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ScienceDirect
Trans. Nonferrous Met. Soc. China 19(2009) 228−234
Transactions of Nonferrous Metals Society of China
www.tnmsc.cn

Flotation of aluminosilicate minerals using alkylguanidine collectors

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Received 19 March 2008; accepted 15 July 2008

Abstract: The flotation mechanism of aluminosilicate minerals using alkylguanidine collectors was studied through flotation experiments, Zeta potential measurements and FT-IR spectrum analysis. It is shown that kaolinite, illite and pyrophyllite all exhibit good floatability with alkylguanidines as collectors at pH 4−12. The flotation recoveries rise with the increase of the carbon chain length. Isoelectric point(IEP) is determined to be 3.5, 3.0 and 2.3 for kaolinite, illite and pyrophyllite, respectively. However, it is anomalous that the presence of cationic collectors has less influence on the negatively charged mineral surfaces. It is explained by the special structure of guanidine which is one of the strongest bases, having two —NH_2 groups. One of them maybe interacts with minerals by electrostatic forces, and the other maybe forms hydrogen bonding with OH^- ions on the aluminosilicate surfaces or in the aqueous solution, increasing the density of negative charge on the aluminosilicate surface and leading unpronounced positive charge to increase on the aluminosilicate. By combining the flotation tests, Zeta potential and FTIR measurements above, the interaction mechanism can be concluded. The simultaneous presence of cationic and neutral amine groups makes it possible for SAG cation to bind on three aluminosilicate minerals by both electrostatic attraction and hydrogen bonding. While in acidic medium, the interaction of the alkylguanidines on the aluminosilicate surfaces is mainly by means of electrostatic force and hydrogen bond; in the alkaline medium, it is by the way of electrostatic effect and hydrogen bond.

Key words: aluminosilicate minerals; alkylguanidine; flotation; adsorption mechanism

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1 Introduction

Bayer process is widely used to treat the bauxite with mole ratio of Al_2O_3 to SiO_2 (A/S) more than 8[1]. Although there are abundant bauxites in China, most of them (more than 90%) are diasporic-bauxite with low ratio of Al_2O_3 to SiO_2 (A/S=4−6)[2]. This type of bauxite is difficult to be treated directly by the Bayer process. It is therefore highly desirable to increase the ratio of A/S by flotation desilication before Bayer process. Direct flotation has been proved to be an efficient method to desilicate for diasporic-bauxite. However, it still has some shortcomings[3], such as more collector consuming, massive forth producing, difficult dewatering and effect of metallurgy. According to the common principle of floating minor rich component and depressing the major constituents, reverse flotation desilication has better prospect than direct flotation[4]. The reverse flotation desilication involves two vital components: the selective depression of diaspore and the enhanced collection of associated gangue minerals. Thus, it is important to find and synthesize new flotation reagents. New cationic collectors have been investigated in recent years, such as alkylamines[5−6], quaternary ammonium salts[7−8], *N*-(2-aminoethyl)-1-naphthalene-acetamide[9], *N*-(3-aminopropyl)-dodecanamide[10], *N*-alkyl-1, 3-diamino-propanes[11−12], *γ*-alkyl-propylamines[13], methyl-naphthaleneamine[14], and RL[15]. Strong flotation capability on aluminosilicates was reported by using these new collectors above, but it was still difficult to apply them in reverse flotation desilication industry, and relatively little work has been done in this field. Therefore, it is of importance to research and develop new reagents with high selectivity and strong flotation ability on aluminosilicates or highly selective depression of diaspore.

The guanidine is one of the strongest bases (pK_a=13.6)[16]. Guanidine functional group attracts interest of chemist and pharmacist mainly due to its bio-

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Foundation item: Project(2005CB623701) supported by the National Basic Research Program of China; Project(50874118) supported by the National Natural Science Foundation of China; Project(2007B52) supported by the Foundation for the Author of National Excellent Doctoral Dissertation of China

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DOI: 10.1016/S1003-6326(08)60257-5

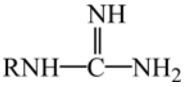
logical activities, hydrogen bonding capability, stability, and positive charge integrity over a wide pH range[17]. Long chain alkylguanidines are widely used as cationic surfactant. They are also applied in detergents, bactericides, fungicides, plant growth inhibitors, anionic extractants, base catalysts and assistants in organic reactions[18]. When considering the special structure and properties of alkylguanidines, they would be a good candidate for cationic collectors in reverse flotation of diasporic-bauxite. In this work, the flotation behaviors of three aluminosilicates with alkylguanidines as cationic collectors were reported, through flotation tests, Zeta potential and FT-IR spectrum measurement. And the adsorption mechanism was further discussed based on structure of the collector.

