Physicochem. Probl. Miner. Process., 54(3), 2018, 992-1003

http://www.journalssystem.com/ppmp

Physicochemical Problems of Mineral Processing

ISSN 1643-1049

Received: November 11, 2017; reviewed; accepted: March 27, 2018

Flotation behavior and separation mechanism of quartz and iron minerals in α-bromolauric acid reverse flotation system

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Abstract: A new type collector α-Bromolauric acid (α-BLA) had been proved to be an efficient collector for quartz flotation. However, the effects of α-BLA on the flotation behavior of iron minerals and quartz-iron separation had not been investigated. In this study, collector α-BLA was synthesized in the laboratory. The flotation behavior of quartz, hematite and magnetite under α-BLA reverse flotation system were investigated and the separation mechanism of quartz-irons was studied by contact angle, zeta-potential and infrared spectroscopy. The results showed that the optimum flotation pH was 11.5 for quartz, 6.45 for hematite and 6.97 for magnetite. The best α-BLA concentrations was 75 mg/dm^3 for quartz flotation, 125 mg/dm^3 for hematite and magnetite flotation. The activator $CaCl_2$ had little effect on the flotation of hematite and magnetite, but the minimum dosage 50 mg/dm^3 of activator $CaCl_2$ was necessary for quartz flotation. On the contrary, starch had no effect on the flotation of quartz, while the recoveries of magnetite and hematite tended to be 0% as starch concentration more than 80 mg/dm^3. The separation mechanism of quartz from iron minerals under α-BLA reverse flotation system was that the starch could be selectively adsorbed on the surface of hematite and magnetite in the form of strong hydrogen bond adsorption. However, the same adsorption of starch did not occur on the surface of quartz, so the α-BLA can be successfully adsorbed on the surface of activated quartz to make the quartz strongly hydrophobic, and then to be floated out.

Keywords: quartz, iron minerals, separation, reverse flotation, α-Bromolauric acid

1. Introduction

Iron is one of the most common elements in earth's crust. The primary industrial types of iron-bearing minerals include magnetite [Fe_3O_4], hematite [Fe_2O_3], goethite [FeO(OH)], limonite [$FeO(OH)\times nH_2O$] and siderite [$FeCO_3$]. These iron minerals mainly come from metamorphic sedimentary iron deposits (Filippov et al., 2014). The share of metamorphic sedimentary iron ores compared to the overall commercial ore production exceeds 74% (Filippov et al., 2014). The Kursk Magnetic Anomaly in Russia, the Hamersley iron province in Australia, the Quadrilátero Ferrífero region in Brazil, the Anshan area in China, the province of Labrador in Canada, the Krivoy Rog basin in Ukraine, the Lake Superior district in the USA and the Singhbhum-North Orissa region in India are among the largest of these types of rock formations (Ma, 2012; Severov et al., 2016). In China, there are more than 11 billion tons metamorphic sedimentary iron ores, accounting for about 50% of the total reserves of iron ore, known as the Anshan iron ore. The main iron minerals of which are magnetite and hematite. Gangue minerals are large amounts of quartz and a small amount of silicate minerals such as feldspar, mica, pyroxene.

In the recent years, the demand for high-quality iron concentrate in the iron and steel industries has increased significantly (Das et al., 2010). However, Major global reserves of iron ores are associated with formations of magnetite-hematite ores of metamorphic sedimentary iron ores (Houot, 1983; Routhier, 1963). Removing quartz from iron ores is of great importance because it represents one of the most common gangue minerals in magnetite-hematite ores (Houot, 1983; Birinci et al., 2010). The effective

DOI: 10.5277/ppmp18101

technologies for the beneficiation of these type iron ores are wet magnetic separation in low intensity magnetic field and reverse flotation of quartz. When dealing with the iron ore from a South African mine with a grade of 30.19% Fe and 41.25% SiO_2, the magnetic separation process could generate only a blast furnace grade pellet feed with the Fe grade <65% and SiO_2 content >6%. However, a iron concentrate with a grade of >69% Fe and SiO_2 content <2% could be obtained by reverse flotation. The result shown that the reverse flotation process could be used as a final cleaning stage to improve the quality of iron concentrate (Frommer, 1967; Bada et al., 2012).

