Application of mixed collectors on quartz-feldspar by fluorine-free flotation separation and their interaction mechanism: A review

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Abstract: Quartz and feldspar are usually exist in symbiosis in nature, and they are difficult to be separated effectively by conventional physical methods owing to their similarities in crystal structures and surface characteristics. Flotation is the most resultful method, and especially, flotation with hydrofluoric acid (HF) is the most efficient way. Because HF may cause serious environmental and health problems, the effective and environmentally friendly separation of quartz and feldspar remains a formidable challenge. The crystal structure, surface broken bonds, surface energy, and solid–liquid interface properties of quartz and feldspar are investigated in this paper. In particular, some types of mixed cationic/anion collectors and their interaction mechanism on the quartz and feldspar surfaces with acidic, alkaline, and neutral media in the absence of fluorine are discussed, and the grade and scheme of quartz and feldspar for the practical application are illustrated. This review proposes concrete research approaches and provides perspectives for the advanced processing of quartz and feldspar in an environmentally friendly and economical way.

Keywords: quartz, feldspar, crystal structure, flotation, mixed collectors, environmentally friendly

1. Introduction

Quartz and feldspar are two of the most abundant types of bulk silicate rock-forming minerals and are widely distributed in the earth's crust (Bayat et al., 2006; Lin et al., 2018；Gaied and Gallala, 2015). Quartz is a basic raw material widely used in multiple emerging industries for the production of glass, photovoltaic, semiconductor and electronic devices (Feng et al., 2018; Lin et al., 2017; Vidyadhar and Rao, 2007; Yuan et al., 2018). Feldspar is a raw material widely used for the production of glass, ceramic, and paint (Gaied and Gallala, 2015; Skorina and Allanore, 2015). Quartz and feldspar usually exist in symbiosis or association with other useful or gangue minerals in nature (Heyes et al., 2012; Wang et al., 2016; Yin et al., 2019; Liu et al., 2013). To meet the demands of above application fields, impurities including magnetite, hematite, rutile, mica, pyrite and tourmaline must be removed. According to the occurrence distribution of detrimental impurity and ore properties, the pretreatment technology before the separation of feldspar and quartz includes crushing, grinding, de-sliming and classification, gravity separation and magnetic separation.

These conventional beneficiation techniques are employed to remove the impurity minerals from quartz and feldspar, but effective separation of quartz and feldspar cannot be achieved owing to their similar physical properties, such as shape, color, electrical and magnet properties, hardness and relative density (Cheng et al., 2019; Mesquita et al., 2003; Liu et al., 2013; Vidyadhar and Rao, 2007). It is well known that various crystal structures possess different exposed surfaces. In addition, the adsorption behaviours of collectors on the minerals is significantly influenced by anisotropic surface characteristics, including the wettability, surface energy, and charge (Ahmed., 2010; Gao et al., 2019; Kou et al., 2015; Mohammadi-Jam et al., 2014; Tian et al., 2017; Zdziennicka., 2010; Xu et al., 2017). Flotation is the crucial

and necessary method to separate quartz and feldspar, which has experienced three development stages of the traditional hydrofluoric acid (HF), fluorine-free with acid (H₂SO₄) and "fluorine-free acid-free"(neutral condition). In the 1940s, most scholars had begun to use the "hydrofluoric acid" method for flotation separation of quartz and feldspar. Considering that HF is hazardous to the environment and health, the United States, Japan and other countries had resort to the "fluoride-free" method in the 1970s, which was widely used in the industry (Yu et al., 2005; Sun et al., 1993). In recent years, under the influence of increasingly strict environmental protection policies, many scholars and plants had begun to resort to "fluorine-free acid-free" method. According to the different working principles, the flotation machine could be divided into three types: stirred flotation machine (mechanical stirring flotation machine, aerated stirring flotation machine), inflatable flotation machine and gas separating flotation machine. The stirred flotation machine was widely used in industry owing to rich foam and high flotation efficiency. In addition, the selectivity of flotation collectors was an essential prerequisite to achieve high quality concentrate and great recovery in the separation process. In the traditional flotation beneficiation process, single collectors, such as EDTA, diamine, sulfonate and oleate were adopted in the separation of quartz and feldspar (Shehu and Spaziani, 1999; Vidyadhar and Rao., 2007). Therefore, the use of mixed collector was a considerable progress in the separation of quartz and feldspar (Gaied and Gallala, 2015; Rao and Forssberg., 1997; Larsen et al., 2019; Larsen and Kleiv, 2016, 2015; Zhang et al., 2018).

Mixed surfactants lead to better flotation performances, including increased recovery and enhanced selectivity to the target mineral (Rao and Forssberg., 1997; Wang et al., 2016, 2014; Xu et al., 2017b., Xie et al., 2020a; Xie et al., 2020b; Shu et al.,2020). Owing to the strong synergistic interactions between two surfactant molecules with oppositely charged head groups, a large number of mixed collectors may lead to low surface tension and lower critical micelle concentration(CMC) (Alexandrova et al., 2009; Rao and Forssberg., 1997; Wang et al., 2016, 2014; Wang et al., 2018; Xu et al., 2017a, 2016). In the flotation process, different types of mixed cationic/anionic collectors are used for surface modification to adjust the wetting properties of feldspar particles. Cationic collectors mainly include alkyl amine, alkyl ether amine, and alkylammonium. Anionic collectors mainly include fatty acids/salts and sulfonates (Abaka-Wood et al., 2017; Chelgani et al., 2015; Kou et al., 2015; Tian et al., 2017., Guo et al., 2020).

In this study, the crystal structure, surface broken bonds, surface energy, and solid–liquid interface properties of quartz and feldspar are compared to design new strategies to improve their flotation separation. Furthermore, the interaction mechanism of mixed cationic/anion collectors with the quartz and feldspar under different pH conditions and in the absence of fluorine are discussed, and the grade and scheme of quartz and feldspar for the practical application are illustrated. We focus on the rational allocation and cascade utilization of resources and consider the comprehensive utilization of the by-products using tailings processing to produce high value products.

2.   Structure and Properties of Quartz and Feldspar

2.1. Quartz surface properties

2.1.1 Crystal Structure

Quartz is mainly composed of SiO₂, which includes α-quartz, β-quartz, and coesite, and generally refers to α-quartz. According to different deposit types, quartz may come from natural crystal, vein quartz, quartz sandstone, quartzite, quartzosesandstone and natural quartz sand, and they have same crystal structure. Quartz crystals belong to trihedral hemihedral crystal family of trigonal systems, and its cell parameters are a = b = 4.973 Å; c = 5.4469 Å; α = β = 90°; γ = 120°; z = 3, and the composition of the unit cells is Si₃O₆ (Xue et al., 2009; Huggins, 1922).