2 Experimental

2.1 Single mineral samples and materials

Kaolinite, pyrophyllite and illite, obtained from Pingdingshan of Henan Province, Qingtian and Ouhai of Zhejiang Province, China, respectively, were hand picked and then crushed and ground in a porcelain mill. The <0.076 mm fractions were used in flotation. The three minerals were all 90% pure by mineralogical analysis, chemical analysis and X-ray diffraction.

Novel collector alkylguanidines synthesized are hexylguanidine sulfate(SAG$_6$), octylguanidine sulfate (SAG$_8$), decylguanidine sulfate(SAG$_{10}$) and dodecylguanidine sulfate(SAG$_{12}$). The structure of alkylguanidine is described as



$$\mathrm{RNH{-}\overset{\overset{\displaystyle NH}{\|}}{C}{-}NH_2} \tag{1}$$

where R represents linear alkyl residues with 6−12 carbon atoms, such as $CH_3(CH_2)_5$, $CH_3(CH_2)_7$, $CH_3(CH_2)_9$, and $CH_3(CH_2)_{11}$.

HCl and NaOH were used as pH modifiers, and distilled water was used in all tests.

2.2 Flotation tests

Flotation tests were carried out with a XFG5−35 flotation machine with 35 mL effective cell volume, at the impeller speed fixed at 1 650 r/min. 3.0 g mineral samples and suitable amount of distilled water were added. Desired pH values were adjusted with 0.01 mol/L hydrochloride acid solution and 0.01 mol/L sodium hydroxide solution. After adding the desired amount of collectors, the suspension was agitated for 3 min, and then the pH value was measured. The flotation was sustained for 5min. The products were collected, dried, and weighed. The recovery was calculated based on the dry mass of the products obtained.

2.3 Zeta potential measurement

Zeta potential was measured on a Delsa−440SX Zeta potential instrument (Brookhaven Corporation, USA). The mineral sample was further ground to <5 μm in an agate mortar. The mineral suspension containing 0.01% (mass fraction) solid was dispersed in a beaker for 15 min and the pH value was measured. 1×10^{-3} mol/L KNO_3 solution was used as a supporting electrolyte. The measurement error was found to be within ±5 mV after at least three measurements in each condition.

2.4 FT-IR spectroscopy

The FT-IR spectra were obtained with AVATAR360 FT-IR (Nicolet Corporation, USA) to characterize the nature of the interaction between the collectors and the minerals. The mineral sample was ground to be less than 2 μm after contacting with the collector.

3 Results and discussion

3.1 Flotation behavior of three aluminosilicates with alkylguanidines as collectors

The flotation recoveries of kaolinite, pyrophyllite and illite with SAG$_6$, SAG$_8$, SAG$_{10}$ and SAG$_{12}$ as collectors of different carbon lengths are shown in Fig.1. The concentration of each collector is 1×10^{-4} mol/L. It can be seen that the floatability of three aluminosilicates is in the order of pyrophyllite>kaolinite>illite. SAG$_8$, SAG$_{10}$ and SAG$_{12}$ all have strong floatability for these three aluminosilicates. Over a wide pH range, the recovery of both kaolinite and illite can reach or exceed 80%, and the floatability is in the order of SAG$_{12}$≈SAG$_{10}$≈SAG$_8$>SAG$_6$. While for pyrophyllite, the order is SAG$_{12}$>SAG$_{10}$≈SAG$_8$>SAG$_6$. When the pulp pH is below 5.5, the recovery decreases with the increase of pulp pH. However, the recovery of pyrophyllite nearly has no change and maintains around 70% over a pH range of 6−12. SAG$_6$ exhibits a stronger collecting power for pyrophyllite than that for kaolinite and illite.

