on montmorillonite in montmorillonite-water systems has also been investigated [16–18]. The adsorption mechanism of dodecyl ammine on the surface of calcite was researched by FTIR, and the conclusion that sodium carbonate decreases the negative charges on the surface of calcite mineral was confirmed [19].

The addition of ions changes the surface properties of minerals, and XPS analysis was used to study these changes. The mechanism underlying the adsorption of mixed dithiophosphate and mercaptobenzothiazole on the surface of copper sulfide ore has been investigated using XPS [20,21]. Results have proven that the F chemistry from  $\text{LiPF}_6$  is the major difference among various coatings, and that the reaction mechanism occurring on the metal oxide surface has been ascertained according to the change in potentials [22,23]. The adsorption mechanisms of organic reagent on mineral surface were also researched by XPS. The adsorption mechanisms of disodium bis (carboxymethyl) trithiocarbonate on the surface of chalcopyrite was researched by using XPS [24].

New methods of feldspar separation were also reported. Hydrofluoric acid (HF) was used in the separation of quartz and feldspar, thus high grades and good recoveries were obtained [25]. Cyclojet flotation cell was used in the beneficiation of low-grade feldspar. The result shows that with cyclojet flotation cell, both  $\text{Fe}_2\text{O}_3$  and  $\text{TiO}_2$  can be removed at a rate of up to 90%, and much better than magnetic separator [26].

The present study aimed to determine the influence of  $\text{BaCl}_2$  on the flotation of K-feldspar with dodecyl amine chloride, and explained the underlying mechanism through FTIR and XPS analyses of solution and surface chemistries.

## 2 Experimental

### 2.1 Materials

High-purity K-feldspar samples were obtained from Shandong Province, China. The chemical composition of the samples is presented in Table 1. The lump-sized materials were crushed with a hammer and ground in an agate mortar followed by dry screening to produce samples ( $d_{80}=56\text{ }\mu\text{m}$ ) for the flotation and XPS studies

and the adsorption experiments. The specific surface area for the size fractions of the K-feldspar samples was  $0.379\text{ m}^2/\text{g}$ .

**Table 1** Chemical composition of K-feldspar (mass fraction, %)

$\text{K}_2\text{O}$	$\text{Na}_2\text{O}$	$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{Fe}_2\text{O}_3$	Others
13.15	1.80	64.84	17.89	0.017	2.303

### 2.2 Reagents

Dodecyl amine chloride was synthesized in the laboratory under  $25\text{ }^\circ\text{C}$  by lauryl amine and hydrochloric with a molecular proportion of 1:1. Barium chloride dehydrate was supplied by Ruijinte Chemicals Co., Ltd., China.

### 2.3 Flotation tests

Single mineral flotation tests were performed in a 50 mL flotation cell with a mechanical agitator. A flotation test sample ( $d_{80}=56\text{ }\mu\text{m}$ ) of approximately 2 g was mixed with 50 mL of deionized water (including the reagent volume) at an impeller speed of 1600 r/min. Conditioning and flotation were performed at the same impeller speed and pulp volume. Firstly, 2.0 g of the mineral sample was conditioned in deionized water for 2 min with stirring. Barium chloride dehydrate was used as a regulator and conditioned for 3 min. Then, dodecyl amine chloride was conditioned for 3 min. The optimum flotation time of 2 min was used in all flotation tests. The concentrate and tailing were dried separately at  $35\text{ }^\circ\text{C}$  and weighed to calculate the productivity and recovery.

### 2.4 Adsorption experiments

Adsorption experiments of  $\text{Ba}^{2+}$  from solution onto the surface of K-feldspar were performed in a beaker. For each experiment, 4 g of powder sample and 40 mL working solution with a specific  $\text{BaCl}_2$  concentration were added into a 100 mL beaker, and the suspension was conditioned for 30 min. After centrifugation, the  $\text{BaCl}_2$  concentration of the water phase was determined by ICP-MS (UV). The adsorption of  $\text{BaCl}_2$  onto the material was calculated as the difference between the initial and final  $\text{BaCl}_2$  concentrations of water [27].