Quartz has a typical crystal structure consisting of a silicon-oxygen tetrahedron with each silicon atom connecting four oxygen atoms with single bonds. The Si-O-Si bond angles are 143.30° and 143.73°; the lengths of the Si-O bonds are 1.620 and 1.624 Å; the lengths of O-O bonds are 2.604 and 2.640 Å. The oxygen atoms in the tetrahedron are shared by two silicon-oxygen tetrahedrons, forming a corner-connecting spatial crystal structure (Fig.1) (Wei et al., 2013; Yan et al., 2016). The silicon atoms and the surrounding four oxygen atoms are connected by atomic bonds, 60% and 40% of which are covalent

and ionic, respectively, with equal bonding force in each direction (Chen et al., 2008; Leeuw et al., 1999; Sahoo et al., 2016; Tsuchiya et al., 2000; Wang et al., 2018).
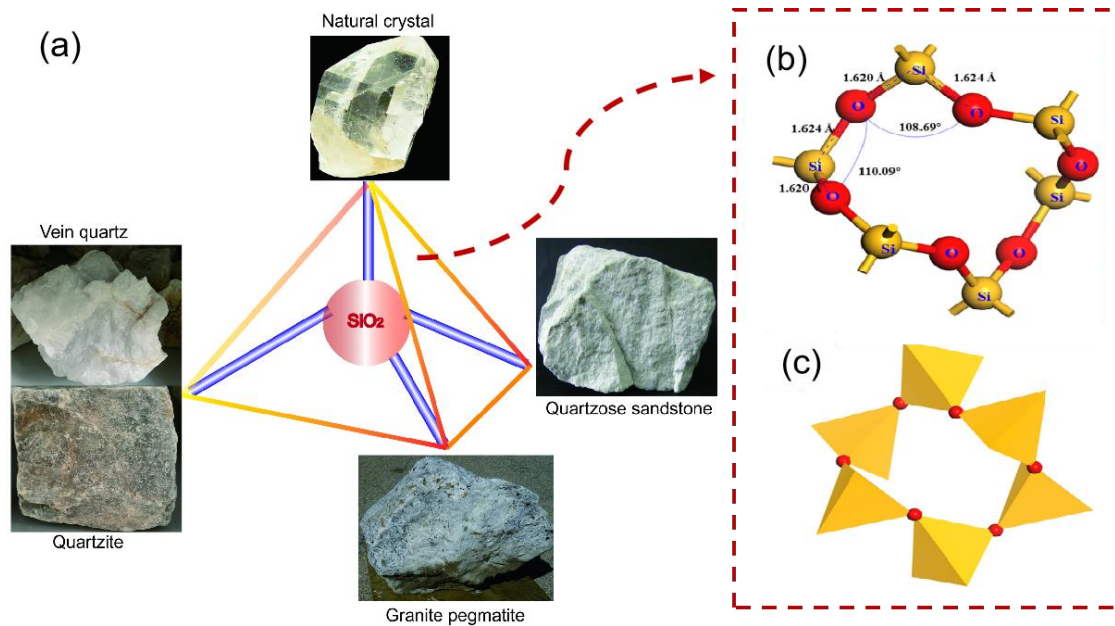

Fig .1. Main quartz deposit (a) and cell with a (b) ball and stick model and (c) polyhedron model: O (red); Si (yellow) (Wang et al., 2018)

2.1.2 Surface broken bonds and surface energy

During the crushing and grinding process, minerals cleave along particular crystal orientations where weaker chemical bonds are present and form new exposed surfaces. The atoms on the exposed surfaces have less coordination and different atoms can possess different broken bonds, which affects the reactivity of the surface, ultimately changing the flotation behaviour of the bulk mineral (Chen and Cheng, 2010; Gao et al., 2019; Leuty and Tsige, 2010; Mohammadi-Jam et al., 2014).

The surface energy provides a criterion to evaluate the surface stability and cleavage difficulty and is closely correlated with the density of broken bonds (Huggins., 1922; Wang et al., 2018; Yan et al., 2016).
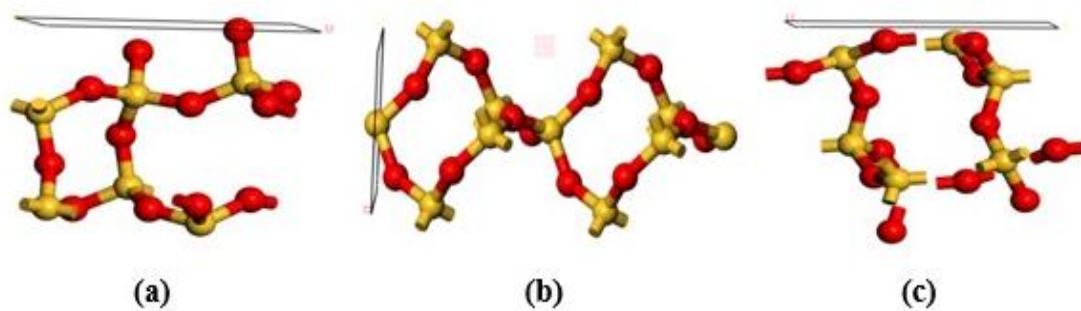

Fig.2. Unit cell of quartz cleave surface: (a) (101) surface, (b) (001) surface, and (c) (011) surface

On the basis of the literature (Bandura et al., 2011; Leuty and Tsige, 2010; Morgane and Gaigeot., 2016; Rath et al., 2014; Wang et al., 2018; Wright et al., 2013; Zhu et al., 2016), the most commonly mentioned crystal surfaces of quartz are (101), (001), and (011) (Fig.2). First-principle and density functional theory (DFT) calculations were performed on the (001) and (101) cleaved surfaces to calculate the surface energies and predict the stability of the quartz surfaces (Wang et al., 2018; Leuty and Tsige., 2010; Wang et al., 2018). According to the calculated surface energy value, quartz (101) have the lowest surface energy (Bandura., 2011; Murashov, 2005).

Table 1. Calculated surface energies obtained by structural optimization of different quartz surfaces (Murashov., 2005)

Surface	101	112	100	001
Surface energy(eV/Å²)	0.071	0.109	0.067	0.139

2.1.3. Quartz–water interface properties

During the crushing and grinding process, a large number of Si-O bonds are broken. When quartz enters into the water solution, the H⁺ or OH⁻ in the solution adsorbed on the broken Si-O bond, which makes the quartz surface charged. Depending on the pH value of the solution , the quartz edges is 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 (Duan et al., 2019; Liu et al.,2015; Huang et al., 2014).
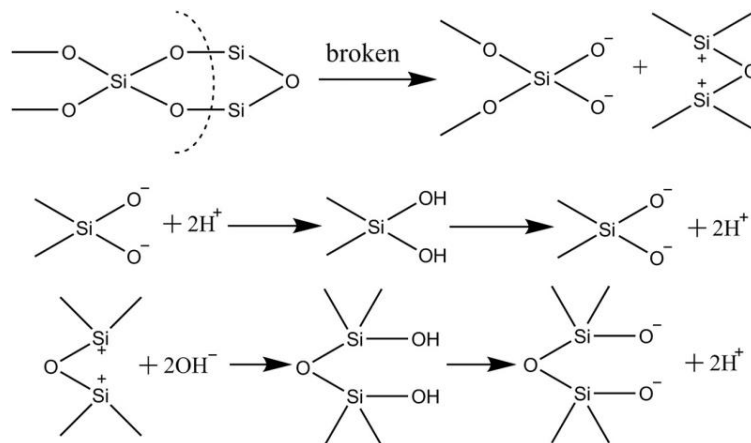