Reverse anion flotation is widely used flotation route in the iron ore industry to obtain high-grade iron concentrate with low silica content (Houot, 1983; Frommer,1964; Sahoo et al., 2016). Some researches (Ma et al.,2011, Lu et al.,2017) had revealed that the major advantage of reverse anionic flotation over reverse cationic flotation was found to be its excellent capability to selectively separate ultrafine particles of quartz and hematite. Uwadiale et al. (1995) used reverse anionic flotation to recover iron from low-grade (31.6% Fe) Muro iron ore. A concentrate with a grade of 70.4% Fe and a recovery of 92.7% Fe was obtained and the result of investigation also revealed that a calcium ion concentration of 50 to 100 ppm was optimum. Based on the flotation research of pure hematite, siderite, and quartz in the oleate-starch-$CaCl_2$ system, a two-step reverse anion flotation process was proved to be very effective by Yin et al. (2010) for the separation of iron concentrate from Donganshan carbonaceous iron ore. For reverse anion flotation of quartz from iron ores, reagents NaOH, corn starch, $CaO/CaCl_2$ and anionic fatty acids are used as pH adjuster, depressant, activator, and collector, respectively (Ma et al., 2011; Houot, 1983; Frommer, 1967;). Activation of quartz with Ca or Mg ions prior to anionic flotation was shown by researches from 1960 to 1980 to be very effective. Ca activation requires the high and not environmentally friendly flotation pH about 12. The research of Sandvik et al. (2014) revealed that Mg ions activation was environmentally friendly because a substantially lower flotation pH of 10.5 was enough, with the magnesium chloride, sodium hydroxide, dextrin, oleic acid used as the activator, pH adjuster, depressant, collector, respectively. During the reverse anionic flotation process, quartz particles attach to air bubbles and float upward into the froth layer leaving iron minerals as sink fraction (Frommer,1964; Birinci et al., 2010).

Currently, new type collectors α-Bromodecanoic acid ($CH_3(CH_2)_7CHBrCOOH$, α-BDA) (Luo et al., 2015) and α-Bromolauric acid ($CH_3(CH_2)_9CHBrCOOH$, α-BLA) (Zhu et al., 2015) were synthesized by solvent-free method (Hell-Volhard-Zelinski reaction). The collectors α-BLA and a-BDA proved to have a good flotation performance at a relatively low temperature of 16 ℃and the adsorption mechanism on quartz surface was established (Zhu et al.,2016). However, the effects of α-BLA and a-BDA on the flotation behavior of iron minerals had not been investigated, as well as the mechanism of separating quartz from quartz-iron system.

In this work, the new type collector α-BLA was synthesized in the laboratory. The effects of different flotation conditions on the flotation behavior of quartz, hematite and magnetite under reverse anion flotation system were investigated by pure minerals flotation tests with the new type collector α-BLA. The separation mechanism of quartz from hematite and magnetite was studied by contact angle, zeta-potential and infrared spectroscopy.

2. Materials and methods

2.1 Minerals

The pure samples of quartz, hematite and magnetite used in this study were all obtained from Sijiaying iron mine, Hebei Province, China. All the samples were carefully hand-picked, crushed with hammer, grinded in a laboratory ball mill and subsequently wet-sieved to obtain the -0.045 mm size fractions. The quartz sample was further purified by digestion in dilute hydrochloric acid and repeated washing with distilled water. Wet low intensity magnetic separator (XCRS-Φ400×240, Wuhan prospecting Machinery Factory) was firstly applied to remove gangue minerals with greater magnetic susceptibility than hematite and then magnetic field was adjusted to separate hematite from the low magnetic gangue minerals. The magnetite sample was purified by wet magnetic separation in low intensity magnetic field. The chemical compositions and X-ray diffraction (XRD) analyses of the obtained quartz hematite and magnetite samples were presented in Table 1 and Fig. 1.

The results of chemical composition analysis showed that the quartz sample consisted of 99.20% (wt.%) SiO_2 and the purity of hematite and magnetite were both more than 96%. XRD data confirmed that there were no obvious impurities in the samples of quartz, hematite and magnetite. which meet the desirable requirement of purity for the experiments.

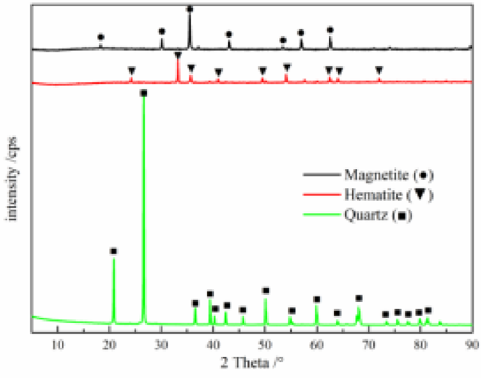

Fig. 1. X-ray diffraction patterns of quartz, hematite and magnetite

Table 1. Chemical composition of the single quartz, hematite and magnetite (wt.%)

Minerals	Fe	FeO	SiO_2	Al_2O_3	CaO	MgO	Purity
Quartz	<0.01	<0.01	99.20	0.67	<0.01	<0.01	99.20
Hematite	67.70	0.25	1.11	0.13	0.01	0.12	96.71
Magnetite	69.77	29.99	0.75	0.08	0.02	0.16	96.63

2.2 Reagents

A product α-Bromolauric acid ($CH_3(CH_2)_9CHBrCOOH$, α-BLA) with purity of 83.78% synthesized in laboratory by solventfree method (Hell–Volhard–Zelinski reaction) (Ogataet al., 1979; Carey, 2008; Zhu et al., 2015;) was used as flotation collector after saponified with 20% NaOH solution at a mass ratio of 1: 1. The element analysis result of synthesizing α-Bromolauric acid was showed in Table 2. Corn starch provided by Anqian iron mine, Liaoning Province, China, was hydrolyzed by 20% NaOH solution, which was used as flotation depressant of hematite and magnetite. Analytical purity of calcium chloride ($CaCl_2$) was used as the activator of quartz supplied by Tianjin Kemiou Chemical Reagent Co., Ltd., China. Solutions of HCl and NaOH 0.10 mol/dm^3 were used to adjust the pH value of the system. Distilled water was used in all tests.

