Investigations on a novel collector for anionic reverse flotation separation of quartz from iron ores

Ji Fang [1], Yingyong Ge [1,2], Shunbing Liu [1], Jun Yu [3], Cheng Liu [1,2]

[1] School of Resources and Environmental Engineering, Wuhan University of Technology, Wuhan 430070, China

[2] Hubei Key Laboratory of Mineral Resources Processing & Environment, Wuhan 430070, China

[3] Chonfar Engineering and Technology Co., Ltd., Changsha 410016, China

Corresponding author: fangji1993@foxmail.com (Ji Fang)

Abstract: It is necessary to exploit an easy and effective way to obtain flotation collector. In this paper, oleic acid was modified by oxidation reaction to obtain an excellent collector. The flotation performances of oleic acid and its oxidation products were systematically investigated and a novel collector ((E)-8,11-dihydroperoxyoctadec-9-enoic acid, EDEA) was obtained. Single mineral flotation tests results showed that EDEA had strong flotation power towards quartz at pH＞11 and hardly floated hematite and magnetite at pH=8~13. The recovery of quartz could achieve 92.35% with 120 mg/L EDEA under the condition of pH=12 and dosage of $CaCl_2$ 60mg/L while the recovery was 62.44% with 120 mg/L oleic acid. Bench scale flotation tests results showed that EDEA had a preferable effect on separating quartz from iron ore especially at low flotation temperature (288K). The mechanism research revealed that EDEA attracted on quartz surface through electrostatic attraction and the neighboring EDEA molecules could form intermolecular hydrogen bonds which resulted in a closer alignment of EDEA on quartz surface.

Keywords: reverse flotation, iron ore, quartz, collector, fatty acid

1. Introduction

Flotation has been regarded as the most effective solution, both technologically and economically, when upgrading iron concentrates (Filippov et al., 2014). Intensive investigation on iron ore flotation began in 1931 and revealed the following flotation routes: the direct anionic flotation of iron oxides and the reverse anionic or cationic flotation of quartz (Nakhaei and Irannajad, 2018; Uwadiale, 1992). Due to the simple processing, relatively low cost and stable flotation indicators, the reverse flotation was widely used. The appropriate collectors play an important role in the reverse flotation.

There are two main types of iron ore collectors, anionic collectors and cationic collectors, used in the flotation processes. The anionic collectors contain a hydrocarbon and alkali salts of straight chain fatty acids, and alkyl aryl sulfonates. The cationic collectors usually contain a hydrocarbon group, and the salts of bases, usually chlorides or acetates (Sahoo et al., 2015). Due to the complicated properties of the iron ores, it is difficult to compare reverse anionic and cationic flotation (Ma et al., 2011). Though the main advantage of reverse cationic flotation over reverse anionic flotation is higher flotation rate, reverse cationic flotation is more sensitive to the slime, which may bring a lot of trouble to flotation operation, and cationic collectors are expensive, which have no advantage in cost compared with anionic collectors. Based on these factors, anionic reverse flotation has been considered as one of the most widely applied technologies for the economical utilization of iron ore resources (Filippov et al., 2014; Nakhaei and Irannajad, 2018).

However, the usual anionic collectors such as oleic acid have a fatal flaw that the flotation pulp should be maintained at a relatively higher pulp temperature (308 - 318 K) which leads to a great deal of energy consumption. The most extensively used types of anionic collectors are long-chain fatty acids and their salts (Quast, 2006). And the solubility of the straight chain, saturated fatty acids containing

between 6 and 18 carbon atoms in water decrease from 8.3×10^{-2} mol/L to 3.0×10^{-7} mol/L with increasing chain length (Johnson and Daniels, 2000). The requirement of higher pulp temperature to maintain the activity and solubility of fatty acid anionic collectors leads to a great deal of energy consumption which promotes the researches to design and develop novel low temperature resistant collectors in hopes of finding a solution in cutting the energy consumption. It is not only to reduce production costs and save resources, but more importantly to protect the ecological environment. Minimizing the emission of carbon dioxide and other greenhouse gases for the protection of the global environment (Sis and Chander, 2003; Zhu et al., 2015).

In order to solve the problem of low-temperature flotation, researchers have made a lot of exploration and experimental research on low-temperature flotation reagents. Low-temperature resistant fatty acid collectors take fatty acids as raw materials, and are modified by introducing various polar functional groups such as carboxyl, hydroxyl, sulfonic acid group, ethoxy group and halogen atom, which is aiming to improve the collection, selectivity, dispersion and solubility. Japanese scientist (Ogata et al., 1979) found that the modified saturated fatty acids with chlorine atom which was introduced into the α-carbon position could improve the solubility of these reagents and the enhancement of electro-negative of fatty acid by Cl atom resulted in a stronger adsorption among active sites of O atoms of carboxyl group with hydroxyl of quartz. According to these findings, some new collectors such as RA-315, RA-515, RA-715, RA-915, KS-II, LKY and DZN-1 were synthesized and applied to reverse flotation of iron ore (Lin et al., 1993; Mei et al., 2009; Zhang and Liu, 2003; Zhu et al., 2012). Besides, bromine atom also has been introduced into the α-carbon position of fatty acid and the α-bromolauric acid ($CH_3(CH_2)_9CHBrCOOH$) and α-bromodecanoic acid ($CH_3(CH_2)_7CHBrCOOH$) were synthesized in the laboratory. Flotation tests presented that they have a good flotation performance at a relatively low temperature of 289 K and the results have indicated that they were more tolerant to lower pulp temperature and fluctuations of the reagents dosages compared with α-chloro fatty acid (Han et al., 2018; Luo et al., 2015; Zhu et al., 2015). In addition, Chinese researcher (Song, 2010) prepared a novel binary carboxylic acid collector called azelaic acid by oxidizing oleic acid with ozone. Flotation tests have proved that it was an excellent low temperature resistant collector due to its good solubility and collecting ability.

However, these synthetic methods have some business or environmental problems. The synthesis of RA-315, RA-515, RA-715, RA-915, KS-II, LKY and DZN-1 requires chlorine as a substrate which is a highly toxic gas. Once the chlorine gas leaks during the synthesis process, it will cause great harm to human and environment. Bromine is one of the important raw materials for the synthesis of α-bromolauric acid and α-bromodecanoic acid, and the high price of bromine cannot be ignored. To some extent, high production costs discourage the commercial use of these two collectors, though they possess satisfactory flotation performance. Owing to the use of ozone in the synthesis process, LKD is also expensive and it is difficult to be widely used.

It is widely accepted that flotation reagents are critical in the flotation separation process (Yu et al., 2018). It is necessary to obtain an effective and low temperature resistant collector for promoting low-temperature flotation result and reducing the high energy consumption in the mineral processing. Oxidation is an easy and effective way to change the properties of fatty acid (Kirpluks et al., 2019). However, the influence of oxidation on fatty acid flotation performances was rarely reported and the systematical research on the characterizations and the flotation performances of fatty acid and its products with different oxidation degree were never conducted. In this paper, an inexpensive and convenient fatty acid, oleic acid, was oxidized to varying degrees. Then, the flotation performances of oleic acid and its oxidation products were investigated by single mineral flotation tests under reverse flotation system. Finally, a novel collector was obtained and its flotation performance for raw iron ores was studied. Meanwhile, Zeta-potential measurement, contact angle and FTIR spectroscopy analyses were used to clarify the interaction mechanisms between this novel collector and minerals.