Fig. 3. The charging mechanism of quartz

When the exposed quartz surface enters into water solution, quartz-water interface properties was greatly changed and the hydroxylated surface was formed due to water adsorption and dissociation action, and these hydroxyl groups structure will possibly in turn influence the surface interfacial chemical reactivity, further affecting the mineral flotation behavior (Bandura et al., 2011; Boily and Rosso, 2011; Chen and Cheng, 2010; Esslur et al., 1997; Niu et al., 2019; Vega et al., 1986; Zhu et al., 2016, Morgane and Gaigeot., 2016). Different types of silanol groups and siloxane bridges on the surface of quartz was shown in Fig. 4 (Zhuravlev., 2000).
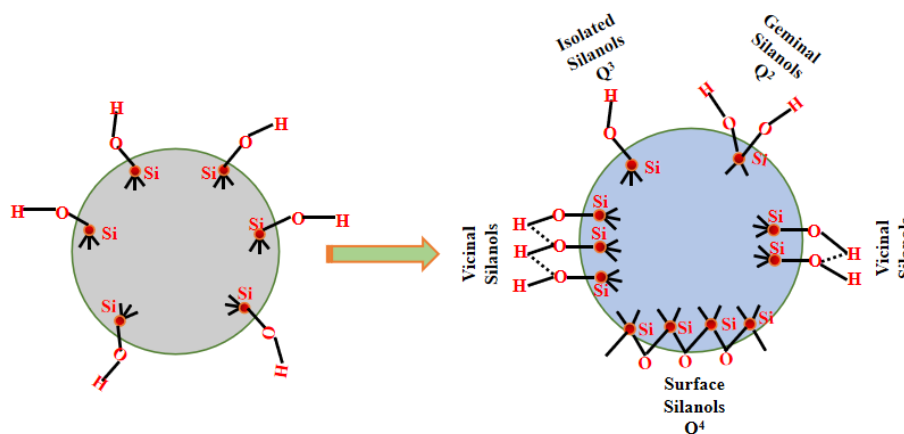

Fig. 4. Different types of silanol groups and siloxane bridges on the surface of quartz

Different surfaces of quartz have different hydroxyl groups structural features while in contact with water solution (Zhuravlev, 2000; Rath et al., 2014). Molecular dynamics simulations method (MDS) had been used by many researchers to investigate the interface charge effect, the adsorption process and mechanism (Adeagbo et al., 2008; Kubicki et al., 2012; Wright and Walsh, 2012; Bandura et al., 2011).

Different silicon hydroxyl compound form on different exposed surfaces. The most notable difference between the (101) and (100) surfaces of quartz is that the former is composed of Q^3 Si-OH, whereas the basic composition of the latter is Q^2 Si-(OH)$_2$(Fig. 5). In the Q^3 Si-(OH) surface, it is relatively easy to form a hydrogen bond network in the aqueous phase (Kubicki et al., 2012).
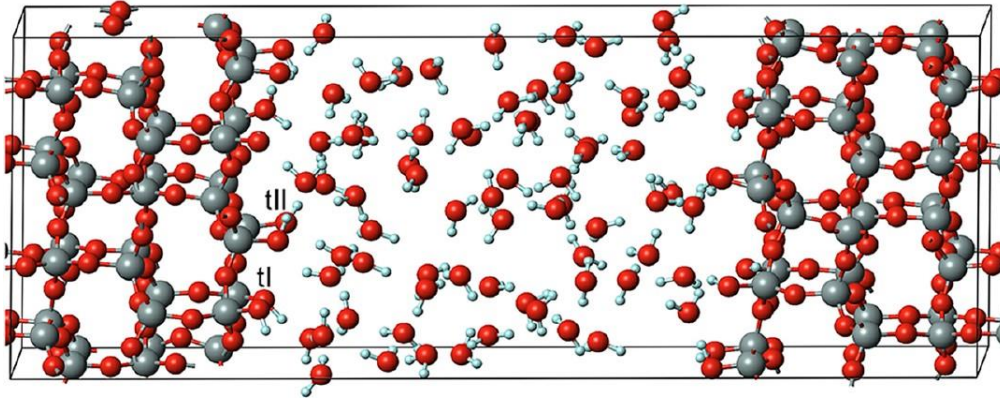

Fig. 5. Quartz (101) and water interface model for the DFT molecular dynamics simulation: O (red); Si (gray); H (light blue)

2.2. Feldspar surface properties

2.2.1. Crystal structure

All the rocks of the feldspar groups are called feldspar. Feldspar is an aluminosilicate mineral containing calcium, sodium, and potassium. The isomorphic substitution is very common in feldspars, and the chemical composition of the compound is often expressed as $Or_xAb_yAn_z$ (x + y + z=100), where Or, Ab, and An represent $KAlSi_3O_8$, $NaAlSiO_8$, and $CaAl_2Si_2O_8$, respectively (Heyes et al., 2012;Bayat et al., 2006). The chemical constitution of alkali feldspars ranges from microcline and orthoclase ($KAlSi_3O_8$) to albite ($NaAlSi_3O8$) (Or-Ab), and their plagioclases range from albite ($NaAlSi_3O_8$) to anorthite ($CaAl_2Si_2O_8$). These subgroups constitute the continuous solid solution series of feldspar (Fig. 6) (Zhang et al., 2018).
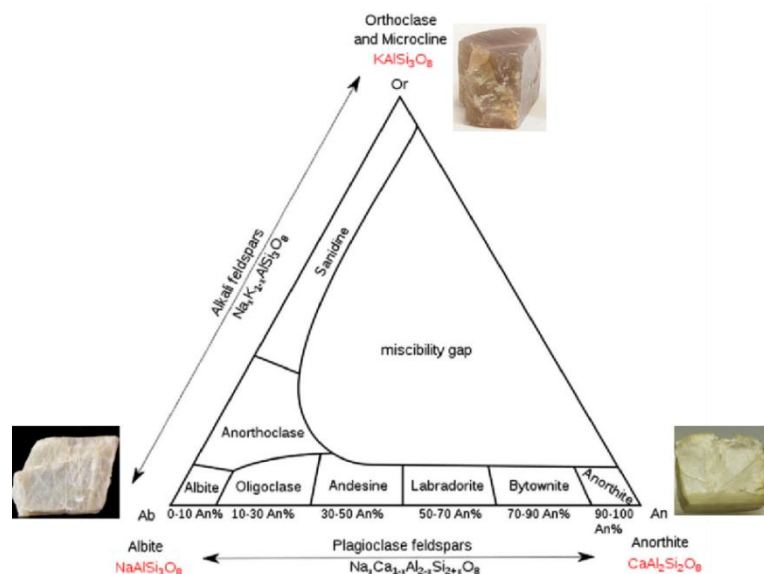

Fig. 6. Compositional phase diagram of the different minerals that constitute the feldspar solid solution