The flotation responses of the aluminosilicates as a function of the concentration of collectors (SAG$_6$, SAG$_8$, SAG$_{10}$ and SAG$_{12}$) are presented in Fig.2. The pulp pH maintains at 5.5. As can be observed from Fig.2, the recoveries of the three aluminosilicates increase with increasing the dosage of collectors. For pyrophyllite, the floatability of the four collectors is in the order of SAG$_{12}$ > SAG$_{10}$ > SAG$_8$ > SAG$_6$, indicating that with the increase of carbon length of alkylguanidines the floatability of alkylguanidines increases correspondingly. The collecting power of SAG$_8$ increases prominently compared with that of SAG$_6$. However, when the carbon

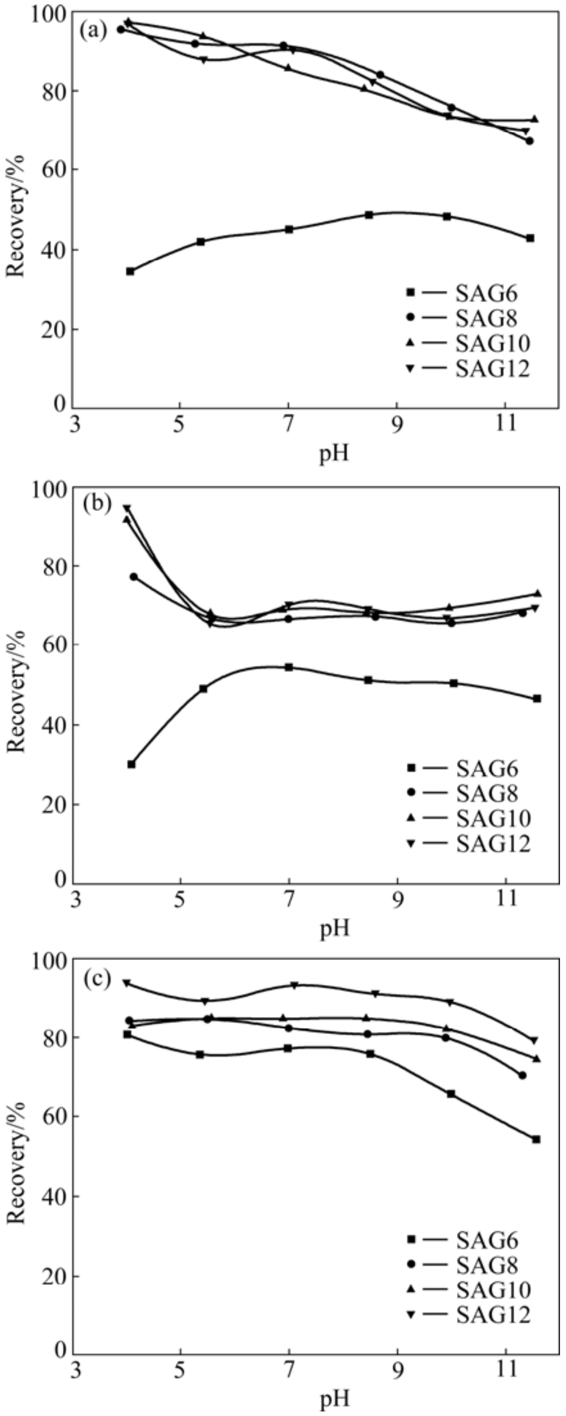


Fig.1 Effect of pulp pH on flotation of aluminosilicates: (a) Kaolinite; (b) Illite; (c) Pyrophyllite