2. Materials and methods

2.1. Minerals and reagents

2.1.1. Pure mineral samples

The pure samples of quartz, hematite and magnetite obtained from Yuanjiacun iron mine, Shanxi

Province, China, were carefully hand-picked, crushed using a hammer, ground in a porcelain mill with zirconia balls (RK/CQM-280×290, Wuhan Rock Grinding Equipment Manufacturing Co., Ltd., China), and wet-sieved to obtain the samples with particle size range -74 µm +44 µm for single minerals flotation tests. High purity quartz was obtained by leaching with dilute hydrochloric acid for flotation tests. To ensure the purity of mineral particles surface, quartz samples was immersed in dilute hydrochloric acid and alcohol for 24 hours before flotation tests. Hematite and magnetite samples were also washed using deionized water before flotation tests. The chemical compositions and X-ray diffraction (XRD) analyses of quartz, hematite and magnetite samples were shown in Table. 1 and Fig. 1. No obvious impurity peaks were observed, confirming the high purity of the three minerals samples. The purities of the samples of quartz, hematite and magnetite exceeded 99%, 96% and 97%, respectively, according to their chemical analysis.
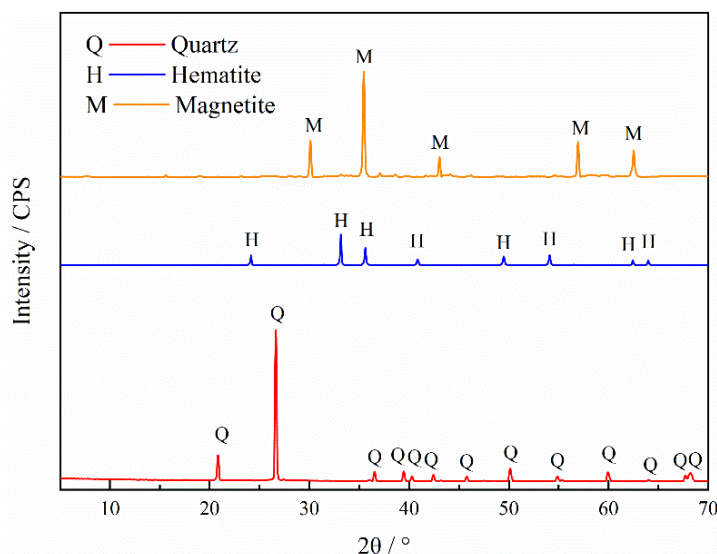

Fig. 1. X-ray diffraction pattern of quartz, hematite and magnetite

Table. 1. Chemical analysis results of single mineral (wt %)

Sample	FeO·Fe$_2$O$_3$	SiO$_2$	Al$_2$O$_3$	MgO	CaO	Others
quartz	0.02	99.73	0.16	0.04	0.04	0.01
hematite	96.89	0.88	0.19	0.17	0.05	1.82
magnetite	97.47	0.65	0.12	0.16	0.07	1.53

2.1.2. Raw iron ores

Raw iron ore, containing ~42.50% TFe from Yuanjiacun iron mine of Shanxi Province in China, was used in bench-scale flotation tests. According to the X-ray diffraction analyses (Fig. 2), the iron bearing minerals in this samples are hematite and magnetite. The main gangue mineral is quartz, the ore also contains a small amount of chlorite. Chemical analysis showed that the content of SiO$_2$ in the iron ore was 34.26%.

2.1.3. Reagents

Oleic acid (C$_{18}$H$_{34}$O$_2$), bought from Sinopharm Chemical Reagent Co., Ltd., China, was used as the raw material for oxidation modification. Calcium chloride (CaCl$_2$), supplied by Sinopharm Chemical Reagent Co., Ltd., China, was used as the activator source of Ca^{2+} in single mineral flotation tests. Calcium oxide (CaO), supplied by Sinopharm Chemical Reagent Co., Ltd., China, was used as the activator in bench scale flotation tests. Corn starch provided by Wokai Chemical Reagent Co., Ltd., Shanghai, China, was hydrolyzed by 5% NaOH solution at 363 K, and it was used as flotation depressant of hematite and magnetite in bench scale flotation tests. HCl (0.10 mol/L) and NaOH (0.10 mol/L) solutions were used to adjust the pH values of the system and deionized water was used in all tests.
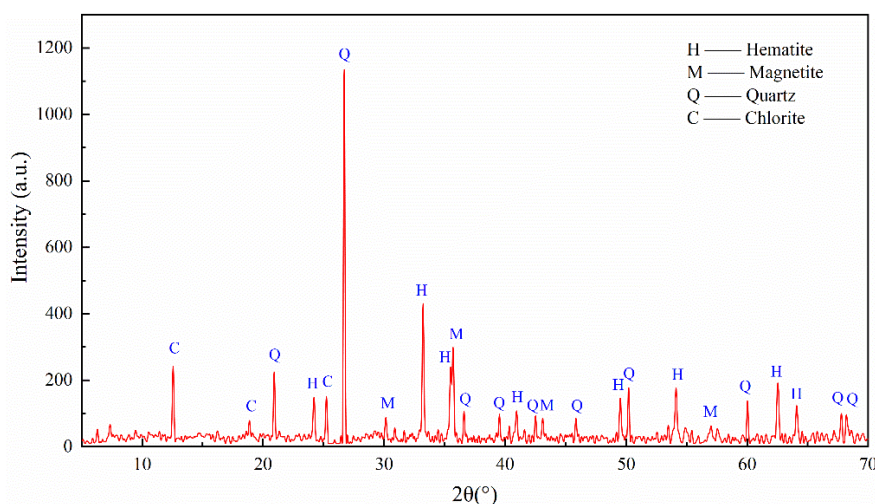
Fig. 2. X-ray diffraction pattern of iron ores

2.2. Oxidation of fatty acid and its products

2.2.1. Synthesis of EDEA

The theoretical and desired oxidation product of oleic acid in this article is (E)-8,11-dihydroperoxyoctadec-9-enoic acid (EDEA). The synthetic route of EDEA was shown in Fig. 3. In brief, 100g oleic acid was added into a 500 cm^3 glass beaker, which was heated and stirred by a heating magnetic stirrer. When the temperature of oleic acid reached 323 K, air was introduced to the oleic acid by a miniature air pump. After 1 hour, 1 g catalyzer was added into oleic acid, and keeping inflating for another several hours. The products with different degree of oxidation can be obtained by controlling the inflating time.
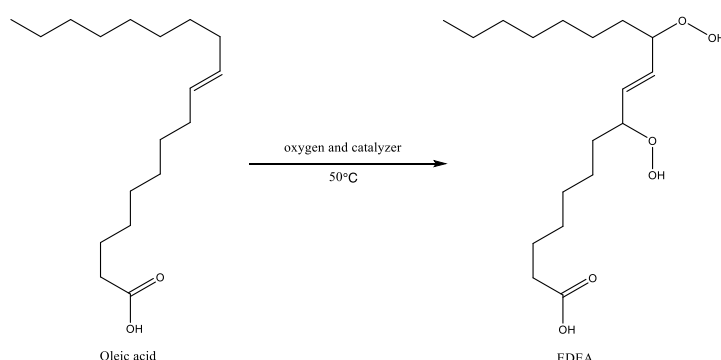

Fig. 3. Scheme of synthetic route of EDEA

The oxidation process of fatty acids is a typical radical reaction. This process can be divided into three reactions: initiation reaction, main reactions and side reactions. A brief description of the oxidation process is shown below:

(1) Initiation reaction:

$$RH \rightarrow R\bullet \tag{1}$$

The initiation reaction process is shown as eq. (1). Where, R is the unsaturated carbon chain of fatty acid. The hydrogen atom H (named α-H) in eq. (1) attached to α-carbon atom is easily attacked by oxygen and departing from carbon chain. Therefore, the formation of free radical R• in this process is sufficiently promoted and the C=C double bond is also not broken. The oxidation process of fatty acid is activated due to the formation of free radical R•.

(2) Main reaction:

$$R\bullet + O_2 \rightarrow ROO\bullet \tag{2}$$

$$ROO\bullet + RH \rightarrow ROOH + R\bullet \tag{3}$$

In this period, the free radical R• reacts with oxygen molecules and produces a new peroxy radical ROO•. The peroxy radical ROO• possesses a strong ability to acquire hydrogen atom H from RH molecule and generates the desired product ROOH. The free radicals ROO• and R• have high reaction activity to keep the oxidation reaction constantly continue. Since there are two α-H atoms (for the C=C double bond) in oleic acid molecule, actually, two peroxide hydroxyls (−OOH) will be introduced into oleic acid molecule.

(3) Side reaction

$$ROO• + R• \rightarrow ROOR \tag{4}$$

$$ROO• + ROO• \rightarrow ROOR + O_2 \tag{5}$$

$$R• + R• \rightarrow R\text{-}R \tag{6}$$

There is a slight side reaction occurs during this process. The free radicals ROO• and R• will possibly react with each other and produce slight byproduct ROOR and R-R as the expending of RH.

2.2.2. Products characterization

Peroxide value (POV) is a conventional and common means of detecting the degree of lipid oxidation (Zhu et al., 2020). In this article, POV was used to estimate the oxidation level of the products with different inflating time. POV of oxidation products was determined using the official method of China mentioned in GB/T5538-1995. For each oxidation product, POV was measured three times, and the average value was reported as the final value.