The basic structure of feldspar is a tetrahedron consisting of four oxygen atoms surrounding either a silicon atom or an aluminum atom. Alkali or alkaline earth metal cations with large radius are located in large voids within the tetrahedron skeleton, and eight (for monoclinic feldspar) or nine (for triclinic

feldspar) cations are attached to the central ion. The most important unit of the crystal structure is the four-membered ring composed of tetrahedron TO_4 (T=Si, Al), which consist of two pairs of nonequivalent [TO_4] tetrahedrons T_1 and T_2 (Fig.7) (Y. Yang et al., 2014). With the isomorphous substitution of Al^{3+} for Si^{4+} in the silica tetrahedra of the crystal lattice, feldspar has an anisotropic crystal chemistry characteristic (Burat et al., 2007).
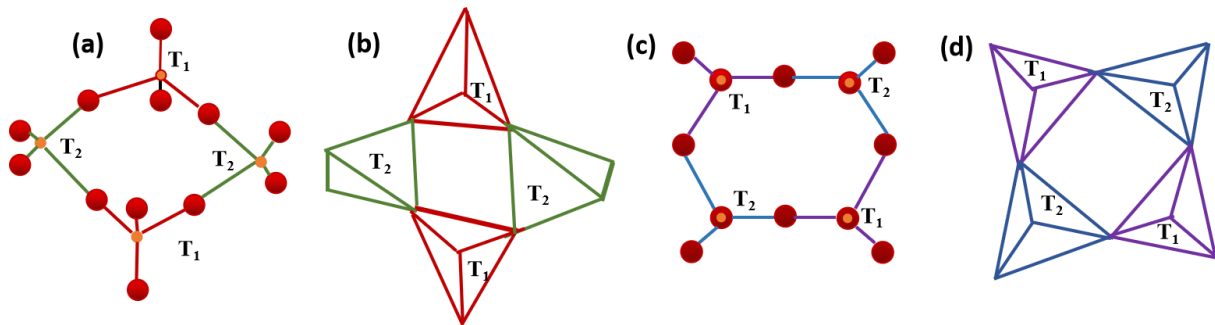

Fig. 7. Basic structure of feldspar: (a) and (b) (010) four-membered ring, (c) and (d) ($\overline{2}$01) four-membered ring

The order-disorder of feldspar group minerals mainly depends on the Al^{3+}/Si^{4+} ratio and their distribution and substitution laws at position T of the tetrahedron [TO_4], which constitutes the crystal structure of feldspar. The order-disorder degree directly affects the symmetry of the crystal. Each four-membered ring in the crystal structure of feldspar represents a complex anion group [(Al, Si)$_4$O$_8$]. Alkali feldspars (K, Na) (AlSi$_3$O$_8$) have an Al: Si ratio of 1:3, and calcium feldspar Ca(AlSi$_3$O$_8$) and barium feldspar Ba(AlSi$_3$O$_8$) have an Al: Si ratio of 2:2 (Yang et al., 2014).

As an example, the cell parameter of microcline are a_0=0.854 nm, b_0=1.297 nm, c_0=0.722 nm, α=90°39′, β=115°56′, γ=87°39′, and Z=4 (Fig. 8).
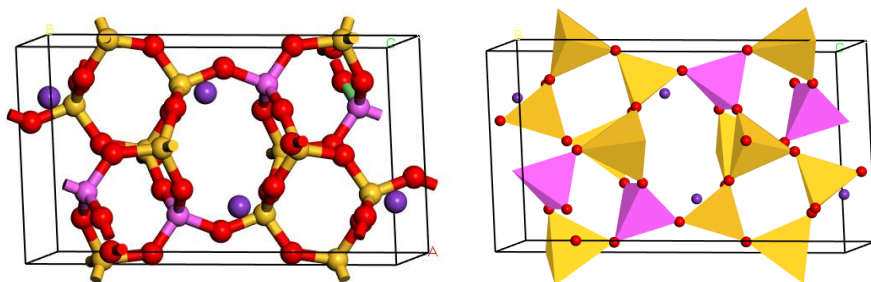

Fig. 8. Cell model of feldspar: O (red); Si (yellow); Al (light purple); K(purple)

2.2.2 Surface broken bonds and surface energy

The crystal structures of feldspar determine the basic types of broken bonds existing on the exposed surfaces, and different types of ions exhibit different numbers of broken bonds (Guan et al., 2009; Xu et al., 2017a, 2014). In the (010) surface, the Si-O and Na-O bonds are broken, whereas the Na-O and Al-O bonds are broken on the (001) surface; Si-O, Na-O, and Al-O bonds are broken on the (110) surface. (Guan et al., 2009; Xu et al., 2017a).

Mineral crystal tends to split along certain crystallographic structural directions during the processing of crushing or grinding, leading to the formation of new cleavage planes. The Lower (higher) surface energies denote that it is easier (harder) for cleavage to be generated along a specfic plane. The surface energies calculated by structural optimization of different feldspar surfaces are presented in Table 2 (Xu et al., 2017a）. According to the above calculated surface energies value, the surface energies of cleavage follows the order (110) > (010) > (001). The (010) and (001) surfaces are the most commonly cleavage planes for feldspar crystals surfaces. Since the (010) and (001) surface energies are basically the same, these surfaces should be the most common cleavage planes for feldspar crystals due to the lowest surface energies(Xu et al., 2017a). The unit cell of feldspar consists of three basic cleave surfaces, as shown in Fig. 9.

Table 2. Calculated surface energies obtained by structural optimization of different feldspar surfaces

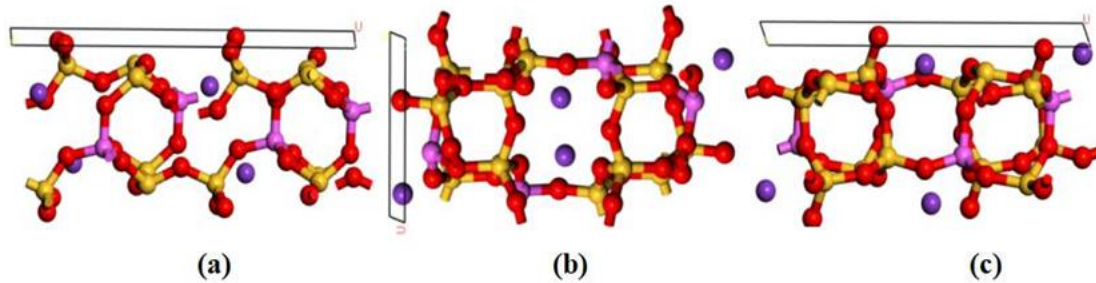| Surface	010	001	110
Surface energy(J/m²)	1.19	1.23	2.06

Fig. 9. Unit cell of feldspar cleave surface: (a) (110) surface, (b) (010) surface, (c) (001) surface