### 2.5 FTIR spectral analysis

The infrared spectra FTIR measurements were performed with 50 mL suspension containing 2 g powder sample and 50 mL water which was conditioned for 2 min. The suspension was added with  $1.1\times 10^{-2}\text{ mol/L}$   $\text{BaCl}_2$  and then conditioned for 3 min. Finally, the suspension was added with 10 mg/L dodecyl amine chloride and then conditioned for 3 min, and the samples were air-dried after filtration. FTIR spectra were

obtained with a Nicolet iS10 FTIR spectrometer with its own attachment, and the average spectrum was 200 scans at  $4\text{ cm}^{-1}$  resolution with a liquid nitrogen-cooled MCT detector. About 25 mg of the air-dried sample was mixed with 125 mg of KBr [28] and then tableted by a sheeter. The untreated K-feldspar powder was used as reference and the absorbance units were defined by the decimal logarithm of the ratio of initial K-feldspar reflectance to that of the sample. The atmospheric water was subtracted from the sample spectrum.

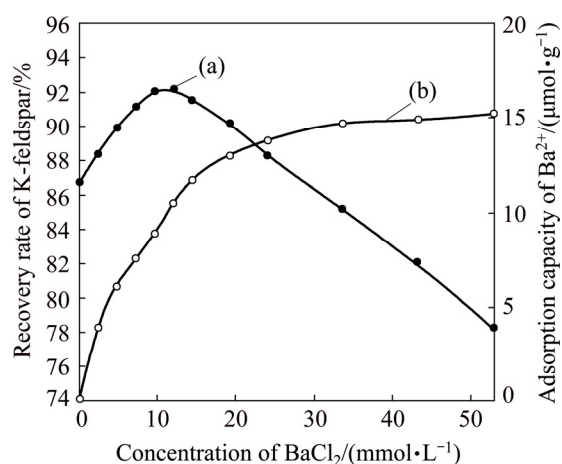
## 2.6 XPS analyses

Approximately 1.0 g of feldspar powder sample was conditioned in 40 mL of water for 25 min with  $\text{BaCl}_2$  concentration of  $1.1 \times 10^{-2}$  and  $5.3 \times 10^{-2}$  mol/L. The XPS studies were performed on a PHI 5000 Versaprobe-II scanning XPS microprobe system with a mono-irradiation Al X-ray source of 50 W. Each analysis started with a survey scan from 0 to 1100 eV and pass energy of 46.95 eV. A value of 284.8 eV was adopted as the standard C1s binding energy [29,30].

## 3 Results and discussion

### 3.1 Flotation and adsorption tests

The flotation experiments were performed with K-feldspar using dodecyl amine chloride to determine the influence of  $\text{BaCl}_2$  on the flotation of K-feldspar. The experiments were performed under the following conditions: pH 7.8, 2 min of mixing time, 1600 r/min of stirring rate, 10 mg/L of dodecyl amine chloride concentration, and 2 min of rising time. The only variable is the amount of  $\text{BaCl}_2$ . Figure 1 shows the flotation results of K-feldspar at different  $\text{BaCl}_2$  concentrations, and the effect of  $\text{BaCl}_2$  concentration on the adsorption capacity of  $\text{Ba}^{2+}$  on the surface of K-feldspar.



**Fig. 1** Recovery rate of K-feldspar versus  $\text{BaCl}_2$  concentration at 10 mg/L of dodecyl amine chloride addition (a) and effect of  $\text{BaCl}_2$  concentration on adsorption capacity of  $\text{Ba}^{2+}$  on surface of K-feldspar (b)

As shown in Fig. 1(a), the recovery rate of K-feldspar was obtained at natural pH as a function of reagent dosage. The results indicated that the recovery rate of K-feldspar increased with increasing dosage when the concentration of  $\text{BaCl}_2$  was lower than  $1.1 \times 10^{-2}$  mol/L. The recovery rate of K-feldspar increased from 86.73% to 92.21% (nearly 5%) when the  $\text{BaCl}_2$  concentration was increased from 0 to  $1.1 \times 10^{-2}$  mol/L. However, the recovery rate of K-feldspar decreased with increasing dosage when the concentration of  $\text{BaCl}_2$  exceeded  $1.1 \times 10^{-2}$  mol/L. The recovery rate of K-feldspar declined from 97.27% to 84.5% (nearly 13%) when  $\text{BaCl}_2$  concentration was increased from  $1.1 \times 10^{-2}$  to  $5.3 \times 10^{-2}$  mol/L.