Iodine value (IV) is an important characteristic for the content of unsaturated fatty acids in fats, fixed oils, emulsifiers and solubilizers (Hilp, 2002). Iodine value is proportional to the degree of unsaturation of the product, so iodine value can be used to characterize the content of the double bond of fatty acid and its oxidation products (Muniyappan et al., 2019; Soares and Rocha, 2018). In present article, the iodine values were analyzed by Hanuš method according to the official method of China (GB/T 13892-2012, Standardization Administration of P.R.C.). Hanuš method for iodine value determination has been reported in several published papers (Hilp, 2002; Imming and Germershaus, 2002). The Iodine value (IV) of each sample was measured three times, and the average value was reported and the standard deviation was calculated.

Acid value (AV) is usually considered to be one of the main parameters to reflect the quality of fatty acid (Zhou et al., 2019). Acid value (AV) was used to characterize the acidity of oleic acid and its oxidation products in present article. Acid value (AV) means the milligrams of potassium hydroxide (KOH) required in tests to neutralize 1 g sample of fatty acid products and its determination has been reported in the previous study (Desta et al., 2020). In this article, Acid value (AV) was measured according to the official method of China (GB/T 5530-2005, Standardization Administration of P.R.C.). In brief, 1.000 g fatty acid or its oxidation products was dissolved in 50 ml of ethanol in 250 ml conical flask and the solution was titrated using a KOH solution (0.042 mol/L) with phenolphthalein as indicator. The acid value of fatty acid or its oxidation products was calculated using the eq. (7):

$$AV(mgKOH/\text{g}) = \frac{V_{KOH}(ml) \times C_{KOH}(mol/L)}{1.000(g)} \times 56 \tag{7}$$

where V_{KOH} is the volume of the solution of KOH consumed in the titration, C_{KOH} is the concentration of KOH solution. The Acid value (AV) of each sample was measured three times, and the average value was reported and the standard deviation was calculated.

2.3. Single minerals flotation tests

Single minerals flotation tests were divided into two parts: (1) quartz micro-flotation tests were implemented to compare the flotation effects of oleic acid and its oxidation products on quartz and then an appropriate oxidation product was selected as the novel collector EDEA, (2) hematite and magnetite micro-flotation tests were implemented to compare their flotation recovery with quartz while oleic acid and EDEA were used as collector.

Single minerals flotation tests were conducted in a 50 ml cell of a XFGII50 laboratory flotation machine (Jilin Prospecting Machinery, China). In each test, 2.0 g of minerals was dispersed in the cell with 45 ml distilled water for 3 min, and the pulp pH was adjusted by HCl or NaOH solutions for 3 min,

then activator ($CaCl_2$), depressant (Corn starch, only for hematite and magnetite microflotation tests) and collector (oleic acid and its oxidation products with different POV) were added into the cell every 3 min continually. The suspension was agitated for 3 min after adding all the desired amount of reagents, and the flotation pulp was conducted for 4 min. Finally, the froth products were weighed as m_K and tailings were weighed as m_T respectively after filtration and drying. The recovery means the rate of froth product weight to the total weight of froth product and tailing. The recovery R was calculated by the following expressions:

$$R = \frac{m_K}{m_K + m_T} \times 100\% \tag{8}$$
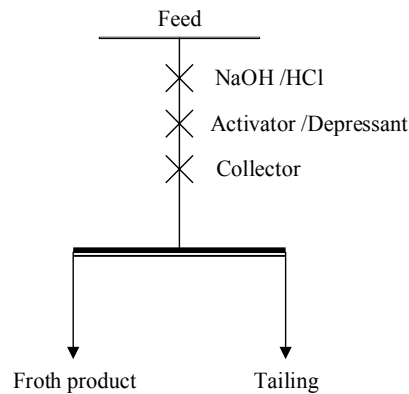
Fig. 4. The flowsheet of single minerals flotation tests

2.4. Bench scale flotation tests

Bench-scale flotation tests were reverse flotation for obtaining the target minerals, hematite and magnetite. Bench-scale flotation was a batch flotation tests conducted on discontinuous flotation devices. The flotation flowsheet and reagent regime were determined on the basis of the previous open-
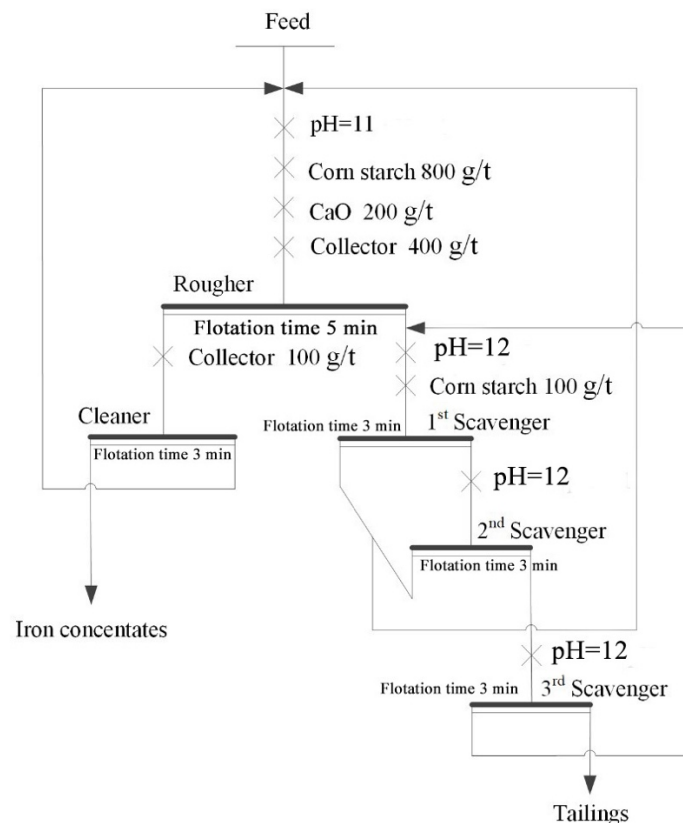
Fig. 5. The closed-circuit flowsheet of actual ore flotation tests

circuit flotation tests. The detailed flotation conditions and the flotation flow sheet of closed-circuit tests were listed in Fig. 5. For rougher flotation, the froth product was tailing and the product left in the tank was concentrate and would be taken once cleaner flotation. Bench-scale flotation tests were performed in XFD-63 flotation cell whose volume for rougher flotation was 1.0 L and for cleaner flotation and scavenger flotation was 0.5 L respectively. In each bench-scale flotation test, the rougher flotation used 300 g raw iron ores and the impeller speed was fixed at 2000 r/min for 3 min. NaOH was added to adjust pulp pH. Subsequently, corn starch was added and the mixture was stirred for 3 min. Then, CaO was added and the mixture was stirred for 3 min. Finally, the collector was added and the mixture was stirred for a further 3 min. The pulp temperature of bench-scale flotation was maintained at 298K (natural pulp temperature). Different to single minerals flotation tests, CaO was used as activator in bench-scale flotation tests to simulate the actual reagent regime in flotation plant. The closed-circuit flotation system reached equilibrium after six cycles. The concentrates and tailings were filtered, dried, weighted, sampled and assayed for TFe and SiO_2 to calculate the recovery.

2.5. Contact angle measurement

Static contact angle values of minerals particle surfaces were carried out with a contact angle apparatus (FT-CAM, Suzhou feitang testing equipment, China) using the free sessile drop method. For each test, the pure mineral sample was immersed in the prepared solution for 5 min. After drying (333 K), the pure mineral samples were pressed into round tablets (d=1 cm) at 10 M pressure for 2 min using a powder compressing machine (FW-4A, Tianjin Tuopu Instrument, China). A drop deionized water was deposited on the tablet surface. At the same time, the build-in high speed camera recorded the droplet changing processes. In each teat, contact angle was generated by analyzing the shape of the droplet on tablet surface. Each sample was measured three times at different sample locations and the average value was reported as a final value.

2.6. Zeta potential measurements

Zeta potentials were measured by a Malvern Instruments Nano-ZS90 zeta potential analyzer (Malvern Instruments, Malvern, UK). For quartz sample, zeta potentials were measured in the absence and presence of $CaCl_2$ and collector (EDEA or oleic acid) at a constant temperature of 298 K. The zeta potentials of hematite and magnetite samples treated with depressant and collector EDEA and untreated with any reagents were also measured at a constant temperature of 298 K. Before the measurements, samples were further ground to below 5 μm. Then, 0.02 g samples were mixed with 50 ml water to obtain the suspension containing 0.04wt.% of the solid content. The pH of suspension was regulated with 0.10 mol/L HCl or 0.10 mol/L NaOH. After that, the reagents with appropriate dosage were added into the suspension in sequence and after being agitated for 10 min with a magnetic stirrer and standing for 5 min, the supernatant liquid of the suspension sucked out and used for zeta potential measurement. The average value from 10 individual measurements was reported in this paper.