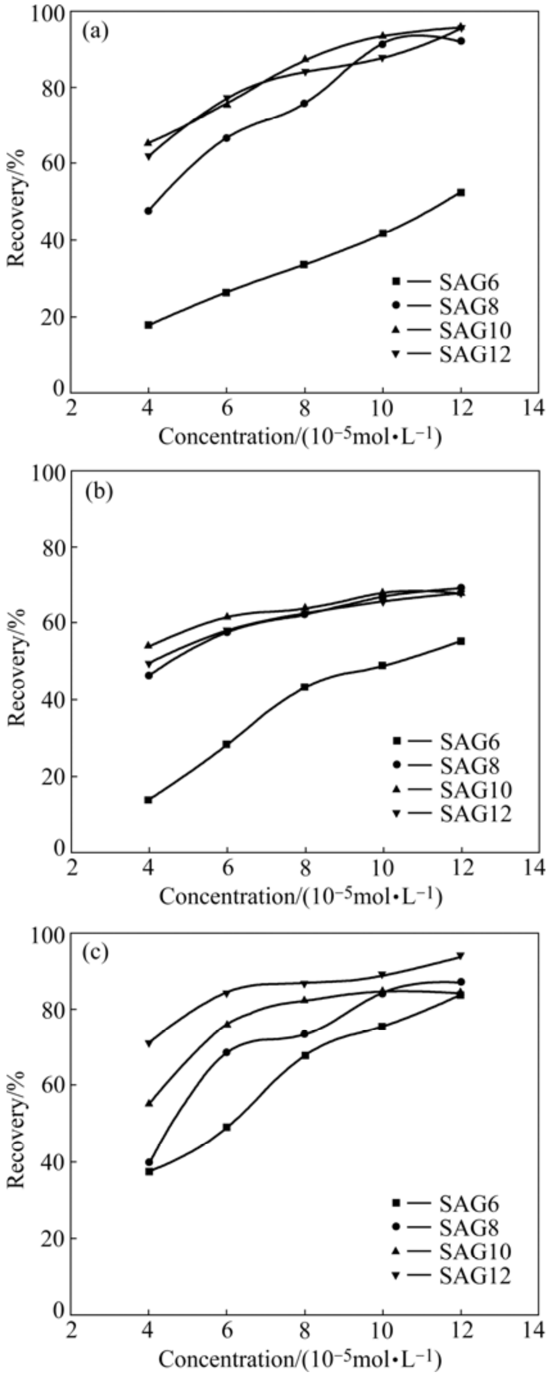


Fig.2 Effect of SAG_6, SAG_8, SAG_{10} and SAG_{12} concentration on flotation of aluminosilicates: (a) Kaolinite; (b) Illite; (c) Pyrophyllite

length of alkylguanidines increases further, there is no increase of flotation recoveries for the three aluminosilicates. SAG_8, SAG_{10} and SAG_{12} exhibit strong collecting ability for kaolinite at the concentration of 1.2×10^{-4} mol/L, and the flotation recoveries are 92.1%, 95.8% and 95.3% respectively. In the case of SAG_6, the collecting power is relatively poor. The four alkylguanidines all exhibit poor floatability for illite and none of them can reach up to 70%. For pyrophyllite, the four collectors all exhibit better collecting abilities than illite, and the flotation recoveries are 84.1%, 87.1%, 84.4% and 94.0%, respectively, at the concentration of 1.2×10^{-4} mol/L.

3.2 Zeta potential results

The floatation capability is enhanced notably with SAG_8 as collector for the three aluminosilicates, as mentioned above. To better understand the interactions between SAG_8 and the three aluminosilicates, electrokinetic phenomenon of mineral suspensions was studied. Zeta potentials of the aluminosilicates in the absence and presence of SAG_8 with concentration of 1.0×10^{-4} mol/L were investigated, and the results are shown in Fig.3.