2.2.3 feldspar–water interface properties

The characteristics of surface reactions for feldspar in aqueous phase are similar to those of quartz. The tetrahedral silica sheets and octahedral alumina sheets are damaged due to external force, leading to the broken of Si–O and Al–O bonds. The charging mechanism(Fig. 10) of the feldspar can be explained with the model of oxides and silicates (Duan et al., 2019; Liu et al.,2015; Huang et al., 2014). The charge of feldspar surface is similar to that of quartz, depending on the pH value of solution. Moreover, K^+ or Na^+ at the edge of feldspar is dissolved in the water solution, and leaving positive charge holes, leading to slightly negatively charged than quartz (Dai et al., 1996). The isoelectric point of quartz and feldspar minerals are at pH 2 and at a slightly lower pH (about pH 1.5), respectively (Vidyadhar and Rao, 2007; Fuerstenau and Pradip, 2005; Liu et al., 2018; Tian et al., 2017b).
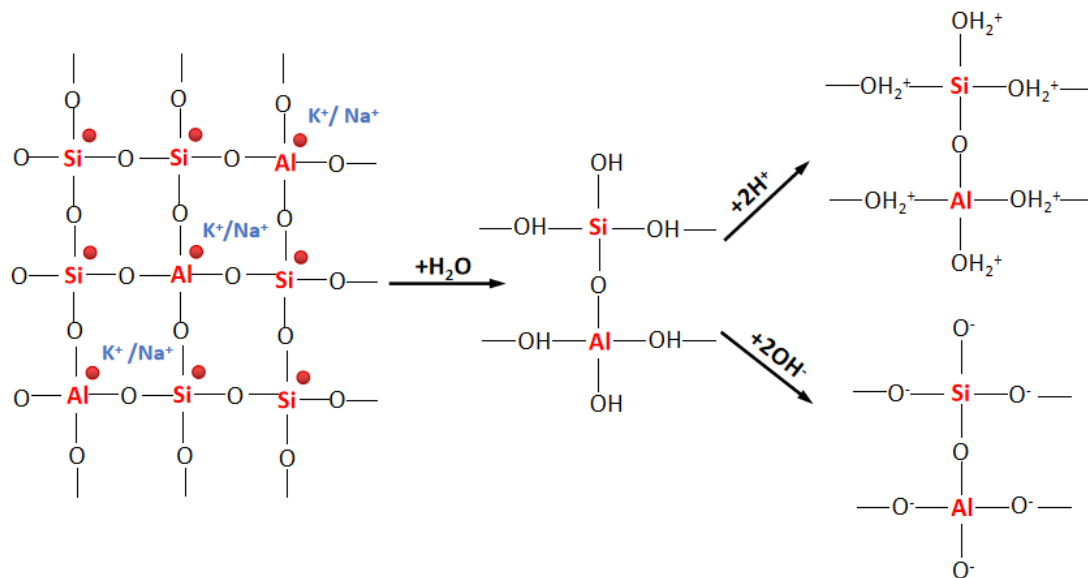

Fig. 10. The charging mechanism of feldspar

Several researchers demonstrated that the specific chemisorption sites for the anionic collector are the Al sites on the surface of aluminosilicate minerals (Xu et al., 2014, 2016; Rai et al., 2011). In the case of feldspar, Al sites only be exposed on the surfaces of (001) and (110) from the Al-O broken bonds, leading to a free Al site. In addition, only the (001) surfaces possessed the Al sites required for anionic collector by anisotropic surface energies and broken bond densities estimated by density functional theory calculations. Schematic illustration of the broken bonds formed on different feldspar surfaces is shown in Fig. 11(Xu et al., 2017a).
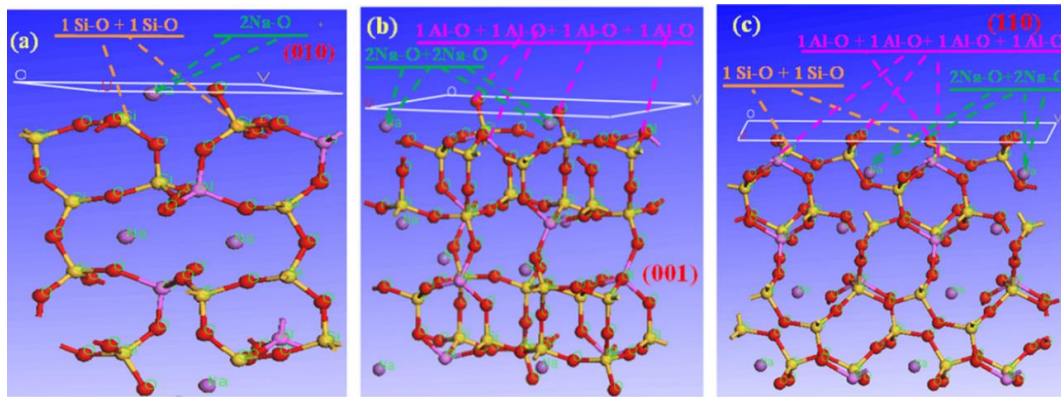
Fig. 11. Diagram of the broken bonds on different crystal surfaces of feldspar: (a) (010), (b) (001), and (c) (110) (Xu et al., 2017a)

3.   Mixed collectors for acid flotation of feldspar

3.1. Current research status and progress on mixed collectors for acid flotation of feldspar

The acid selective flotation of feldspar from quartz was utilized due to their differences in surface characteristics under highly acidic conditions(pH<2). The selection of flotation collectors is essential for beneficiation separation of quartz and feldspar. Mixed collectors have become increasingly popular owing to their excellent selectivity and recovery in separation flotation (Vidyadhar et al., 2002; Rao and Forssberg., 1997;Liu et al., 2020).

In the flotation process, different types of mixed cationic/anionic collectors are used for surface modification to adjust the surface properties of feldspar particles. Cationic collectors mainly include alkyl amine, alkyl ether amine, and alkylammonium. Anionic collectors mainly include fatty acids/salts and sulfonates. Sodium hexametaphosphate and water glass can be used as quartz depressing agents (Abaka-Wood et al., 2017; Chelgani et al., 2015; Kou et al., 2015; Tian et al., 2017; Guo et al., 2020). The cation/anion mixed collector has been recommended to the flotation separation of quartz and feldspar without fluorine, and has attracted great attention from many domestic and international researchers. A mixed of cationic diamine (tallow-1,3-propanediamine) and anionic alkyl aryl sulfonate collector and a combined cationic/anionic collector of diamine–dioleate (Duomeen TDO) were used through Hallimond flotation tests, and albite can be selectively floated from quartz at pH 2. An albite recovery exceeding 85% was achieved from a feed material containing about 50% albite (Vidyadhar and Rao., 2007). Especially, selection of cation in mixed reagents was much more important, which will directly affect the recovery of concentrate. Compared with dodecylamine system, both sodium oleate and sodium dodecylbenzene sulfonate have relatively high recovery beyond 80% under oleylamine system (Liu et al., 2013). Some collectors used for the acid flotation of feldspar from quartz are summarized in Table 3.

