ADSORPTION AND ACTIVATION OF METAL IONS ON KYANITE①

Dong Hongjun, Chen Jin
Department of Mineral Engineering,
Central South University of Technology, Changsha 410083

ABSTRACT It was discovered that the adsorption of metal ions on mineral surface had much to do with their activation for mineral in flotation. The authors proposed a percentage of adsorptive precipitation(PAP) to represent activation power of metal ions. The greater the PAP of the metal ion, the stronger its activation power. When the PAP was small to a certain extent, the metal ion showed a depression effect on mineral in flotation.

Key words metal ion kyanite sodium oleate adsorption flotation

1 INTRODUCTION

The influences of metal ions in pulp on mineral floatability are very complicated. Take quartz, the most common silicate mineral, for example, most of the metal ions can activate its flotation, and there are two kinds of viewpoints in explaining their activation mechanism. In one opinion, it is the hydrolysate of a metal ion, MOH^{n+}, that activates quartz floation[1]; in another opinion, it is the metal hydroxide precipitation that does the same thing[2]. In common, both of them agree that the adsorption of metal ion on mineral surface, no matter what ingredients of ion, is the prerequisite to activate mineral flotation. It has been proposed that the adsorption behaviors of metal ions associate closely with their activation power[3]. In this paper, the relationship between adsorption and activation of metal ions on kyanite in the presence of sodium oleate is investigated in detail.

2 ADSORPTION BEHAVIORS OF METAL IONS ON KYANITE SURFACE

2.1 Quantum chemistry calculation of adsorption strength of metal ions on kyanite

Diatomic energy, $\varepsilon(O—M)$, determined by quantum chemistry calculation, can be used to represent the adsorption strength of metal ion on mineral surface. When the value of $\varepsilon(O—M)$ is below zero, it indicates that a covalent bond is formed between oxygen atom on mineral surface and metal atom in the solution; when above zero, an ionic bond is formed. The greater the absolute value of $\varepsilon(O—M)$, the stronger the chemical bond. The diatomic energies between oxygen atom on kyanite surface and metal ions added have been calculated using quantum chemistry calculation[4]. The results are shown in Table 1. According to their diatomic energies, the adsorption intensities of metal ions on kyanite can be arranged as: $H^+ > Fe^{3+} > Al^{3+} \gg Mg^{2+} > Ca^{2+}$, which is further confirmed through measuring their adsorption amount.

2.2 Adsorption amount of Me^{n+} on kyanite

Upon previous study on adsorption mechanism, metal ions adsorb on mineral surface in two forms, metal ion complex and surface precipitation. Both of them should be included in adsorption amount, which is indicated as the percentage of adsorptive precipitation (PAP). By residual concentration measurement, PAP can be obtained:

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$$PAP(\%) = \frac{C_0 - C}{C_0} \times 100$$

where C_0 stands for initial concentration of adsorbate; C stands for residual concentration after adsorption.

The PAPs of metal ions Al^{3+}, Fe^{3+}, Ca^{2+}, Mg^{2+} in pulp were measured with ICP-AES. The four metal ions in the form of chlorides were added simultaneously into the pulp made up of 2 g kyanite(75~ 150 μm) and 40 mL secondary distilled water in the presence of 5×10^{-4} mol/L sodium oleate. The operation procedure is the same as that in reference [3]. The PAPs of metal ions as a function of pH are shown in Fig. 1. It can be seen that:

Fig. 1 PAPs of metal ions on kyanite as functions of pH

1—Fe^{3+}; 2—Al^{3+}; 3—Ca^{2+}; 4—Mg^{2+}

(1) In weak acidic medium of pH= 4~ 6, the sequence of PAPs is $PAP_{Fe} > PAP_{Al} \gg PAP_{Ca} > PAP_{Mg}$, which is in agreement approximately with that of diatomic energies and completely with that of metal ions' solubility products(see Table 1).