Table 2. Element analysis result of synthesizing α-Bromolauric acid (wt.%)

C	H	Br	O	Purity
54.27	9.13	24.33	12.27	83.78

2.3 Flotation tests

The micro-flotation tests were conducted in a 50 cm^3 flotation cell of a XFGII50 laboratory flotation machine (Liu et al., 2010). Taking 5 g single mineral sample (quartz, hematite or magnetite) in the flotation cell with ultra-pure water filled. The pulp was stirred for 3 min at a rotating speed of 1992 rpm, then the pH regulator (HCl or NaOH solution), activator $CaCl_2$, depressant starch and collector α-BLA were added into the cell every 3 min continually, and the flotation was conducted for 4 min. Finally, the froth products and tailings were weighed respectively after drying, and the recovery was calculated based on the weight of the products.

2.4 Contact angle measurements

Hand-picked pure mineral samples (quartz, hematite or magnetite) were polished and cut to a proper size approximately 2×1.5×1 cm. The cleaned sample pieces were immersed in 80 mg/dm^3 starch solutions or 75 mg/dm^3 α-BLA solution (quartz sample piece activated by 50 mg/dm^3 $CaCl_2$), respectively, with the suitable pulp pH of 11.5 for quartz, 6.45 for hematite and 6.97 for magnetite and then air-dried at ambient temperature for 24 h before contact angle measurements (Zhu et al., 2015). A contact angle device XG-CAMB was used to measure the contact angle of the samples with the free sessile drop method. In this method, a stable water drop of 3-4 mm diameter was slowly transferred to the mineral surface using a microsyringe to measure the contact angle value. Each sample was measured three times at different sample locations and averaged with an accuracy of ± 2°.

2.5 Zeta potential measurements

Zeta potentials were measured by Malvern Instruments Nano-ZS90 zeta potential analyzer. Before the measurement, samples (quartz, hematite or magnetite) was further ground to below 0.005 mm and configured as a 0.06 wt.% suspension. The zeta potentials of samples surface were measured in the presence of depressant starch and collector α-BLA (quartz activited by $CaCl_2$), respectively, or just in water at a constant temperature of 25 °C. After agitated for 10 min with a magnetic stirrer, 0.10 mol/dm^3 HCl or 0.10 mol/dm^3 NaOH was used to regulate the pulp pH. Each measurement was repeated for three times and the average was taken.

2.6 Fourier transform infrared spectroscopy

Before measuring infrared spectrum of minerals acted with agents, the minerals (quartz, hematite or magnetite) used for this purpose were ground to -0.002 mm in an agate mortar. 5 g of quartz, hematite or magnetite was added to 50 cm^3 aqueous solution with 80 mg/dm^3 depressant starch and then treated with 125 mg/dm^3 collector α-BLA (quartz was activated by 50 mg/dm^3 $CaCl_2$ first) at pH 11.50, 25 °C. After being stirred for 0.5 h, the pulp was filtered, washed with distilled water for three times, and dried in a vacuum oven at 50 °C. The analyses were carried out by Nicolet 380 FT-IR spectrometer with a thin slice pressed by a mixtrue fo 1 mg sample and 100 mg KBr.

3 Results and discussion

3.1 Micro-flotation tests

Flotation recoveries of quartz activated by 100 mg/dm^3 $CaCl_2$, unactivated quartz, hematite and magnetite as a function of pH were presented in Fig. 4. The results showed that the recovery of unactivated quartz was tend to 0% in the whole pH range of 2-13. For activated quartz, when the pH of the pulp was less than 8, it had no effect on the flotation recovery, and the optimum flotation pH was 11.5 with an excellent flotation recovery of 98.35%. The suitable flotation pH of magnetite and hematite was in range of 4 to 8. However, the natural pulp pH of magnetite and hematite were 6.97 and 6.45, respectively, therefore, the optimum flotation pH value of magnetite and hematite were the natural pulp pH.

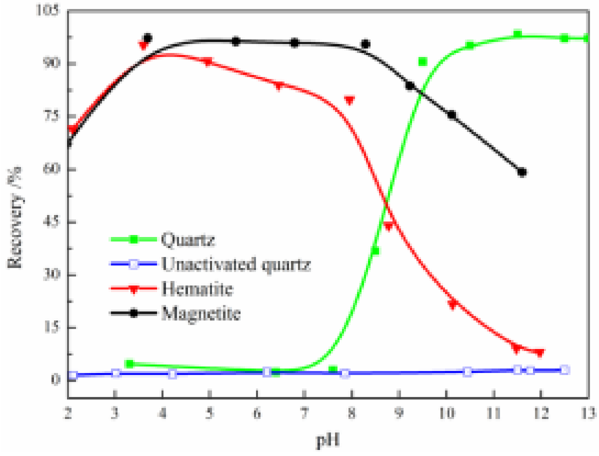

Fig. 4. Flotation recoveries of quartz activated by 100 mg/dm^3, inactivated quartz, hematite and magnetite as a function of pH with collector α-BLA concentration of 100 mg/dm^3, at 25 ℃