The results of flotation tests indicated that the  $\text{BaCl}_2$  concentrations exerted a distinct influence on the flotation of K-feldspar using dodecyl amine chloride as the collector. In specific, low  $\text{BaCl}_2$  concentration activated the flotation of K-feldspar, whereas high  $\text{BaCl}_2$  concentration inhibited this process.

As shown in Fig. 1(b), the adsorption capacity of  $\text{Ba}^{2+}$  on the surface of K-feldspar increased throughout the test range of  $\text{BaCl}_2$  concentration. The adsorption capacity of  $\text{Ba}^{2+}$  can be divided into three stages. The first stage is the rapid rise stage, which occurs when the concentration of  $\text{BaCl}_2$  is less than  $7.2 \times 10^{-3}$  mol/L. In this stage, the adsorption capacity of  $\text{Ba}^{2+}$  increased from 0 to  $7.6 \times 10^{-3}$  mol/g. The second stage is the steady rise stage, which occurs when the concentration of  $\text{BaCl}_2$  is greater than  $7.2 \times 10^{-3}$  mol/L and less than  $2.1 \times 10^{-2}$  mol/L. In this stage, the adsorption capacity of  $\text{Ba}^{2+}$  increased from  $7.6 \times 10^{-3}$  to  $1.3 \times 10^{-2}$  mol/g. The third stage is the slow rise stage, which occurs when the concentration of  $\text{BaCl}_2$  exceeds  $2.1 \times 10^{-2}$  mol/L. In this stage, the adsorption capacity of  $\text{Ba}^{2+}$  approached the saturation state, after which the adsorption capacity of  $\text{Ba}^{2+}$  increased very slowly.

Figures 1(a) and (b) were compared, and the following results were obtained. In the rapid rise stage of the adsorption capacity of  $\text{Ba}^{2+}$ , the recovery rate of K-feldspar increased with the increase of the adsorption capacity of  $\text{Ba}^{2+}$ . In the steady rise stage, the recovery rate of K-feldspar initially increased and then decreased. However, the recovery rate exceeded 90% and was in the narrow fluctuation range. In the slow rise stage, the recovery rate of K-feldspar decreased as the adsorption capacity of  $\text{Ba}^{2+}$  increased.

### 3.2 FTIR spectral analysis

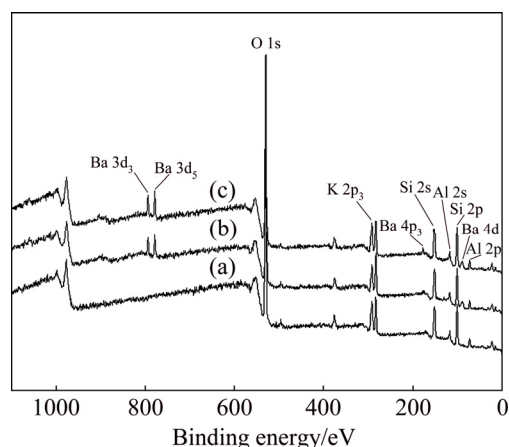
The FTIR absorption bands in the K-feldspar tests were mainly Si—O and Al—O groups, and the range of feldspar spectra was mainly  $1200\text{--}300\text{ cm}^{-1}$ . The FTIR spectra of K-feldspar, the K-feldspar reaction with dodecyl amine chloride, and the K-feldspar reaction with



from that in Fig. 2(b), proving an obvious effect of  $\text{BaCl}_2$  on the adsorption of dodecyl amine onto the surface of K-feldspar. The peaks of  $-\text{OH}$  in Fig. 2(c) were simpler than those in Fig. 2(b) (only  $3416.18\text{ cm}^{-1}$ ), which can be attributed to the stretching vibration of the H-bond between the O atom of the mineral and the H atom of amine, and the bending vibration of  $-\text{OH}$  was obviously lower in Fig. 2(c) than that in Fig. 2(b). The peak of the  $\text{N}-\text{H}$  group was not found in Fig. 2(c). Thus, when  $\text{BaCl}_2$  acted as an inhibitor, the adsorption of  $\text{RNH}_3^+$  onto the mineral surface with a covalent bond was more sensitive than that of  $\text{RNH}_2$  with H-bond.