2.7. FTIR spectrum measurement

The infrared spectra of collector and samples before and after treated by $CaCl_2$ and collector were recorded by the FTIR spectrometer (Nicolet IS-10). Before measuring infrared spectrum, the mineral samples used for this purpose were ground to below 2 μm in an agate mortar. 5 g of quartz was added to 50 ml aqueous solution and then treated with 125 mg/ml collector (quartz was activated by 50 mg/ml $CaCl_2$ first) at pH 11, 298 K. 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 323 K for 24 h, and then recorded infrared adsorption spectra through KBr disks from 400 cm^{-1} to 4000 cm^{-1}.

3. Results and discussion

3.1. Oxidation of fatty acid and its products

The products with different degree of oxidation were obtained by controlling the inflating time. The iodine value (IV) and Acid values (AV) of six kinds of oxidation products with different POV (respectively were 43.3, 58.6, 80.2, 108.6, 119.0 and 155.3 meq/kg) and oleic acid (POV=0 meq/kg) were
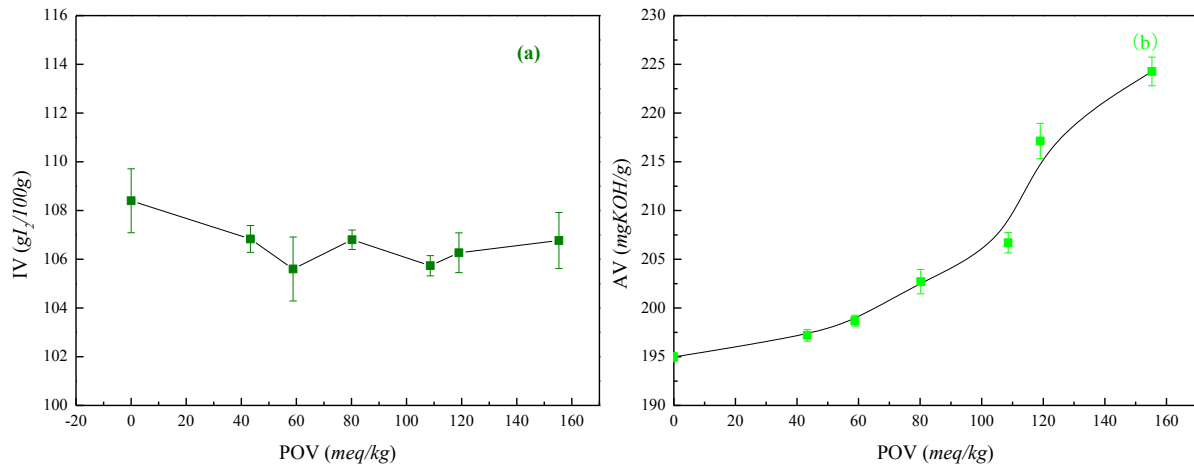
Fig. 6. IV (a) and AV (b) of oleic acid and its oxidation products as a function of POV

measured and the results were showed in Fig. 4 (a) and (b), respectively.

Iodine value (IV) is an index of the degree of unsaturation of a fatty tissue: the more the tissue is rich in saturated fatty acids, the lower is the IV value, and vice versa (Foca et al., 2016). The number of double bonds of fatty acid are crucial for the determination of IV (Kyriakidis and Katsiloulis, 2000). The degree of unsaturation of oleic acid depends on the carbon-carbon double bond in oleic acid molecules. Therefore, iodine value can be used to characterize the content of the double bond of oleic acid and its oxidation products in this article. As shown in Fig. 6(a), the iodine values (IV) of the oxidation products with different POV were basically same as that of oleic acid, which indicated that there were no significant changes on the amount of double bonds (-C=C-). In other words, the double bond (-C=C-) didn't participate in oxidation and was not broken during the oxidation process.

Acid value (AV) is an important standard for the food industry (Gong et al., 2019). It has reported that high acid value could favor the application of fatty acid and its oxidation products as a collector in flotation systems (Oliveira et al., 2019). As shown in Fig. 6(b), the acid value (AV) was significantly increased as the increase of POV. It meant that the increase of the oxidation degree of oleic acid could enhance its acidity. The acidity of fatty acid was usually influenced by the saponification process (Poulenat et al., 2003). Moreover, the oxidation process could introduce some functional groups, such as carbonyl (–C=O), carboxyl (–COOH) and peroxide hydroxyl (−OOH), which alter the polarity functionality along the carbon chains of fatty acid (Fletcher et al., 2020). In this article, the increase of acidity was largely dependent on the introduction of peroxide hydroxyl (−OOH). The increase of acidity signified that the molecular polarity and solubility of oleic acid had been enhanced. Therefore, the solubility of oleic acid was significantly increased attribute to the oxidation reactions.

3.2. Single mineral flotation tests

Oleic acid and its oxidation products with different POV (respectively were 43.3, 58.6, 80.2, 108.6, 119.0 and 155.3 meq/kg) were used as collectors in single mineral flotation tests for exploring the influence of oxidation degree on flotation performance. Effects of pulp pH, dosage of collectors, pulp temperature and dosage of $CaCl_2$ on the flotation recoveries of quartz were showed in Figs. 7 - 10.

3.2.1. Effect of pH

It can be seen from Fig. 7 that the flotation recoveries of quartz increased with the pulp pH value. The results in Fig. 7 also showed that the favorable pH values for collecting quartz were 12 - 13 and the pulp pH values less than 11 would decrease the flotation recovery of quartz. Compared with oleic acid, the oxidation products exhibited superior collecting ability to quartz under the same flotation pH condition. What's more, as the POV increasing, the recoveries of quartz increased visibly. This result suggests that the oxidation product with a higher degree of oxidation possesses a better collecting capability to quartz. Especially, the oxidation product with POV=155.3 meq/kg exerted the best collecting ability towards quartz. It also can be seen from Fig. 7, for the the oxidation product with POV=155.3 meq/kg,

the increase of quartz recovery principally happened between pH=9 and 11. The collecting ability nearly approached maximization at pH=11-12 for the oxidation product with POV=155.3 meq/kg. While for other oxidation products, the optimal pH for quartz flotation was above 12. The different performances of oleic acid and its oxidation products for quartz flotation mainly depended on the oxidation degree. As described in the previous section, the acidity of the oxidation product with POV=155.3 meq/kg was greater than other oxidation products and oleic acid. It meant that the dissociation degree of carboxyl (-COOH) of the oxidation product with POV=155.3 meq/kg was greater than other oxidation products and oleic acid. Therefore, the oxidation product with POV=155.3 meq/kg possesses a better performance for quartz flotation under the same flotation pH condition.
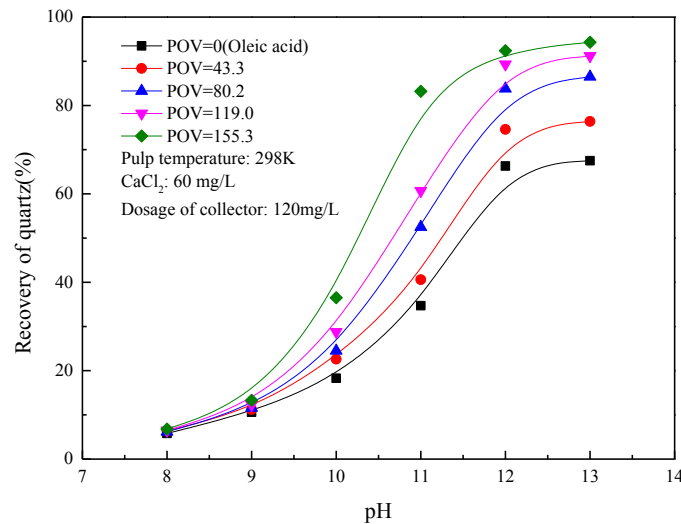
Fig. 7. Recovery of quartz as a function of pulp pH