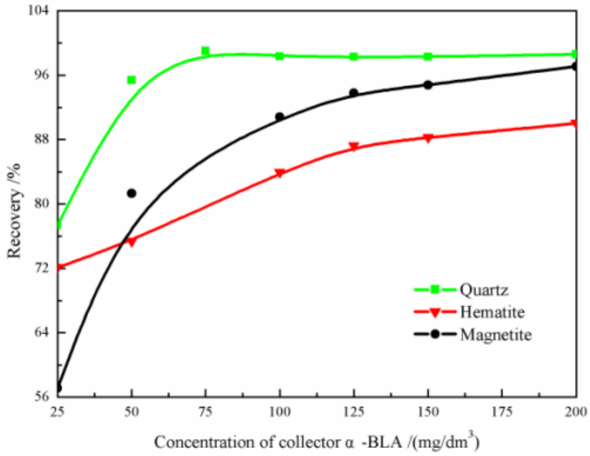

Fig. 5. Flotation recoveries as a function of α-BLA concentration. The pulp pH was 11.5 for quartz (activated by 100 mg/dm³ $CaCl_2$), 6.45 for hematite and 6.97 for magnetite, at 25 ℃

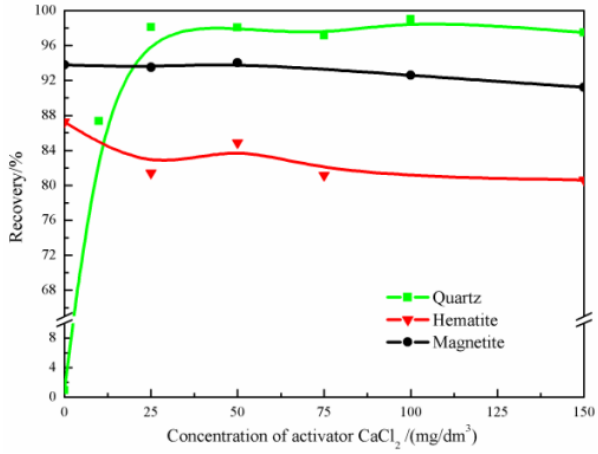

Fig. 6. Flotation recoveries as a function of $CaCl_2$ concentration, at 25 ℃. (Quartz flotation: α-BLA 75 mg/dm³, pulp pH=11.5. Hematite flotation: α-BLA 125 mg/dm³, pulp pH=6.45. Magnetite flotation: α-BLA 125 mg/dm³, pulp pH =6.97)

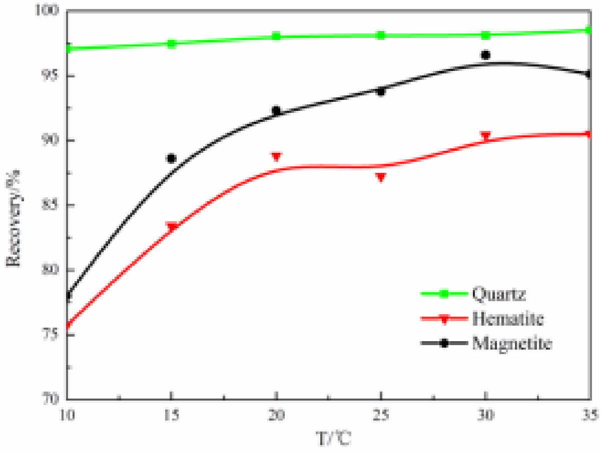

Fig. 7. Flotation recoveries as a function of pulp temperature. (Quartz flotation: $CaCl_2$ 50 mg/dm³, α-BLA 75 mg/dm³, pulp pH=11.5. Hematite flotation: α-BLA 125 mg/dm³, pulp pH=6.45. Magnetite flotation: α-BLA 125 mg/dm³, pulp pH =6.97)

Fig. 5 showed the recoveries of quartz, hematite and magnetite as a function of concentration of collector α-BLA, at their respective optimum flotation pH values (11.5, 6.45 and 6.97) and flotation temperature at 25 ℃. The results showed that the effect of collector α-BLA on the flotation of three minerals was similar. With the concentration of collector α-BLA increasing, the flotation recoveries significantly increased first and then started to stabilize or increase slowly at a certain value. The best collector α-BLA concentrations of magnetite, hematite and quartz flotation were 125 mg/dm^3, 125 mg/dm^3 and 75 mg/dm^3, respectively, and the corresponding flotation recoveries were 93.78%, 87.25% and 99.00%.

As shown in Fig. 6, the effect of activator $CaCl_2$ on the flotation of quartz, hematite and magnetite was investigated. The results showed that $CaCl_2$ had little effect on the flotation of magnetite and hematite, but it had a significant effect on the flotation behavior of quartz. For quartz flotation, the recovery rapidly increased from 3.00% to 98.12% with the increase of the $CaCl_2$ concentration from 0 mg/dm^3 to 50 mg/dm^3. When the concentration of $CaCl_2$ exceeded 50 mg/dm^3, quartz flotation recovery was almost no longer changing. Therefore, a concentration of $CaCl_2$ about 50 mg/dm^3 was appropriate for collector α-BLA to float quartz.