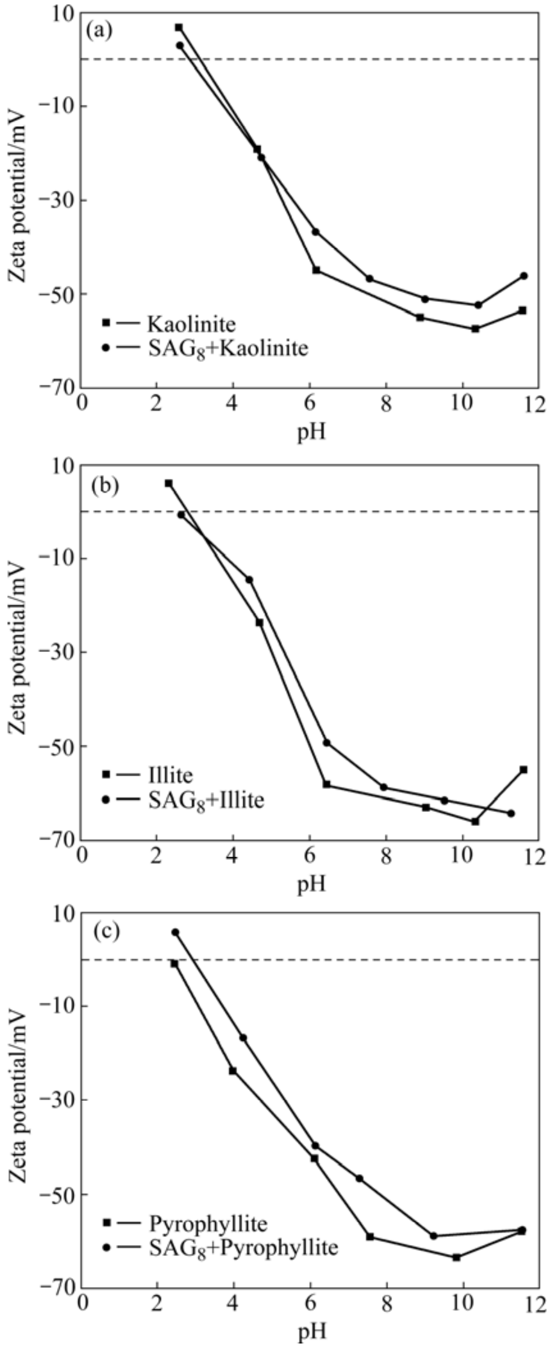


Fig.3 Relationship between Zeta potential and pulp pH: (a) Kaolinite; (b) Illite; (c) Pyrophyllite

The three aluminosilicate surfaces are all negatively charged over a wide range of pH value, which can be explained in view of the crystal structures of the three aluminosilicates[19−20]. Isoelectric point(IEP) is determined to be 3.5, 3.0 and 2.3 for kaolinite, illite and pyrophyllite, respectively, and these values are in excellent agreement with those reported in Ref.[21]. The negative Zeta potential of three aluminosilicates increases with the increase of the pulp pH at a lower pH range. However, there is nearly no increase when the pulp pH is above 8.

Zeta potentials of kaolinite, illite and pyrophyllite are higher in the presence of SAG_8 than in the absence of SAG_8, which indicates that SAG_8 is adsorbed on the surface of aluminosilicates, leading the positive charges on the aluminosilicates surface to increase. It is anomalous that the presence of SAG_8 has less influence on the negatively charged mineral surfaces, which can be explained as follows. The guanidine is one of the strongest bases, which has two kinds of NH_2 groups in its cationic ions. When the cationic collector is introduced into the pulp, one of the NH_2 groups may be attracted by electrostatic forces on the aluminosilicates surface. Meanwhile, another may form hydrogen bond with OH^- ions on the aluminosilicates surface or in the aqueous solution. Thus, the concentration of OH^- increases on the surface of aluminosilicate, resulting in the unnoticeable positive charge increase on the surface of aluminosilicates. The influence of SAG_8 on Zeta potential for three aluminosilicates is in the order of pyrophyllite > kaolinite > illite, indicating that the floatability of three aluminosilicates is in the order of pyrophyllite>kaolinite>illite, which is in accordance with the flotation results.

It is known that cationic collector exhibits different existence states in different pH values. In the case of the guanidine collector, it is anomalous that SAG exhibits the same influence on the change of Zeta potential at different pH values. This anomalous phenomenon can be explained as follows. The guanidine is one of the strongest bases (pK_a=13.6) with strong hydrogen bonding capability and integrity positive charging over a wide pH range. SAG is in the form of cationic ions in aqueous solution over the entire experimental pH range. Therefore, SAG displays the same influence on the change of Zeta potential for three aluminosilicates in the whole experimental pH range.