Mixed collectors for acid flotation of feldspar had been widely applied in practice. The quartz sand dressing plant in the Huangshan work area of Anhui province have applied H_2SO_4 as modifier, N-dodecyl 1, 3-propanediamine and petroleum sodium sulfonate as mixed collectors for flotation of feldspar from quartz, generating the final products with SiO_2 grade of beyond 99.50%, Fe_2O_3 grade 0.0030~0.010%. The obtained quartz product can be used as raw materials for optical glass, photovoltaic glass, information display glass, neutral medical glass and electronic grade silica powder according to the requirements of the market. The granitemine located in Hezhou City of Guangxi province, which used fatty amine and petroleum sodium sulfonate as mixed collectors for selective flotation of feldspar from quartz, obtaining the quartz product with SiO_2 grade 99.00%, which can be used as raw materials for automotive glass and electronicglass. The obtained feldspar product contained Fe_2O_3 grade 0.10%, K_2O grade 9.05% and Na_2O grade 2.88%, which can be used as raw materials for ceramic industry.

3.2. Interaction mechanism on the feldspar surfaces with mixed collectors

Advanced modern analysis and testing techniques, solution chemistry calculation, and density

Table 3. Collectors used for the acid flotation of feldspar from quartz

Cationic collector	Anion collector	Modifier	Studies	Reference
alkyl-l,3-propandiamine salts 2-propanol	Petroleum sulfonate	H_2SO_4	Flotation	(Shehu and Spaziani, 1999)
N-tallow-1,3-propanediamine–dioleate/Tallow-1,3-diaminopropane	Sodium oleate	H_2SO_4/NaOH	Flotation and Adsorption	(Vidyadhar etal., 2002)
AERO 3030C (amine acetate)	R801-R825（derivatives of petroleum）	H_2SO_4	Flotation	(Sekulić et al., 2004)
Tallow-1,3-diaminopropane	Sodium dodecyl sulfonate/sodium oleate	HCl/NaOH	Flotation and Adsorption	(Vidyadhar and Rao., 2007)
Dodecyl amine	Sodium dodecyl sulfonate	H_2SO_4/NaOH	Flotation and Adsorption	(Zhang et al., 2012)
N-dodecyl 1, 3-propanediamine	Sodium dodecyl sulfate	H_2SO_4	Flotation	(Wang et al., 2013)
oleylamine	Sodium oleate/sodium dodecylbenzene sulfonate	H_2SO_4	Flotation and Adsorption	(Liu et al., 2013)
Cutusamine 9007 (amine acetate)	E526 (petroleum sulfonate)	H_2SO_4	Flotation	(Gaied and Gallala, 2015)

functional theory (DFT) calculations have been introduced to investigate the synergistic adsorption mechanism of mixed collectors onto the mineral surfaces (Kubicki et al., 2012; Morgane and Gaigeot, 2016; Xu et al., 2014; Zhu et al., 2016; Zheng et al., 2018).

Electrostatic force and specific chemisorption play a crucial role on the adsorption of collectors on the feldspar surface (Wang et al., 2016). Mixed cationic-anionic collectors affect feldspar because of two main reasons. First, at pH 2, which is near the isoelectric point of quartz, the charge of feldspar surface is negative, while the quartz surface is neutral. Moreover, K^+ or Na^+ at the surface of feldspar is dissolved in the water solution, and leaving positive charge holes. The positively charged NH_3^+ head group of amine is bound to the negative areas of the feldspar surface via electrostatic attraction at first. Meanwhile, the oleate/sulfonate are not adsorbed on the quartz surface but are adsorbed on feldspar surface by the interaction between oppositely charged heads and hydrophobic association with amine (Vidyadhar and Rao, 2007; Wang et al., 2016, 2014). Second, the aluminum sites on the feldspar surface are amenable to complexation with adsorbing oleate molecules for specific chemisorption. Al sites exposed on the (001) surfaces of feldspar in aqueous solution can associate with the oleate/sulfonate for specific chemisorption (Rai et al.,2011; Xu et al., 2016a; Zhu et al., 2018). Moon and Fuerstenau (Moon and Fuerstenau, 2003) presented that oleate molecule is able to distinguish/discriminate (and thus recognize) the nature of different Al sites present on the two different crystal planes and between the nature of Al sites present on the cleavage planes of different silicate minerals. Moreover, Xu et al (Xu et al., 2016b)presented that NaOL prefers to bind in a monodentate chelating complex configuration to the most stable surface plane, the (110) plane, which has two broken Al-O bonds. The (110) plane of spodumene is more favorable for chemisorbing NaOL than the (001) plane, which has two broken Al-O bond. In other words, there are no Al atoms with broken bonds on the quartz surface, and the surface consists of Si and O atoms only. However, there are Al atoms with one broken bond on the feldspar (001) surface making it more favorable to oleate adsorption as compared to the quartz surface. What's more, the presence of sulfonate increases the adsorption of diamine due to a decrease in the adjacent surface alkyl ammonium electrostatic head-head repulsion(Vidyadhar and Rao., 2007). There for, the

mixed cationic-anionic collectors added to the pulp system are only weakly adsorbed on the quartz surface via electrostatic interaction, but they can be synergistically adsorbed on the feldspar surface by chemisorption and electrostatic interaction. The association of alkyl diamine and sulfonate is most preferred. And only when the amount of alkyl diamine dominates (larger than 50%), good collector adsorption with more ordered structures occurs at the feldspar surface (Vidyadhar and Rao, 2007; Shrimali et al., 2017; Tian et al., 2017; Xu et al., 2016a, 2017a).

Take dodecylamine (DDA) and sodium dodecylsulfate (SDS) as collectors, schematic illustration of the synergistic adsorption mechanism of mixed collectors onto the feldspar surfaces are given in Fig. 12.
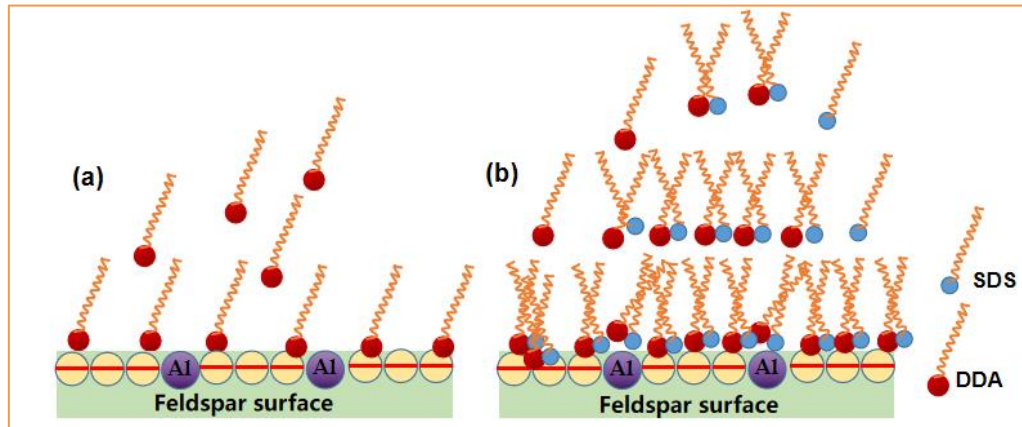

Fig. 12. schematic illustration of the synergistic adsorption mechanism of mixed collectors onto the feldspar surfaces

4. Mixed collectors for alkali flotation of quartz

4.1. Current research status and progress on mixed collectors for alkali flotation of feldspar

The alkali positive selective flotation of quartz from feldspar consists in adopting multivalent metallic ions as activators and anion collectors at high alkaline pH ranges (PH=11~12), in which quartz can be activated but feldspar can not respond to flotation with these reagent systems (Chakraborty et al., 2015; El-Salmawy et al., 1993; Malati and Estefan, 1967; Moudgil, 2005). The recovery of quartz sharply increase with the increasing of Ca^{2+} concentration under sodium oleate system, and the maximum flotation recovery of quartz was beyond 80% at pH=12 (Cong et al., 2018). Various multivalent metallic ions commonly used in the activation of quartz are summarized in Table 4.