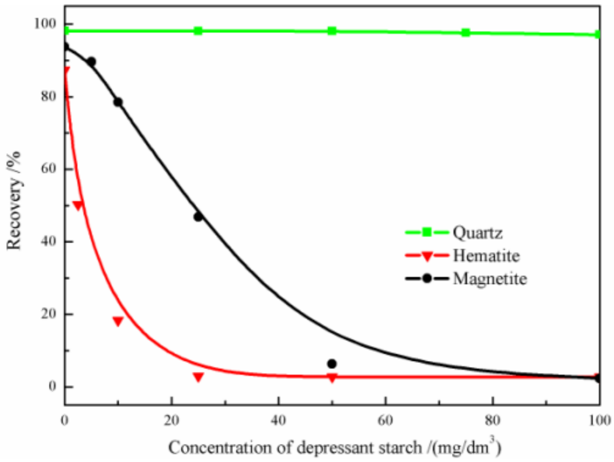

Fig. 8. Flotation recoveries as a function of starch concentration, at 25 ℃. (Quartz flotation: $CaCl_2$ 50 mg/dm^3, α-BLA 75 mg/dm^3, pH=11.5. Hematite flotation: α-BLA 125 mg/dm^3, pH=6.45. Magnetite flotation: α-BLA 125 mg/dm^3, pH =6.97)

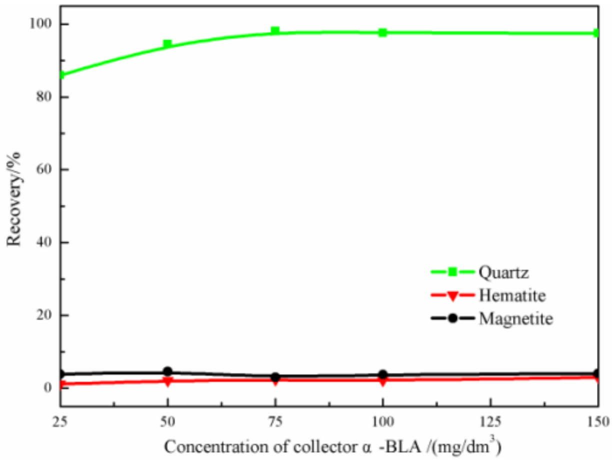

Fig. 9 Floatability difference of the three pure minerals with different α-BLA concentration in reverse anion flotation system. (50 mg/dm^3 $CaCl_2$ as the activator, 80 mg/dm^3 starch as the depressant and pulp pH=11.50, at 25 ℃)

Fig. 7 showed the effect of flotation temperature on the flotation behavior of quartz (activated by 50 mg/dm^3 $CaCl_2$), hematite and magnetite at their respective optimum flotation pH and collector α-BLA dosage. As the pulp temperature rising, the flotation recoveries of magnetite and hematite increased, which relatively stabilized until the temperature higher than 20 ℃. However, the temperature of the pulp had little effect on the flotation behavior of quartz. In the temperature range from 10 ℃ to 35 ℃, the flotation recovery of quartz was about 98%, which indicated that a high pulp temperature is not much helpful for the reverse flotation of quartz with α-BLA as the collector, and a room temperature between 20 ℃ to 25 ℃ was enough.

The effect of depressant starch on the flotation behavior of quartz, hematite and magnetite was presented in Fig. 8. The flotation results showed that the starch had little effect on the flotation behavior of quartz, but which could effectively inhibit the flotation of magnetite and hematite. When the concentration of starch was more than 80 mg/dm^3, the magnetite and hematite could be completely inhibited at the bottom of the flotation cell resulting in the recoveries tend to be 0%.

The results of micro-flotation conditions tests revealed that activator $CaCl_2$ only affected the flotation of quartz. In contrast, starch only had a great influence on the flotation of hematite and magnetite. In this work, the flotation behavior differences of the three minerals under different concentration of collector α-BLA was investigated in reverse anion flotation system with the conditions of pH=11.50, 50 mg/dm^3 $CaCl_2$ as the activator, 80 mg/dm^3 starch as the depressant and flotation temperature at 25 ℃. As the results showed in Fig. 9, the flotation recovery of quartz was almost 100%，under the proper reverse anion flotation system, at the same time, magnetite and hematite were completely inhibited.

3.2 Contact angle analyses

The adhesion energy (W_{sl}) indicates the density of the unsaturated bond on the mineral surfaces and the reactivity of mineral surfaces with water molecules. A larger W_{sl} value means that the mineral surface is more hydrophilic. Adhesive work can be calculated by the contact angle between water and the surface of the mineral. The adhesion energy of mineral surface is calculated by the following equation (Sotiropoulou and Nikolopoulos, 1993; Mohammadi-Jam et al., 2014):

$$W_{sl} = \gamma_L \times (1+\cos\theta) \tag{1}$$

where W_{sl} is the adhesion energy (J/m^2) of mineral surface, θ is the contact angle (°) of water on mineral surface. The γ_L is the surface tension parameter of the water, which value is 7.2×10^{-2} J/m^2 at 25 ℃.