3.3 FT-IR spectra analysis of alkylguanidine adsorption on aluminosilicates

Based on the same reason above, SAG_8 was chosen for the FT-IR spectra analysis. The FT-IR spectra of SAG_8, three aluminosilicates and aluminosilicates in the presence of SAG_8 are presented in Fig.4. The FT-IR spectra of kaolinite, illite and pyrophyllite observed are in great agreement with those reported in Ref.[22].

It can be seen that slight spectrum shift of three aluminosilicates is observed after they are conditioned by SAG_8. The spectra of three aluminosilicates affected by

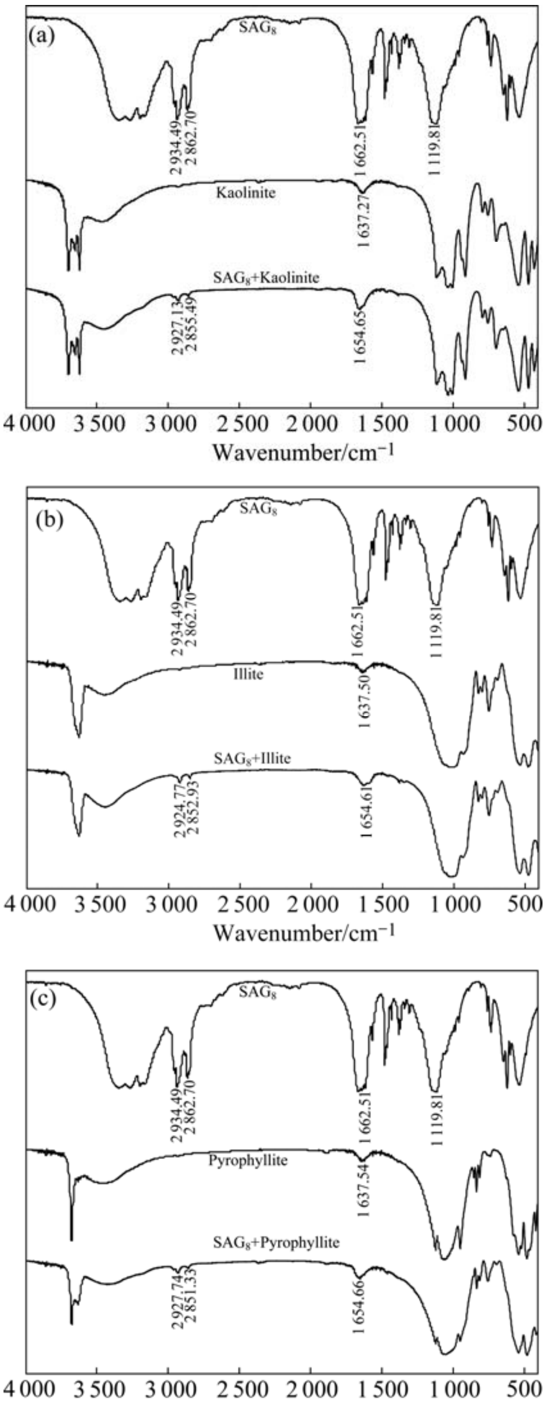


Fig.4 FT-IR spectra of aluminosilicates with and without collector: (a) Kaolinite; (b) Illite; (c) Pyrophyllite

SAG_8 exhibit weak peaks at 2 927.13 cm^{-1} and 2 855.49 cm^{-1}, 2 924.77 cm^{-1} and 2 852.93 cm^{-1}, 2 927.74 cm^{-1} and 2 851.33 cm^{-1}, respectively, which attributes to the stretching bends of CH_3 and $—CH_2$. These results indicate that the adsorption of SAG_8 on three aluminosilicates is dominated by physical electrostatic adsorption [23]. Meanwhile, the spectrum of SAG_8 exhibits the bending mode of NH_2 at 1 662.51 cm^{-1}[24]. The weak peak at 1 637.27 cm^{-1} in the spectrum of kaolinite attributing to the bending mode of H—O—H indicates the existence of little free water[9]. After being conditioned by SAG_8, spectrum of kaolinite exhibits a peak at 1 654.65 cm^{-1}, which may be caused by the formation of the N—H—O hydrogen bond between the group of NH_2 in SAG_8 molecule and the oxygen of kaolinite surface[25]. Therefore, the electronegativity of N is weakened, leading the peak to shift to a higher wavenumber. While for the O of hydroxyl on kaolinite surface, the electronegative is enhanced, leading the peak to shift to the lower wavenumber relatively. Similar to kaolinite, the hydrogen bond is formed for illite and pyrophyllite as well. The peak of 1 637.50 cm^{-1} shifts to the higher wavenumber of 1 654.61 cm^{-1} for illite, while the peak of 1 637.54 cm^{-1} shifts to 1 654.66 cm^{-1} for pyrophyllite. To summarize, the adsorption between SAG_8 and three aluminosilicates is mainly by means of electrostatic force and hydrogen bond. As no other peak shift is observed, it can be concluded that there is no chemical adsorption between the collectors and the aluminosilicates.