Table 4. Various multivalent metal ions commonly used in in the activation of quartz

Metal ions category	Collector	Modifier	Reference
Ca^{2+}	Sodium oleate	HCl/NaOH	(Cong et al., 2018)
Al^{3+}	Sodium oleate	HCl/NaOH	(Zhang et al., 2018)
Fe^{3+}	Sodium oleate	HCl/NaOH citric acid	(Niu et al., 2019)
Ca^{2+}/Mg^{2+}	Dodecyl sulfobetaine	HCl/NaOH	(Hu et al., 2010)
$Ca^{2+}/Mg^{2+}/Fe^{3+}$ /$Fe^{2+}/Pb^{2+}/Cu^{2+}$	Butyl xanthate	HCl/NaOH	(Qin et al., 2017)
$Ca^{2+}/Mg^{2+}/Ba^{2+}/Sr^{2+}$	Sodium dodecylsulfate	1-Dodecanol HCl/NaOH	(El-Salmawy et al., 1993)

4.2. Interaction mechanism on the quartz surfaces with mixed collectors

Recently, several studies have been conducted that the formation of the hydroxy complexes was the main activation factor for quartz flotation(El-Salmawy et al., 1993; Ozkan, et al., 2009; Hu et al., 2010).

Quartz exhibits poor floatability over the whole pH range in the presence of oleate, probably owing to the lack of reactive sites to interact with the collector. (Fig.13) (Wang et al., 2018; Feng et al., 2018a; Li et al., 2017; Luo et al., 2020). The previous study has shown that a large amount of water was adsorbed on quartz in an orderly manner, but without oleate molecules (Li et al., 2017).

Multivalent metal ions may exhibit various forms of hydroxy complexes under different pH regions in aqueous solutions and the existing form of metal ions could influence the mineral flotation behavior (Fig. 15) (Feng et al., 2018; Wang et al., 2018; Zhang et al., 2014; Qin et al., 2017). Recently, the adsorption model and mechanism of calcium ion activated on quartz (101) surface in aqueous have been investigated by DFT method. The primary hydrated complex of $[Ca(H_2O)_4]$ (II) and $[Ca(OH)(H_2O)_3]$(I)
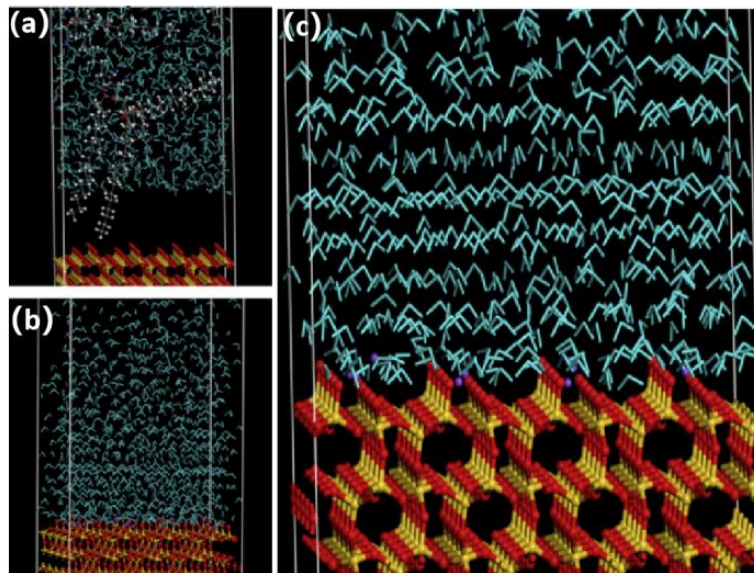
Fig. 13. Models of quartz-reagent complex (a) before and (b) after oleate adsorption. (c) details of oleate solutions on quartz surface (Li et al., 2017)
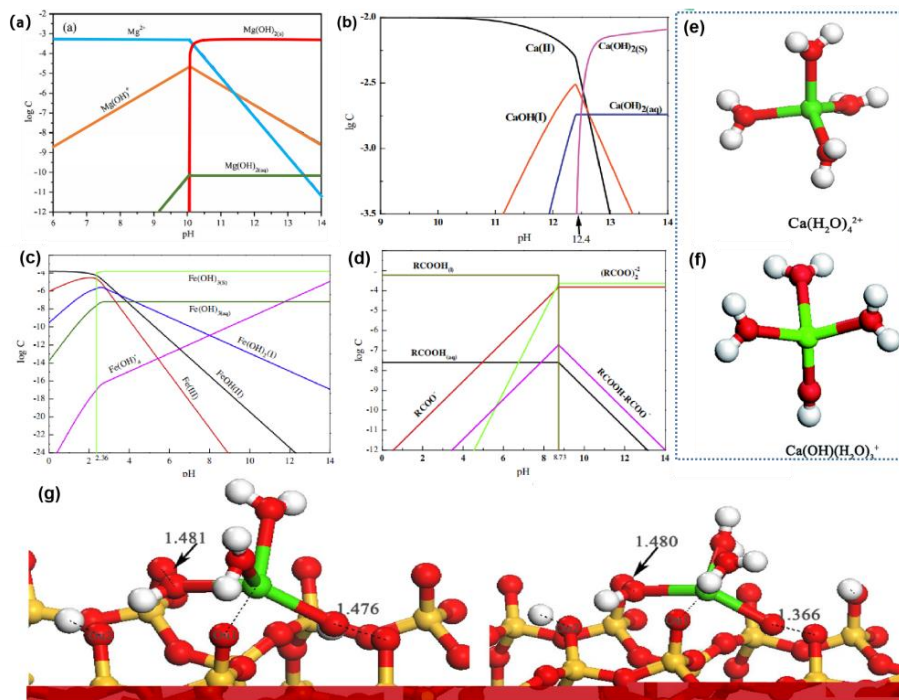
Fig. 15. Distribution of (a) magnesium($5×10^{-4}$ mol/L) ,(b) calcium($1.0×10^{-2}$ mol/L), (c)iron($1.5×10^{-4}$ mol/L), (d)NaOL ($6×10^{-4}$ mol/L) as a function of pH . equilibrium geometries of hydration structures of calcium^{2+} (e) and $Ca(OH)^+$ (f), optimized structures of configurations of $[Ca(OH)(H_2O)_3]^+$complex on quartz (101) surface. (Atom of Ca and H are shown in green and white, respectively) (Feng et al., 2018; Wang et al., 2018; Zhang et al., 2014)

were determined as the activation components (Fig. 15e,f). The calcium ion activation on the quartz surface were closely related to the formation of Ca-O (calcium ion in aqueous and O atom on quartz surface) bond and hydration process of quartz surface. In addition, the hollow site of the same Si center and the top sites of O atoms have been determined to be the major adsorption sites(Fig. 15g)(Wang et al., 2018). Previous studies also demonstrated that multivalent metal ions with a high valence state and small radius were adsorbed on quartz surfaces mainly in the form of hydroxide precipitates species (Me(OH)n) in the pulp solution. However, multivalent metal ions with low valence state and large radius are adsorbed mainly in the form of hydroxo complexes (Me(OH)$^+$) (Demira et al., 2003; Ejtemaei et al., 2012; Gülgönül et al., 2012; Hu et al., 2010; Peretti et al., 2012).