Table 3. The contact angle and adhesion energy between water and mineral

Minerals	Samples to be tested	Contact angle/°	Adhesive work /1.0×10^{-3} J/m^2
Quartz	Quartz	24	137.8
	Quartz with starch	23	138.3
	Activated quartz with α-BLA	89	73.3
Hematite	Hematite	38	128.7
	Hematite with starch	20	139.7
	Hematite with α-BLA	125	30.7
Magnetite	Magnetite	34	131.7
	Magnetite with starch	24	137.8
	Magnetite with α-BLA	129	26.7

The adhesion energy based on the contact angle was calculated. The results were presented in Table 3. As it could be observed, quartz, hematite and magnetite had a great adhesion energy, with natural hydrophilic. After interacted with the depressant starch, the adhesion energy of hematite and magnetite increased by 11.0×10^{-3} J/m^2 and 6.1×10^{-3} J/m^2, respectively, while the adhesion energy of quartz did not change. Indicating that the hydrophobicity of hematite and magnetite were increased, but had no significant changes for quartz, which mean starch might be adsorbed on the surface of the hematite and magnetite but not on the quartz surface. When treated with collector α-BLA, the adhesion energy of the three minerals decreased significantly, indicating that the collector α-BLA could adsorb on the surface of all the three minerals to reduce the hydrophilicity of their surface. However due to the addition of starch, α-BLA did not adsorb in the hematite and magnetite surface. These results were in agreement with the results of flotation experiments in Fig. 5 and Fig. 8.

3.3 Zeta potential analyses

The contact angle analysis could reflect the effects of the reagents on the wettability of minerals surface, but there was no intuitive representation of whether the reagents could adsorb on the minerals surface. In this study, the zeta potential for quartz, hematite and magnetite as a function of pH were measured to reveal the changes in zeta potential of minerals surface, owing to the adsorption of the reagents.

The zeta potential data of quartz in Fig. 10a indicated that the quartz surface was negative within the pH range from 2 to 14. As the pH value of the pulp raised, the concentration of OH^- ions in the solution increased and more OH^- ions were adsorbed onto the double layer of quartz's surface leading to the compression of the double layer (Forbes et al., 2011). As a result, the zeta potential decreased. After interacting with depressant starch (Fig. 10b), the changes in zeta potential of quartz surface were not obvious, indicating that the starch did not adsorb on the quartz surface. This was also in agreement with the conclusion obtained from contact angle analyses (in Table 3).

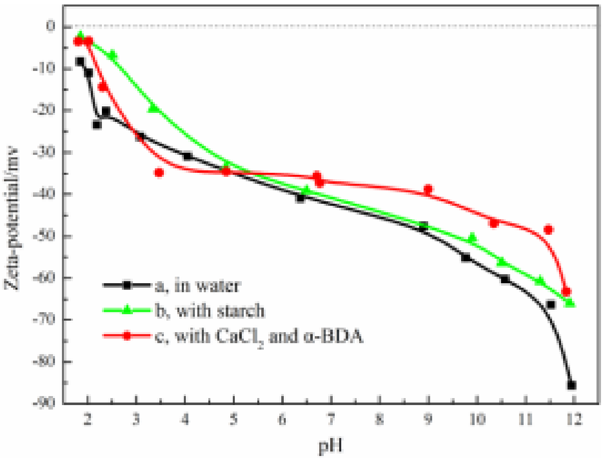

Fig. 10. Zeta potentials of quartz as a function of pH in the absence (a), or presence of 80 mg/dm^3 depressant starch (b), and 75 mg/dm^3 collector α-BLA (c)

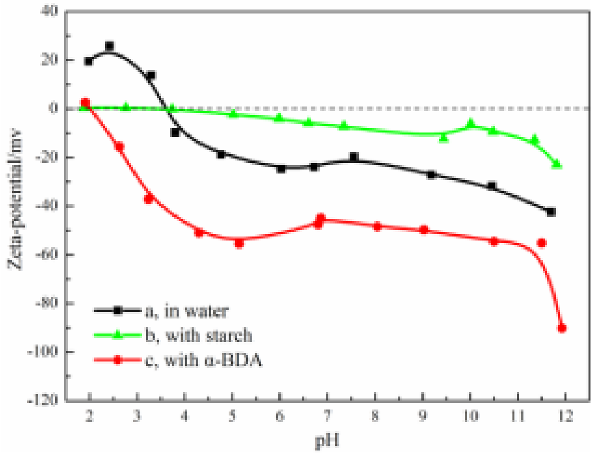

Fig. 11. Zeta potentials of hematite as a function of pH in the absence (a), or presence of 80 mg/dm^3 depressant starch (b), and 75 mg/dm^3 collector α-BLA (c)

The zeta potential curve (Fig. 10c) of quartz treated with $CaCl_2$ and collector α-BLA shifted to less negative values in a range of pH 7-12, compared to the curve of Fig. 10a. It was due to collector α-BLA anions $RBrCOO^-$ and $(RBrCOO^-)_2$ accounted for the majority (Liu et al., 2015), when the pulp pH value was higher than 7, which overcame the electrostatic repulsion with the negative activated quartz surface and adsorbed on the calcium ions active sites in the form of bond adsorption, resulting in zeta potential changed. This observation indicated that collector α-BLA could adsorbed onto the surface of activated quartz under alkaline conditions.