(2) In neutral medium, the PAP of Al^{3+} reaches its maximum and is greater than that of Fe^{3+} because amphiprotic $Al(OH)_3$ is stablest in neutral condition. Besides, as Al^{3+} appears in kyanite ($Al_2O_3SiO_2$) lattice, Al^{3+} in pulp is more easily adsorbed on kyanite surface.

(3) The pH values at which PAP approaches 100% are 3 for Fe^{3+}, 5 for Al^{3+}, 11 for Mg^{2+} and 12 for Ca^{2+}, which is in agreement with those at which metal hydroxides precipitate from the solution[5]. It is evident that the adsorption of metal ions on mineral surface is in close relationship with their hydroxide precipitation.

Table 1 K_{sp}, ε(O—M) (atome unit) of metal ions and pH values

Metal ions	Fe^{3+}	Al^{3+}	Ca^{2+}	Mg^{2+}
pH[1]	2. 78	5. 16	13. 32	10. 50
K_{sp}[5]	34. 2	30. 2	15. 4	13. 8
ε(O—M)	– 0. 365	– 0. 243	– 0. 104	– 0. 109

Notes: K_{sp}—the solubility product of oleate;
pH—the value at which metal ions start to form hydroxide precipitation.

The best pH range for kyanite flotation when sodium oleate is taken as collector is from neutral to weak basic, at which the PAP order of metal ions can be arranged as $PAP_{Al} > PAP_{Fe} \gg PAP_{Ca} > PAP_{Mg}$(see Fig. 1). So, Al^{3+} and Fe^{3+} can activate kyanite flotation, while Ca^{2+} and Mg^{2+} depress it because most of them exist in bulk solution and consume collectors.

3 KYANITE FLOTATION BEHAVIOR

3.1 Flotation behavior of kyanite in the absence of metal ions

Kyanite flotation recovery as functions of pH and collector concentration in the absence of metal ions are shown in Fig. 2 and Fig. 3 respect-

Fig. 2 Kyanite recovery(R) as a function of pH

(sodium oleate 5×10^{-4} mol/L)

ively. It can be seen from Fig. 2 that in the pH range of 7~ 8, kyanite floats best. From Fig. 3, when pH= 7. 2~ 7. 5, at the highest kyanite recovery, the optimum sodium oleate concentration is more than 4×10^{-4} mol/ L.

Fig. 3 Kyanite recovery as a function of sodium oleate concentration
(pH= 7. 2~ 7. 5)

3. 2 The influence of metal ions on kyanite floatability

The influence of metal ions with a concentration of 1×10^{-4} mol/ L on floation behavior of kyanite-sodium oleate system is shown in Fig. 4. It is clear that Al^{3+} and Fe^{3+} activate kyanite flotation but Ca^{2+} and Mg^{2+} depress it. The recoveries of kyanite under the influence of metal ions are in the following order: $R_{Al} > R_{Fe} > R_{Ca} > R_{Mg}$, which is agreeable completely to that of PAPs of metal ions adsorbed on kyanite surface. In other words, PAP stands for activation power of metal ion in mineral flotation. The larger the PAP, the stronger the activation power of the ion. When the PAP of metal ion is small to a certain extent, it will depress mineral flotation.

The influence of metal ion concentrations on flotation behavior of kyanite-sodium oleate system is shown in Fig. 5. It indicates that both optimum concentrations of Al^{3+} and Fe^{3+} are about 1×10^{-4} mol/ L, and that Al^{3+} has a stronger activation effect than Fe^{3+} ion does.

Fig. 4 Kyanite recoveries as functions of pH in the presence of sodium oleate and metal ions
1 —Al^{3+} ; 2 —Fe^{3+} ; 3 —Ca^{2+} ; 4 —Mg^{2+}

Fig. 5 Kyanite recoveries as functions of metal ion concentrations
1 —Al^{3+} ; 2 —Fe^{3+}

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