3.2.2 Effect of dosage of collector

As it could be observed from Fig. 8, the recovery of quartz rapidly increased with increasing dosage of collector when it was less than 120 mg/L. While the dosage above 120 mg/L, the growth of quartz recovery had a slower trend for the oxidation products. However, the recovery of quartz still remained remarkable increase for oleic acid (POV=0). The oxidation product with higher POV value means that it contains more EDEA molecules. Oleic acid (POV=0) hardly contains EDEA molecule and its effect on
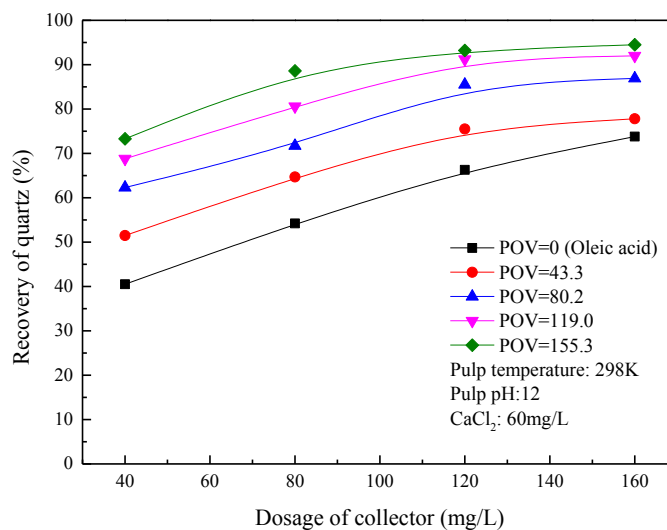
Fig. 8. Recovery of quartz as a function of dosage of collector

quartz flotation is relatively poor. To achieve the maximum recovery of quartz, the dosage of oleic acid (POV=0) is greatly more than its oxidation products. Therefore, the recovery of quartz remains

increasing in collector dosage >120mg/L while oleic acid (POV=0) used as collector. The results shown in Fig. 8 demonstrated that the oxidation products with higher degree of oxidation exhibited superior collecting performances for quartz.

3.2.3. Effect of pulp temperature

The effect of temperature on the recovery of quartz was shown in Fig. 9. As the pulp temperature rising, the flotation recovery of quartz increased. Meanwhile, as POV increasing, the recovery of quartz clearly increased at the same pulp temperature. Especially, at the condition of low pulp temperature (288 K), the recovery of quartz in the presence of oleic acid was 37.82% while the recovery was 68.84% in the presence of the oxidation product with POV=155.3 meq/kg. The results suggested that oxidation reaction had a great effect on enhancing oleic acid collecting capability and low temperature resistance.

In addition, the above flotation tests indicated that the oxidation product with POV=155.3 meq/kg possessed the most satisfactory effect on separating quartz from iron ores. Due to the desired oxidation product of oleic acid was EDEA, the oxidation product with POV=155.3 meq/kg was selected as the collector in the next flotation tests and named EDEA in the following sections.
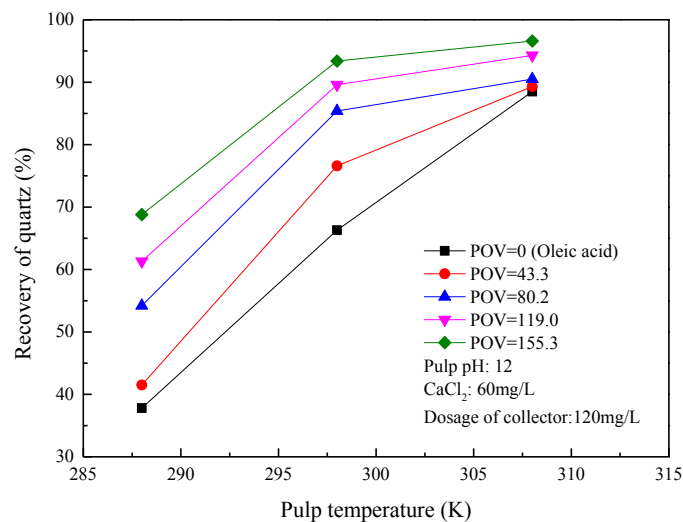
Fig. 9. Recovery of quartz as a function of pulp temperature

3.2.4. Effect of dosage of CaCl$_2$

The recovery of quartz as a function of CaCl$_2$ dosage in the presence of 120 mg/L collector were presented in Fig. 10. As shown in Fig. 8, the CaCl$_2$ dosage significantly affected the flotation behaviors of quartz. It can be seen that the recovery of quartz increased with the increase of CaCl$_2$ dosage. In detail, the recovery of quartz increased as CaCl$_2$ dosage increased from 0 to 60 mg/L, and then remained over 90% at the dosage over 60 mg/L in presence of EDEA. However, the recovery of quartz remained less than 75% as CaCl$_2$ dosage over 80 mg/L in presence of oleic acid. Both EDEA and oleic acid performed very poor flotation ability for quartz while the CaCl$_2$ was not added into pulp. These results indicated that CaCl$_2$ had strong activation on quartz flotation and EDEA had stronger flotation power towards quartz than oleic acid.

3.2.5. Comparison flotation tests

The effect of pulp pH on the recovery of quartz, hematite and magnetite was presented in Fig. 11. With activator CaCl$_2$ concentration (60mg/L), depressor starch concentration (80mg/L), collector EDEA /oleic acid concentration (120mg/L), the recovery of hematite and magnetite was never more than 10% in the pH range of 8-13. The recovery of quartz increased from 8.8% to 93.2% with the raising pulp pH from 8 to 13 in the presence of EDEA. These results indicated that the pH had a crucial effect on quartz flotation but can not promote hematite and magnetite flotation. Compared with Fig. 7, Fig. 11 also indicated that depressant starch hardly influenced the flotation performance of quartz, which corroborated with results reported in the previous literature (Yu et al., 2018).
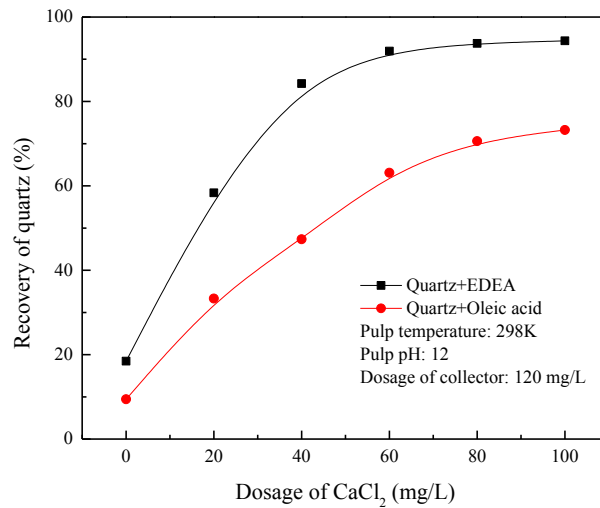
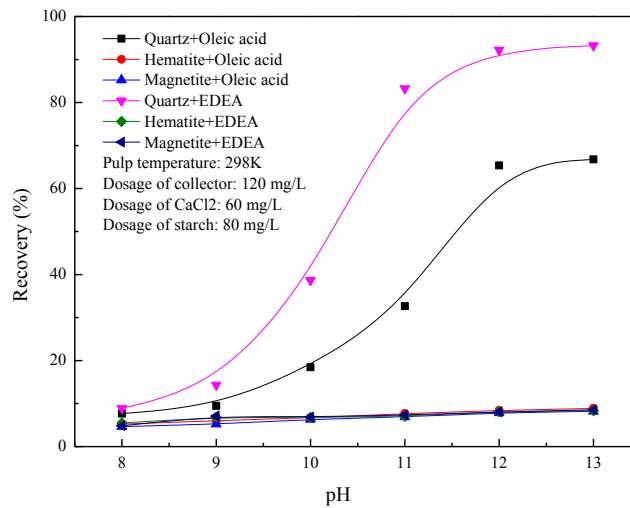Fig. 10. Recovery of quartz as a function of CaCl₂ dosage

Fig. 11. Recoveries of quartz, hematite and magnetite as a function of pH
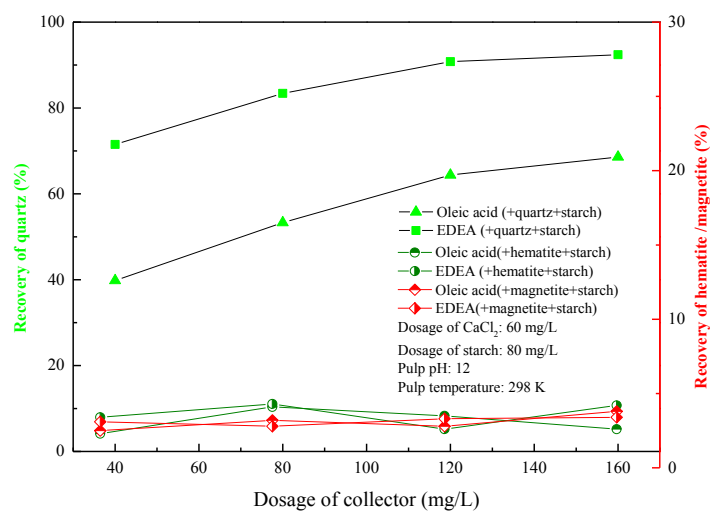

Fig. 12. Recoveries of quartz, hematite and magnetite as a function of collector dosage

Fig. 12 showed the recoveries of quartz, hematite and magnetite at different collector dosage under the condition of pulp temperature 298 K and pH = 12. Different from the above flotation tests, the

depressant corn starch was also added to quartz flotation pulp in order to comparing the flotation performance to hematite and magnetite in this part. The flotation results indicated that the starch had little effect on the flotation behavior of quartz, but which could effectively inhibit the flotation of magnetite and hematite. The oxidation of oleic acid didn't promote its collecting capability for hematite and magnetite. These tests provided evidence that the oxidation products of oleic acid with high POV could be used as collector to remove quartz from iron ore.