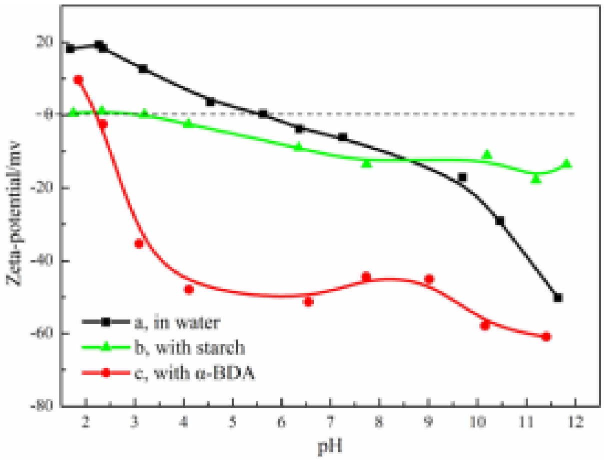

Fig. 12. Zeta potentials of magnetite as a function of pH in the absence (a), or presence of 80 mg/dm³ depressant starch (b), and 75 mg/dm³ collector α-BLA (c)

Fig. 11a and Fig. 12a showed the zeta potential curves for hematite and magnetite, respectively. The point of zero charge (PZC) for the mineral samples correspond to pH values of approximately 3.6 for hematite and 5.8 for magnetite, which was in agreement with the values reported in the literature (Mesquita et al., 2003). After interacted with the starch (Fig. 11b and Fig. 12b), similar changes were observed in the surface properties of both minerals. The PZC for the two minerals disappeared in the whole pH range 1-12, and the zeta potential of both samples kept electrically neutral in a short range of pH 1-4, while the zeta potential shifted to weakly negative electronegativity as the pulp pH> 4. The adsorption of starch on hematite and magnetite samples would be a result of hydrogen or chemical bonding interaction, since there is no electrostatic interaction between the electrically neutral starch molecules and the charged mineral surface.

After conditioned with the collector α-BLA as shown in Fig. 11c and Fig. 12c, there was a displacement in the pH values corresponding to the PZC, shifting from 3.6 to 2.0 in the case of hematite, and from about 5.8 to 2.2 in the case of magnetite, and in the whole pH range from 1.0 to 12， the zeta potential values was decreased compared to which of the hematite and magnetite untreated with any reagents. This indicated that specific adsorption of collector α-BLA onto the surface of hematite and magnetite were prevalent at all pH conditions. The mechanism for collector α-BLA adsorption onto the surface of hematite and magnetite surfaces could be described as chemisorption, when the pulp pH higher than the PZCs (3.6 for hematite and 5.8 for magnetite), because electrostatic repulsion would be expected between the anionic collector ions and the negative mineral surface. Therefore, a strong force of chemisorption should exist to overcome the electrostatic repulsion to make the adsorption occur.

3.4 Infrared spectra analyses

The characteristic absorption peaks of the infrared spectra can be used to analyze the adsorption mechanisms between flotation reagents and the mineral surface (Lima et al., 2005). The FT-IR spectras of quartz, hematite and magnetite conditioned with 80 mg/dm³ starch or treated by 80 mg/dm³ and 125 mg/dm³ collector α-BLA, was shown in Fig. 13a to Fig. 13f.

In the FT-IR spectra of quartz treated by starch (Fig. 13a), those characteristic absorption peaks belonging to starch or starch adsorption did not appear. The strong absorption peaks at 3128 cm^{-1} and 1400 cm^{-1} were due to the stretching vibration and bending vibration of -OH from water adsorpted onto surface of quartz (Luo et al., 2016). The peak located at the position of 1082 cm^{-1} belonged to Si-O-Si asymmetric stretching vibration which was the first characteristic absorption peak of quartz (Zhou et al., 2008). The peaks near 795 cm^{-1} and 461 cm^{-1} were assigned to symmetric stretching vibrations of Si-O-Si, while the peak of 693 cm^{-1} belongs to symmetric bending vibrations (Wu et al., 2002).