3.4 Interfacial characteristic of three aluminosilicates

Kaolinite is a two-layer-structured aluminosilicate, which can form two different planes (basal planes and edge planes) with different properties during crashing [22, 26]. The basal planes displaying an inert siloxane structure are constantly negatively charged both in acidic and in alkaline media due to the isomorphous substitution of Al^{3+} for Si^{4+} and Mg^{2+}/Fe^{3+} for Al^{3+}, which makes kaolinite only have the moderate floatability. However, the atomic structure of the edges on kaolinite is totally different from that of the basal planes. At the edges, the tetrahedral silica sheets and octahedral alumina sheets are destroyed, resulting in a surface of broken Si—O and Al—O covalent bonds. The presence of these broken bonds affects the physicochemical properties of the resultant surfaces and their interactions with flotation reagents. The charging mechanism of the edges can be described with the traditional model for oxides and silicates. Depending on solution pH, the edges are positively charged due to H^+ ion adsorption in acidic solution or negatively charged by adsorption of OH^- or by dissociation of H^+ in alkaline solution.

Pyrophyllite is a three-layer-structured aluminosilicate. Similar to the kaolinite, the basal planes of pyrophyllite are constantly negatively charged due to isomorphous substitution, and the edges exhibit pH-dependent surface charging behavior. Hence, pyrophyllite exhibits excellent natural floatability, and the solution pH hardly affects its flotation, which is consistent with the above flotation results.

Illite has similar crystal structure as pyrophyllite, and is also a three-layer-structured aluminosilicate. However, Al^{3+} substitutes isomorphically for some of Si^{4+} lattice of tetrahedral silicates along with varying substitution degree of water for hydroxides lattice in illite. The compensating ions are usually potassium that bridges two neighbouring layers[27]. Due to the cleavage planes being hydrophilic entirely and with permanent negative charges, illite exhibits the lowest floatability among three aluminosilicate minerals, which is confirmed by the flotation results.

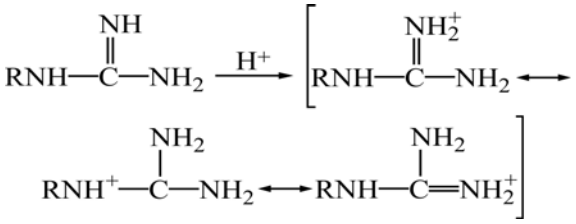
The ratio of the broken Al—O to Si—O bonds per unit area on the various edge surfaces is in the order of kaolinite > illite > pyrophyllite. This trend is in the reverse order of hydrophobicity of the three aluminosilicates in cationic solutions, suggesting that the ratio of broken Al—O to Si—O bonds on various edge surfaces appears to play a dominant role in determining the surface properties of various aluminosilicates and their flotation response in collector solutions.

3.5 Interaction of SAG with aluminosilicates

Based on the unique molecule structure of SAG, the FT-IR spectra of aluminosilicates and the Zeta potential of the pulp, the adsorption mechanism between mineral and collector is proposed as follows.

The guanidine is one of the strongest bases (pK_a=13.6) with strong hydrogen bonding capability and integrity positive charging over a wide pH range, indicating that SAG is in the form of cationic ions in aqueous solution over the entire experimental pH range of 4−12.