3.3. Bench scale flotation tests

Based on the excellent flotation results of pure mineral tests, the raw iron ores were prepared to further investigate the flotation performance of EDEA. Meanwhile, the flotation tests with oleic acid as a collector also implemented to compare flotation performance with EDEA. Table. 2 and Table. 3 listed the results of the flotation tests, respectively.

Table. 2. Reverse flotation results of iron ores with EDEA as a collector

Temperature (K)	product	Yield (%)	Grade (%)		Recovery (%)	
			Fe	SiO_2	Fe	SiO_2
288	concentrate	58.18	64.07	5.89	87.85	10.01
	tailings	41.82	12.32	73.63	12.15	89.99
	feed	100.00	42.43	34.22	100.00	100.00
293	concentrate	57.39	65.44	3.62	88.72	6.09
	tailings	42.61	11.20	75.25	11.28	93.91
	feed	100.00	42.33	34.14	100.00	100.00
298	concentrate	56.62	66.41	3.19	88.41	5.23
	tailings	43.38	11.36	75.48	11.59	94.77
	feed	100.00	42.53	34.55	100.00	100.00

Table. 3. Reverse flotation results of iron ores with oleic acid as a collector

Temperature (K)	product	Yield (%)	Grade (%)		Recovery (%)	
			Fe	SiO_2	Fe	SiO_2
288	concentrate	53.26	61.32	6.12	78.08	9.47
	tailings	46.74	19.62	66.67	21.92	90.53
	feed	100.00	41.83	34.42	100.00	100.00
293	concentrate	54.76	64.52	6.42	83.43	9.97
	tailings	45.24	15.51	70.17	16.57	90.03
	feed	100.00	42.35	35.26	100.00	100.00
298	concentrate	56.46	66.32	6.62	87.40	10.52
	tailings	43.54	12.39	73.00	12.60	89.48
	feed	100.00	42.84	35.52	100.00	100.00

The results in Table. 2 showed that the iron grade of concentrate increased and the SiO_2 content of concentrate decreased with the increase of temperature. When the pulp temperature was 293 K, the recovery of iron in concentrate reached 88.72%, and the grade of iron in concentrate exceeded 65%. As can be seen in Table. 2, the purpose of removing quartz from iron ore can be achieved at the temperature of 288 - 298 K with EDEA as a collector.

The results shown in Table. 3 indicated that the flotation performance of oleic acid was inferior to EDEA, especially under the condition of a low pulp temperature (288 K). Therefore, EDEA was verified to be a collector for anionic reverse flotation to separate quartz from magnetite and hematite at a relatively lower pulp temperature.

3.4. Contact angle analyses

Contact angles of quartz untreated and treated with $CaCl_2$ and collector (EDEA or oleic acid) were measured at different pH values, and the results were presented in Fig. 9.

As can be observed in Fig. 13, the contact angle of quartz was small in distilled water, and the quartz is natural hydrophilic. In the pH range of 2.0 to 8.0, the contact angles of quartz in the solution of CaCl$_2$ 2×10^{-4} mol/L and collector 6×10^{-4} mol/L only a little higher than its nature contact angle and these results indicated that few collectors adsorbed on quartz surface. While, in the pH range of 8.0 to 13.0, rapidly increasing contact angle indicated that the adsorption of collectors on the surface of quartz increased with the increase of the pulp pH. Within the pH range of 8 to 10, contact angle of quartz treated with CaCl$_2$ and EDEA was obviously higher than that of treated with CaCl$_2$ and oleic acid. It can be inferred that at pH is 8 to 10, because of the higher acidity of EDEA, it is more easily dissolved for EDEA molecules in the slurry than oleic acid molecules. According to the electrostatic adsorption theory, the negatively charged molecule (EDEA$^-$) formed from EDEA dissolution is the main substance adsorbing on quartz surface. Therefore, EDEA can more obviously change the wettability of quartz surface at pH 8-10. In the pH range of 11 to 13, the differences of the effect on contact angle between EDEA and oleic acid were insignificant. This shows that both EDEA and oleic acid can significantly change the wettability of quartz surface in a strong alkaline solution. Moreover, in the whole pH range, contact angle of quartz treated with CaCl$_2$ and EDEA was higher than that of treated with CaCl$_2$ and oleic acid. It could be inferred that the adsorption quantity of EDEA on quartz surface was larger than that of oleic acid on quartz surface.
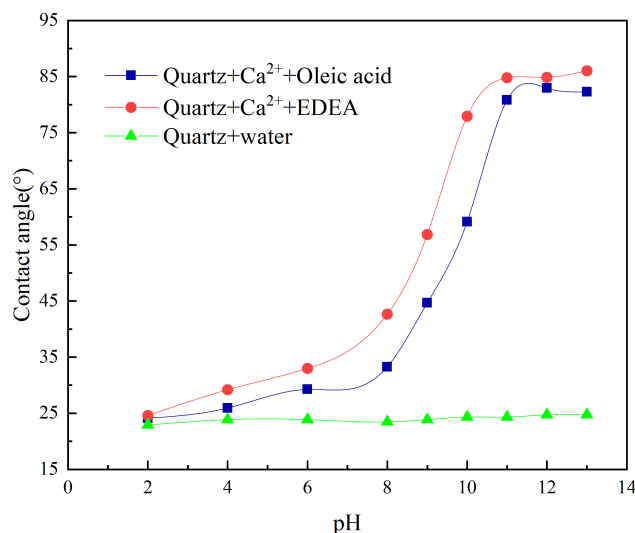

Fig. 13. Contact angle of quartz as a function of pH

Table. 4. Contact angle of minerals before and after reagent conditioning (pH value, 12; CaCl$_2$, 2×10^{-4} mol/L; Starch, 80 mg/L; EDEA, 6×10^{-4} mol/L)

Test materials	Quartz	Quartz + Ca^{2+}	Quartz+Ca^{2+} + Starch + EDEA
Contact angle (°)	18	2.4	85.8
Test materials	Hematite	Hematite + Starch	Hematite+Ca^{2+} + Starch + EDEA
Contact angle (°)	54.6	16.8	18.4
Test materials	Magnetite	Magnetite +Starch	Magnetite+ Ca^{2+} + Starch + EDEA
Contact angle (°)	46.8	20.4	22.4

The contact angles of quartz, hematite and magnetite were measured in the presence and absence of Ca^{2+}/starch and EDEA and the results are given in Table 4. Quartz particles exhibit strong hydrophilicity in deionized water, and their hydrophilicity is stronger after conditioning with calcium ions. After the addition of EDEA, the quartz surface showed hydrophobicity with a contact angle of 85.8°. EDEA could enhance the hydrophobicity of quartz after conditioning with calcium ions and increase its flotation recovery. These results indicated that calcium ions could change the property of quartz surface and make EDEA easier to adsorb on quartz surface. As shown in Table 4, starch can adsorb on the hematite and magnetite surface, thus significantly reducing the contact angle of hematite and magnetite. Therefore, EDEA exerts slight effect on the contact angle of hematite and magnetite. It

could be inferred that EDEA could easily adsorb on quartz surface in the presence of CaCl$_2$ but hardly on hematite and magnetite surface.