The selective separation of quartz may be closely related to the ability of forming neutral complexes, which co-adsorb with collectors on the quartz surface and stimulate the formation of hemimicelle (El-Salmawy et al., 1993; Malati and Estefan, 1967). Current researchers consider that these neutral complexes play a regulatory role in promoting the formation of hemimicelle on the quartz surface. The neutral complexes not only change the hydrophilicity of quartz surfaces but also provide active sites for the chemical adsorption of sodium oleate (Fig. 16) (Filippov et al., 2012; Zajac et al., 1997; Feng et al., 2018; Wang et al., 2019).
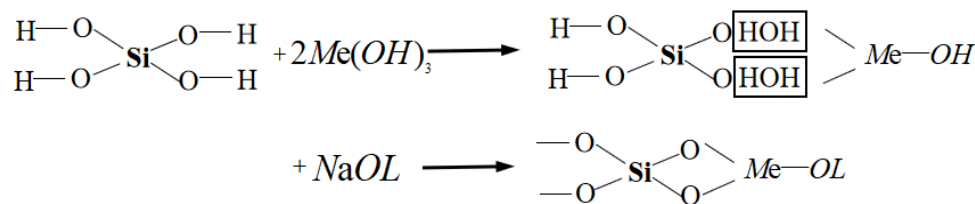

Fig. 16. Schematic of the combination of alkali metal ions with a quartz surface and NaOL

El-Salmawy et al (El-Salmawy et al., 1993) insisted that the floatation separation of quartz from feldspar by using metal ions as activators under high alkaline condition was attribute to the formation of different hydrated layer structure on the surface of quartz and feldspar. The surface of feldspar was exhausted in silica and enriched in alkali ions under high alkaline condition. The lower adsorption density of Ca^{2+} on feldspar surface in comparison to that of quartz owing to the composition of hydrated layer structure. Movable cations, such as aluminum and potassium on the feldspar surface, may exchange and compete with Ca^{2+} cations, which affects the formation of neutral complexes on the surface at high alkaline conditions. However, quartz is a three-dimensinal framework silicate does not exist in any exchangeable constituent (Liu et al., 2019; Wang et al., 2019).

5.   Mixed collectors for neutral flotation of feldspar

5.1. Current research status and progress on mixed collectors for neutral flotation of feldspar

The neutral flotation of feldspar consists in the separation of feldspar from quartz at pH 6–7. Few studies have been published on the selective flotation separation of feldspar from quartz in neutral media (Table 5).

Table 5. Mixed collectors for quartz-feldspar flotation

Cationic collector	Anion collector	Non-ion collector	Activator/Inhibitor Modifier	Reference
Ether amine	/	/	Aluminum salt and sodium silicate	(Mao et al.,1986)
Diamine	Sodium oleate	/	/	(Zheng et al., 2015)
C8, C10, C12, C14, and C16 alkyl amines	/	Alcohols	/	(Vidyadhar e tal., 2002; Vidyadhar et al., 2003)

Although the indexes of feldspar and quartz products under neutral condition were slightly worse than those acidic conditions, the neutral flotation method has also adopted by many mineral processing enterprises owing to environmental protection issues. At present, the quartz sand dressing plant in the Tongliao work area of Inner Mongolia has applied fatty amine and petroleum sulfonate as mixed collectors for flotation of feldspar from quartz at pH 6–7, generating feldspar product with Fe_2O_3 grade 0.15% , K_2O grade 9.48%, which can be used as raw materials for ceramic industry. The quartz product obtained contains SiO_2 grade 98.50%, Fe_2O_3 grade 0.078%, which can be used as raw materials for float glass.

5.2 Interaction mechanism on the feldspar surfaces with mixed collectors

Although the surfaces of feldspar and quartz are negatively charged overall, they also contain local area that was positively charged, where the anionic collector acts on the mineral surface via electrostatic interactions to form a certain adsorption area under the action of molecular forces and hydrogen bond association. However, the local positively charged physical adsorption is reversible, leading to the low strength and reversibility of adsorption of anionic collectors on quartz surfaces. Nevertheless, Al sites exposed on the (001) and (110) surfaces of feldspar in aqueous solution can associate with the anionic collectors for specific chemisorption. Future research should focus on identifying or developing inhibitors that can effectively prevent amine cationic collectors from adsorbing on the quartz surface while exerting having small effects on the feldspar surface (Dai et al., 1996; Zheng et al., 2015; Vidyadhar et al., 2002; Vidyadhar et al., 2003).

6. Conclusion and future perspectives

With the rapid depletion of high-quality quartz and feldspar mineral resources, the production of high-grade quartz and feldspar from those resources will be lower in the future. Equal attention should be paid to the comprehensive utilization and clean production of quartz and feldspar. Research should be conducted on the rational allocation and cascade utilization of resources to produce high-grade products while considering the comprehensive utilization of the by-products, using tailings processing to produce high valued products.

The flotation separation of feldspar and quartz has been successfully applied for industrial production by using N-dodecyl 1,3-propanediamine and petroleum sodium sulfonate as collectors and H_2SO_4 as modifier in acid media. The obtained quartz concentrates can satisfy the requirements of optical glasses, photovoltaic glasses and high-grade electronic-grade silica powder, and the feldspar concentrates can be used as high-grade ceramic glaze. However, this processing method involves additional costs associated with the treatment of wastewater, which can only partly be reduced by recycling. Therefore, focus should be put in the development of amphoteric collectors with lower critical micelle concentration (CMC), low cost, and high degradability. Furthermore, attempts should be made to improve the quartz and feldspar medium flotation with environmentally friendly collectors and without acid or alkaline chemicals.

The separation of quartz and feldspar is a difficult process and worldwide issue. Most researchers have attempted to elucidate the mechanism underlying the flotation separation of feldspar from quartz and other minerals. Research should be conducted on the identification of minerals and occurrence of impurity minerals, which was an essential prerequisite to improve selectivity and recovery of target mineral in separation processing. In addtion, the foundation theories should be strengthen by cutting-edge testing and analysis techniques based on the solution chemistry calculations and molecular simulations. The relationship between genesis and the separability of mineral should be established. Furthermore, new collectors suitable for materials with different crystal structures and surfaces properties should be designed and developed.

Acknowledgments

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