### 3.3 XPS analysis

XPS analysis was used to study the effect of  $\text{BaCl}_2$  on the surface of K-feldspar. The XPS spectra are presented in Fig. 3, and the change of atoms in mole fraction on the mineral surface is provided in Table 2.



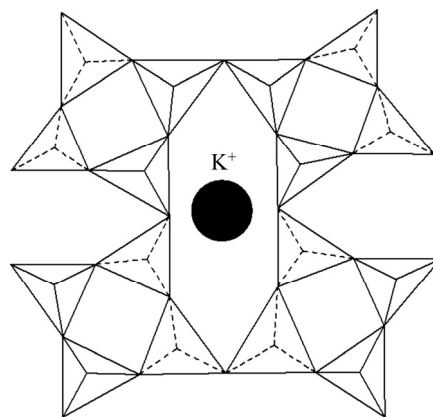
**Fig. 3** XPS spectra of K-feldspar in the absence and presence of  $\text{BaCl}_2$  on natural pH, respectively: (a) K-feldspar leaching with pure water for 25 min; (b) K-feldspar leaching with  $1.1 \times 10^{-2}$  mol/L  $\text{BaCl}_2$  dehydrated solution for 25 min; (c) K-feldspar leaching with  $4.8 \times 10^{-2}$  mol/L  $\text{BaCl}_2$  dehydrated solution for 25 min

**Table 2** Mole fractions of atoms on mineral surface and their proportional shift

Sample No.	Mole fraction/%				
	O	Al	Si	K	Ba
a	73.33	2.51	14.58	9.58	—
b	67.57	2.36	13.32	8.01	8.74
c	67.19	2.42	13.29	8.13	8.97
Sample No.	Proportional shift/%				
	O	Al	Si	K	Ba
a	—	—	—	—	—
b	−7.85	−5.98	−8.64	−16.39	—
c	−8.37	−3.59	−8.85	−15.14	2.63

Figure 3 confirms that  $\text{BaCl}_2$  can be adsorbed on the surface of K-feldspar with a chemical bond. The mole fractions in Table 2 indicate that mole fraction of  $\text{Ba}^{2+}$  was increased by 2.63% when  $\text{BaCl}_2$  concentration was increased from  $1.1 \times 10^{-2}$  to  $4.8 \times 10^{-2}$  mol/L. The adsorption result in Fig. 1 shows that  $\text{BaCl}_2$  was adsorbed on the mineral surface. According to the XPS spectra in Fig. 3, it can be confirmed that  $\text{Ba}^{2+}$  can be adsorbed on the mineral surface through chemisorption when the  $\text{BaCl}_2$  concentration was lower than  $1.1 \times 10^{-2}$  mol/L. Table 2 shows that the mole fraction of Ba on mineral surface changed from 8.74% to 8.97% when the  $\text{BaCl}_2$  concentration was increased from  $1.1 \times 10^{-2}$  to  $4.8 \times 10^{-2}$  mol/L. In consideration of the adsorption result in Fig. 1, it can be speculated that the  $\text{Ba}^{2+}$  adsorbed onto the mineral surface mainly through physical adsorption when  $\text{BaCl}_2$  concentration exceeded  $1.1 \times 10^{-2}$  mol/L.

The proportional shift in Table 2 confirms that the shift rate of K was more obvious than that of O, Al and Si. The frame structure of K-feldspar under the ideal condition is illustrated in Fig. 4.  $\text{K}^+$  entered the skeleton as counterbalance ion and was easily diffused into the pulp.  $\text{Ba}^{2+}$  had a similar ionic radius to  $\text{K}^+$  and easily entered into the crystal skeleton by filling the vacancy caused by the dissolution of  $\text{K}^+$ . The positron of  $\text{Ba}^{2+}$  was twice that of  $\text{K}^+$ . Thus, the adjacent crystal lattice had no more need for extra positron from  $\text{K}^+$ , and the shift rate of  $\text{K}^+$  became nearly twice those of the other atoms.