3.5. Zeta potential analyses

The surface charge is widely used to characterize the solid surface interactions with reagents in flotation (Fuerstenau and Pradip, 2005). The interactions between quartz surface and collector in the absence and presence of CaCl$_2$ were investigated by zeta potential measurements. The zeta potential of quartz particles as a function of pH in the absence and presence of CaCl$_2$ ($2×10^{-4}$ mol/L), and CaCl$_2$ ($2×10^{-4}$ mol/L)+EDEA or oleic acid ($6×10^{-4}$ mol/L) was presented in Fig. 14, respectively. It indicated that the Point of Zero Charge (PZC) of quartz was about pH 2.0, which was close to the reported value reported in the previous literature (Li and De Bruyn, 1966; Liu et al., 2019; Vielra and Peres, 2007). In the absence and presence of CaCl$_2$ and collector, quartz surface carries strong negative charge in the pH range of 3-13. Because of dissociation of −Si−OH to −Si−O− sites and hydration of −Si$^+$ sites to −Si···OH, quartz's surface acquired negative charge with the increase of OH$^-$ ions in solution (Fuerstenau and Pradip, 2005). With the increasing of pulp pH, more OH$^-$ ions adsorbed onto quartz's surface which resulted in the decreasing of zeta potential. However, when pH value exceeded 10, the zeta potential of quartz particles increased instead of decreasing due to the shielding effect of the negatively charged electrons (Filippov et al., 2014; Wang et al., 2014).
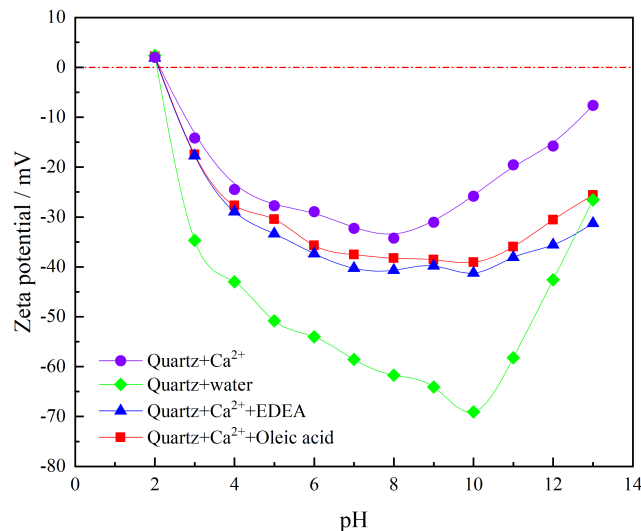

Fig. 14. Zeta potentials of quartz as a function of pH

After being activated by Ca^{2+}, the PZC had no obvious change, but the zeta potentials shifted significantly towards the positive direction when pH > 2. According to the species distribution in Fig. 15, it was supposed that the adsorption of the positively charged Ca^{2+} or Ca(OH)$^+$ ions on quartz surfaces had caused the positive shift of the potentials (Feng et al., 2013; Kou et al., 2016; Ozkan et al., 2009; Shi et al., 2013).

In the presence of $2×10^{-4}$ mol/L CaCl$_2$ and $6×10^{-4}$ mol/L collector (EDEA or oleic acid), the zeta potentials decreased in the whole pH range in comparison of absence of collector. The results illustrated that the collector adsorbed on −Si−O−Ca$^+$ in anionic form by weak electrostatic force due to the weak activation of Ca^{2+}. Moreover, the zeta potentials of the quartz that treated by Ca^{2+} and EDEA was lower than that of treated by Ca^{2+} and oleic acid. Therefore, it can be inferred that EDEA was more likely to adsorb on the quartz's surface compared with oleic acid.

The zeta potential of magnetite and hematite as a function of pH in the absence and presence of starch (80mg/L), and starch (80mg/L)+EDEA ($6×10^{-4}$ mol/L) was presented in Fig. 16, respectively. According to Fig. 16, the potential zero charge (PZC) of magnetite and hematite in aqueous solution was found to about pH 5.5 and 5.0, respectively, which were in agreement with previous studies (Nan et al., 2019; Zhao et al., 2019). In deionized water, the zeta potential of magnetite and hematite was decreasing with the increasing of pulp pH that can be attributed to the adsorption of OH$^-$ ions on

magnetite and hematite surface. It can be seen in Fig. 16, the zeta potentials of magnetite and hematite were negatively shifted when pH＜PZC and positively shifted when pH＞PZC in the presence of starch compared to the zeta potentials in deionized water, which indicated that starch adsorbed onto magnetite and hematite surface and reduced the influence of OH⁻ ions on the zeta potentials of magnetite and hematite. According to Fig. 16, the addition of EDEA caused little influence on the zeta potential of the magnetite and hematite surfaces which had been treated with starch. The zeta potential data confirmed the adsorption of the non-charged starch on magnetite and hematite surfaces could impede the interaction between magnetite and hematite and EDEA. The results from these experiments confirms that the novel collector EDEA can be used for separation of quartz from magnetite and hematite when starch is used as depressant.
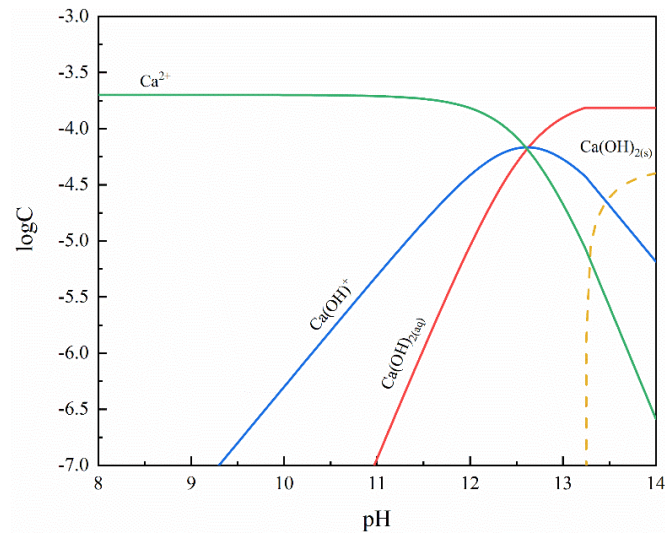

Fig. 15. Species distribution diagram of Ca(II) 2×10-4 mol/L as a function of pH
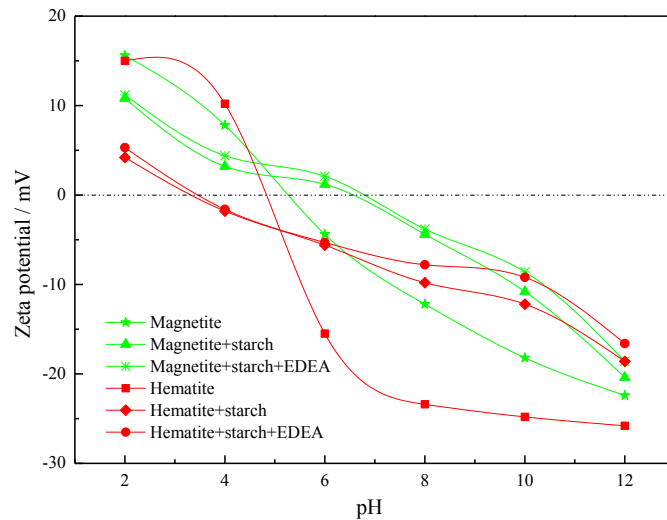

Fig. 16. Zeta potentials of magnetite and hematite as a function of pH

3.6. FTIR spectrum analyses

In Fig. 17(a), the asymmetrical stretching vibration of O−Si−O led to a broad and intense band centred at 1080 cm⁻¹. Peaks at 778 cm⁻¹ and 459 cm⁻¹ belonged to the symmetrical stretching vibration of Si−O−Si. The absorption peak at 694 cm⁻¹ corresponded to the symmetrical bending vibration of Si−O. The observation of these peaks agreed with the results reported in the previous literature (Huang et al., 2014; Luo et al., 2018; Sahoo et al., 2016).

The spectrum of collector EDEA in Fig. 17(b) shows the peaks characteristic of alkyl chains at

positions of 3009, 2929,2859, and 1462 cm^{-1} was assigned to asymmetric stretching of $-CH_3$ group, asymmetric/ symmetric stretching and scissoring of $-CH_2$ group, respectively. Peaks at 1561 cm^{-1} assigned to the asymmetric stretching vibration of $-C=O$ of $-COOH$ group of EDEA (Li et al., 2017; Luo et al., 2015). The carboxy ($-COOH$) vibrations at about 1446, 1425 and 924 cm^{-1} also appeared in the FTIR spectra. The absorption peak at 823 cm^{-1} shows the introduction of $-C-O-OH$ into oleic acid structure (Kirpluks et al., 2019).