The forming process of the SAG cationic surfactant is shown in formula (2). The formed cationic surfactant has three kinds of syntonous structures, which can exist stably in solution[28].



$$\mathrm{RNH{-}\overset{\overset{\displaystyle NH}{\|}}{C}{-}NH_2} \xrightarrow{H^+} \left[\mathrm{RNH{-}\overset{\overset{\displaystyle NH_2^+}{\|}}{C}{-}NH_2} \longleftrightarrow \mathrm{RNH^+{-}\overset{\overset{\displaystyle NH_2}{|}}{C}{-}NH_2} \longleftrightarrow \mathrm{RNH{-}\overset{\overset{\displaystyle NH_2}{|}}{C}{=}NH_2^+}\right] \quad (2)$$

As seen from the formula (2), SAG has two kinds of NH_2 functional groups on their cationic ions. One is the SAG-cation group of $—CH_2NHC\ (NH)\ N^+H_3$ that can absorb on the negatively charged mineral surface through electrostatic effects. The other is the SAG-amine group shown in formula (2) which can absorb on the $Si—O^-$ and $Al—O^-$ sites through its —N—H atoms by $Si—O^-$---H—N and $Al—O^-$---H—N hydrogen bonding. In a word, the adsorption of SAG on three aluminosilicates is dominantly by electrostatic attraction or hydrogen bonding, consistent with previous studies.

In the pH range of 4−7, the basal planes of kaolinite are negatively charged, and the edges are positively charged. The interaction between SAG^+ cationic ions is predominated by electrostatic attraction. In the pH range of 8−12, OH^- ion will bond with H atom on the kaolinite surface and cationic ion SAG^+ in aqueous solution, which increases the negative charge of kaolinite surface and decreases the amount of SAG^+ cations in aqueous solution. As a result, the floatability of kaolinite slightly decreases with increasing pH, which is consistent with the experimental results.

The interaction between SAG and illite and pyrophyllite is similar to kaolinite. However, pyrophyllite exhibits excellent natural floatability, and the solution pH hardly affects its flotation, which is consistent with the experiment results. While for illite, the situation is also slightly different from the kaolinte. The flotation recovery decreases sharply at first with pulp pH going up to 6 and then maintains constant at relatively lower recovery around 70% with increasing pH further. Increasing concentration of OH^- ions enhances the reactive ability of OH^- with SAG^+ cationic ions, which weakens the adsorption ability of SAG^+ on the illite surface. Another possible reason to explain the above situation is the compensatory ions on the surface of illite. The compensatory ions (neutralising the negative charge caused by isomorphous substitution of Si^{4+} by Al^{3+} on the surface of illite) such as K^+, Na^+, Mg^{2+} and H^+ can dissolve in aqueous solution. The solubilities of those ions increase with increasing pH. As a result, in the pH range of 8-12, the adsorption competition between SAG collectors and above compensatory ions onto the illite surface weakens the adsorption ability of SAG^+ cations and then decreases the flotation response, which confirms the lowest floatability among three aluminosilicate minerals.

4 Conclusions

1) The floatability of three aluminosilicates is in the order of pyrophyllite>kaolinite>illite. For kaolinite and illite, SAG_8, SAG_{10} and SAG_{12} exhibit much better collecting power than SAG_6 which shows a much stronger floatability for pyrophyllite than for kaolinite and illite.

2) The floatability of kaolinite decreases slightly with increasing pH value of the pulp with SAG_8, SAG_{10} and SAG_{12} as collectors. The lowest flotation recovery is above 70%. The flotation recovery is less variable and is around 70%. For illite, when the pulp pH is over 6, the pH value of the pulp has less influence on the floatability of the pyrophyllite.

3) The isoelectric point of kaolinite, illite and

pyrophyllite are 3.5, 3.0 and 2.3, respectively. The Zeta potentials of three aluminosilicates all change after they are treated by SAG_8, which confirms the fact that alkylguanidines using as collectors are all attracted on the surface of aluminosilicates.

4) FT-IR spectra of three aluminosilicates in the presence of alkylguanidines indicate that the cationic collector is adsorbed mainly by the way of electrostatic forces and hydrogen bond. It seems no chemical reaction observed.

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(Edited by YANG Bing)