**Fig. 4** Framework structure of idealized K-feldspar

The FTIR and XPS spectral analyses of the flotation mechanism can be explained as follows. The activation of  $\text{BaCl}_2$  at a low concentration was caused by the ion exchange on the mineral surface, and the replacement of  $\text{K}^+$  by  $\text{Ba}^{2+}$  increased the lattice vacancies and adsorption sites on the mineral surface [34]. With the increase in  $\text{BaCl}_2$  concentration, the balance of ion exchange was achieved,  $\text{Ba}^{2+}$  adsorbed on the mineral surface by chemisorption reached the maximum, and maximum recovery rate of K-feldspar was reached. Subsequently,

some of the adsorption sites were covered by  $\text{Ba}^{2+}$  adsorbed on the mineral surface and hindered the adsorption of dodecyl amine chloride with the continuous increase in concentration. The dissociation equilibrium of dodecyl amine chloride existed in the pulp, as shown by Eq. (4). The concentration of  $\text{Cl}^-$  increased with increasing  $\text{BaCl}_2$  concentration, and the equilibrium moved to the left, which means that the concentration of  $\text{RNH}_3^+$  decreased and the concentration of the collector with reactivity increased.



The ion exchange adsorption, physical absorption, and chemical equilibrium in the pulp are the main influencing factors of K-feldspar flotation with  $\text{BaCl}_2$  as the regulator and dodecyl amine chloride as the collector.

## 4 Conclusions

1) The flotation of K-feldspar with  $\text{BaCl}_2$  and dodecyl amine chloride shows that within the scope of the test  $\text{BaCl}_2$  concentration, the recovery rate of K-feldspar increases with the increase of the  $\text{BaCl}_2$  concentration when it is below  $1.1 \times 10^{-2}$  mol/L, and decreases with the increase of the  $\text{BaCl}_2$  concentration when it is beyond  $1.1 \times 10^{-2}$  mol/L.

2) Dodecyl amine chloride is adsorbed on the surface of K-feldspar with three forms and causes three peaks at 3548.18, 3475.56, and 3414.35  $\text{cm}^{-1}$ .

3) The ion exchange between  $\text{K}^+$  and  $\text{Ba}^{2+}$  is a major factor of the low concentration of  $\text{BaCl}_2$  and promotes the flotation of K-feldspar. The physical absorption of  $\text{Ba}^{2+}$  increases with the increase of the concentration of  $\text{BaCl}_2$  when the concentration of  $\text{BaCl}_2$  exceeds  $1.3 \times 10^{-2}$  mol/L, and the physical absorption becomes a major influencing factor of flotation. The chemical equilibrium of dodecyl amine chloride ionization form  $\text{RNH}_2 \cdot \text{HCl}$  increased and also had some impact on the inhibition of K-feldspar flotation.

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## 自然 pH 条件下 $\text{BaCl}_2$ 对钾长石盐酸十二胺浮选的影响

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**摘要:** 采用浮选试验、吸附量测定、傅里叶转换红外光谱分析(FTIR)以及 X 射线光电子能谱分析(XPS)研究自然 pH 条件下  $\text{BaCl}_2$  对钾长石盐酸十二胺浮选的影响。研究表明, 低浓度  $\text{BaCl}_2$  对钾长石的浮选具有活化作用, 高浓度  $\text{BaCl}_2$  对钾长石浮选具有抑制作用。位于 3548.18、3475.56 和 3414.35  $\text{cm}^{-1}$  的红外光谱谱峰表明盐酸十二胺与钾长石表面作用后有 3 种不同—OH 基团存在。XPS 分析结果表明,  $\text{Ba}^{2+}$  在钾长石表面吸附后, 长石表面 K 原子的浓度降低程度是 Si、Al 和 O 原子的两倍。低浓度下  $\text{BaCl}_2$  的活化作用可归因于矿物表面  $\text{K}^+$  和  $\text{Ba}^{2+}$  的离子交换作用; 高浓度下  $\text{BaCl}_2$  的抑制作用可归因于矿物表面  $\text{Ba}^{2+}$  的物理吸附; 同时矿浆中  $\text{Cl}^-$  浓度的增加也会导致盐酸十二胺溶解平衡的移动,  $\text{RNH}_2\text{H}^+$  的浓度降低。

**关键词:** 钾长石; 氯化钡; 盐酸十二胺; 活化作用; 浮选

(Edited by Wei-ping CHEN)