The FT-IR spectra of hematite treated by starch (Fig. 13c) was similar to the FT-IR spectra of magnetite treated by starch (Fig. 13e). The absorption peaks at 1090~1097 cm^{-1} and 465~466 cm^{-1} were due to the bending vibration of the Fe-O bond, while the characteristic peak at the position between 545 cm^{-1} and 567 cm^{-1} was the typical stretching vibration absorption peak of the Fe-O bond (Kar et al., 2013). the strong absorption peaks at 3131~3134cm^{-1} and 1401cm^{-1} were assigned to the stretching vibration and bending vibration of -OH from the adsorption water. On both spectrums Fig. 13c and Fig. 13e, the band recorded at 1628~1636 cm^{-1} was related to the vibration of bound water molecules (Heyn, 1974; Kar et al., 2013). This water band was dependent on the number of water molecules associated with the starch molecules. In addition, the absorption peak of C-H stretch vibration in starch molecules could be seen at the position near 2990 cm^{-1} (Yan and Zhang, 2011; Pavlovic and Brandao, 2003) and the peck located at 3445 cm^{-1} illustrated the presence of hydrogen bond adsorption between starch molecules and the surface of hematite and magnetite (Luo et al., 2015). However, those characteristic absorption peaks associated with starch adsorption did not appear in the spectrum of quartz treated by starch. Therefore, it was proved that the starch could not adsorb on the quartz surface but could adsorb on the surface of hematite and magnetite in the form of hydrogen bond adsorption.

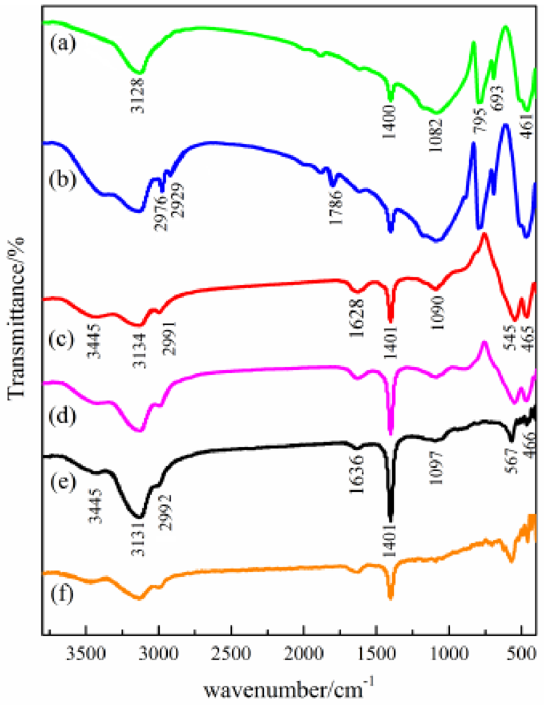

Fig. 13. FT-IR spectra of quartz treated by starch (a), hematite treated by starch (c), magnetite treated by starch (e), activated quartz conditioned with starch and α-BLA (b), hematite conditioned with starch and α-BLA (d), magnetite conditioned with starch and α-BLA (f)

As shown in FT-IR spectra (Fig. 13b) of activated quartz treated by treated by starch and followed by collector α-BLA at pH 11.50, stretching vibration absorption peaks of -CH_3 group, -CH_2 group and C=O group could be seen at the positions near 2976 cm^{-1}, 2929 cm^{-1} and 1786 cm^{-1} (Sahoo et al., 2015; Han et al., 2017), respectively. However, these peaks did not appear in both spectrums of hematite (Fig. 13d) and magnetite (Fig. 13f) conditioned with starch and the collector α-BLA. Therefore, the starch could be preferentially adsorbed on the surface of the hematite and magnetite to prevent the adsorption of the collector α-BLA. In contrast, the adsorption of starch did not occur on the surface of quartz, and the collector α-BLA could be successfully adsorbed on the surface of activated quartz, which was the key to separating the quartz from hematite and magnetite.

4 Conclusions

The flotation behavior of quartz, hematite and magnetite under α-BLA reverse flotation system were investigated. The flotation test results showed that collector α-BLA had a good flotation performance for quartz in the temperature range from 10 ℃ to 35 ℃. The optimum pH value of pulp for quartz flotation was about 11.5, and for hematite and magnetite flotation were in the range 4-8. The best α-BLA concentrations was 75 mg/dm^3 for quartz flotation, 125 mg/dm^3 for hematite and magnetite flotation. Quartz flotation must be activated by activator $CaCl_2$, and the minimum activator $CaCl_2$ concentration was 50 mg/dm^3. However, activator $CaCl_2$ had no obvious effect on the flotation behavior of hematite and magnetite. The results of starch concentration test showed that hematite and magnetite were completely inhibited when the starch concentration in the pulp was more than 80 mg/dm^3, but the addition of starch had little effect on quartz flotation. For the single mineral flotation under reverse anion flotation system, the recovery of quartz tended to 100%, while the hematite and magnetite were completely inhibited and could not be floated. The results of contact angle, zeta-potential and infrared spectroscopy showed that the separation mechanism of quartz from hematite and magnetite was that the starch could be selectively adsorbed on the surface of hematite and magnetite in the form of strong hydrogen bond adsorption, while the adsorption of starch did not occur on the surface of quartz, and then the collector α-BLA could be successfully adsorbed on the surface of activated quartz to make the quartz strongly hydrophobic and to be floated out.

Acknowledgments

The authors gratefully acknowledge and appreciate the financial support provided by the National Natural Science Foundation of China (Grant No.51274056 and 51474055).

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