The spectrum of quartz treated by $CaCl_2$ and EDEA was shown in Fig. 17(c), the most intense peaks at 2922, 2852 and 1541 cm^{-1} assigned to asymmetric stretching of $-CH_3$ group, asymmetric stretching of $-CH_2$ group and asymmetric stretching of $-C=O$ group, respectively, suggesting that the collector EDEA has adsorbed on the quartz surface. Moreover, the peak-shift from 1561 cm^{-1} to 1541 cm^{-1} may indicate the chemical adsorption of $-COOH$ onto $-Si-OH$ sites of quartz surface.
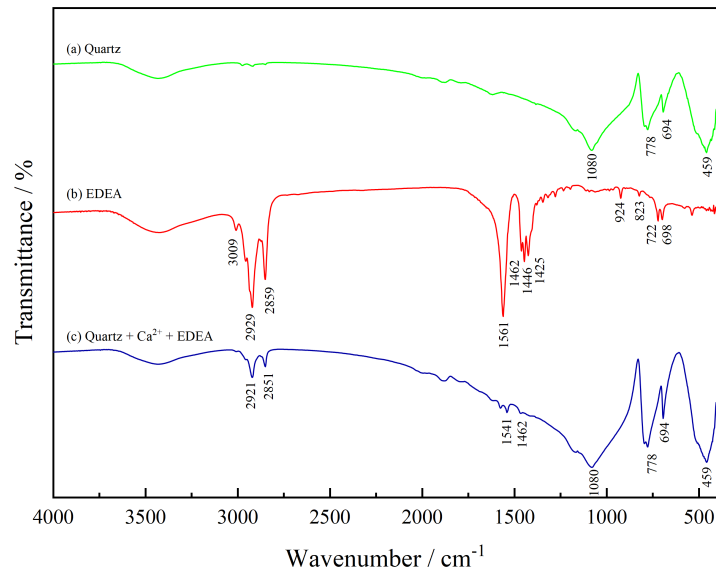

Fig. 17. FTIR spectra of quartz (a), EDEA (b) and quartz treated by 2×10^{-4} mol/L $CaCl_2$
and 7×10^{-4} mol/L EDEA (c)

3.7. Discussion

EDEA contains four parts which was shown in Fig. 18: (a) $C_7H_{15}-$ is a long hydrophobic group; (b) two peroxide hydroxyl groups are introducd to the α-carbon position; (c) C6 aliphatic chain is a hydrophobic linker group; (d) carboxy group is the hydrophilic group. Different from oleic acid, EDEA is introduced two peroxide hydroxyl groups with the $-C=C-$double bond remaining intact.

When electron-donating group is introduced into the molecular structure of fatty acid, the electron density of carboxyl ($-COOH$) would increase and cause an enhancement on its O−H bond. On the contrary, an electron withdrawing group will weaken the electron density of carboxyl ($-COOH$) and reduce the intensity of the O−H bond (Guo et al., 2020b, 2020a). In present article, the peroxide hydroxyl($-OOH$) is a strong electron withdrawing group and can weaken the electron density of carboxyl ($-COOH$) and, as a result, make the hydrion (H$^+$) dissociate from carboxyl($-COOH$) more ea-
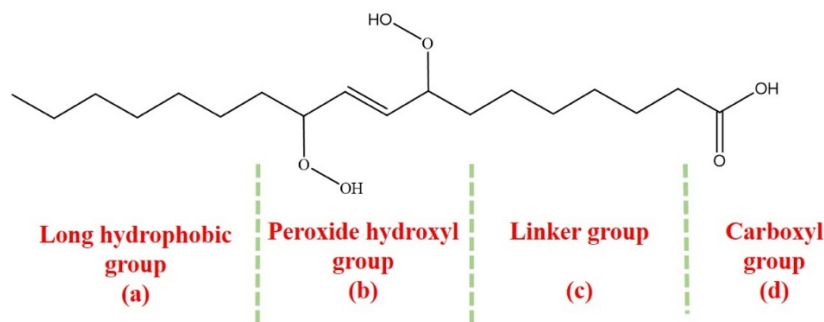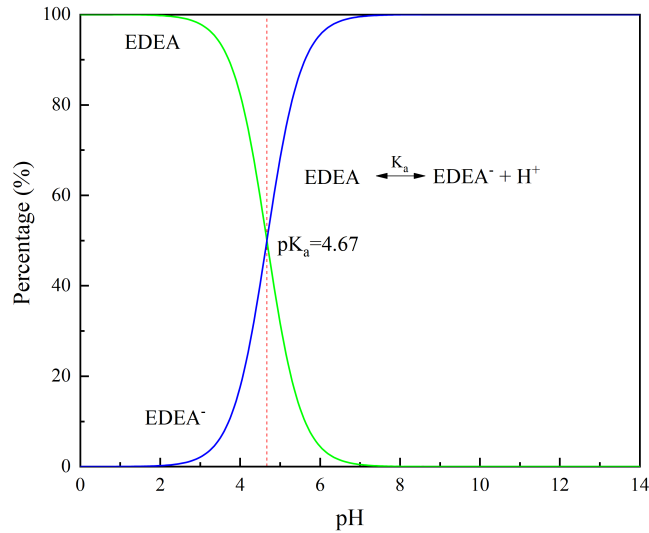

Fig. 18. The components of EDEA

Fig. 19. Percentage distribution of dissociative species of EDEA

sily and the solubility of EDEA is enhanced in a certain extent.

The percentage distribution of EDEA species as a function of aqueous pH values was presented in Fig. 19. Fig. 19 demonstrated that at pH > 4.67, the carboxy group of EDEA lost proton to form negatively charged molecule (EDEA⁻).

According to the species distribution of Ca(II) in solution as shown in Fig. 15, Ca^{2+} absorbs on the negatively charged quartz surface by electrostatic force in the form of Ca^{2+} (pH < 9.0) and Ca^{2+}/ $Ca(OH)^{+}$(pH > 9.0). It should be noted that the proportion of $Ca(OH)^{+}$ achieve maximum when pH values changed from 12.0 to 13.0.

At pH > 4.67, the negatively charged molecule (EDEA⁻) attract the positively charged Ca^{2+}/ $Ca(OH)^{+}$ on mineral surfaces through electrostatic attraction, thereby the zeta potentials of quartz shifting towards the positive direction as shown in Fig. 14. Especially, at pH around 11.0 - 13.0, the interaction of EDEA with quartz surfaces is further enhanced own to hydrogen bonds between $Ca(OH)^{+}$ and −C=O in carboxyl groups of EDEA⁻ as shown in Fig. 20. Therefore, the collector EDEA exhibits an optimal collecting ability to quartz at pH > 11. Furthermore, the neighboring EDEA species coating on quartz surfaces could form intermolecular hydrogen bonds by the peroxide hydroxyl groups (−OOH), resulting in a closer alignment of EDEA on quartz surface as shown in Fig. 20. From the above, these intense interactions of EDEA with quartz surfaces result in an excellent efficiency in separating quartz from iron ores.
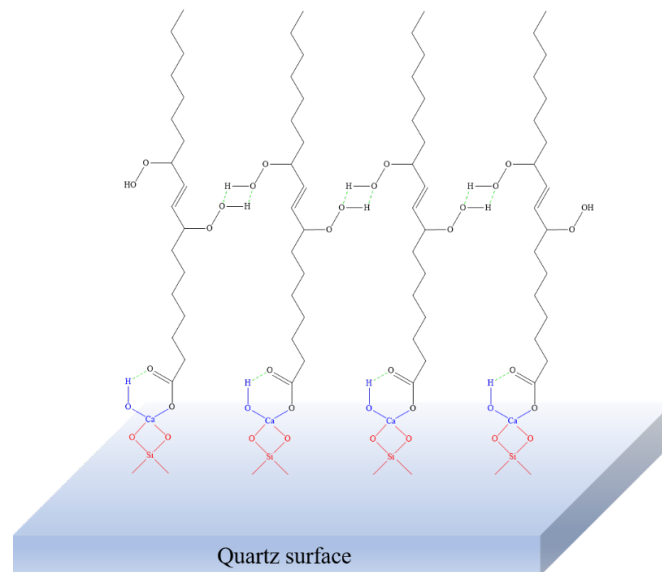

Fig. 20. Schematic view on the potential interaction within a layer of EDEA adsorbed on quartz

4. Conclusions

(1) A novel collector EDEA was synthesized based on the oxidation of fatty acid which was a commercially viable and environmentally resource alternative. EDEA was an efficient collector with excellent collecting performance for the quartz flotation at a relatively lower temperature of 293 K.

(2) The measurements of iodine value (IV) indicated that the double bond ($-C=C-$) was not broken during oxidation process. The oxidation reaction of oleic acid could enhance its acidity and promote the molecular polarity and solubility.

(3) The optimum pH value for quartz flotation with EDEA in the presence of activator $CaCl_2$ was between 11 and 12. The results of bench scale flotation showed that EDEA was a more effective collector to remove quartz from iron ores in comparison with oleic acid at pulp temperature 288 K - 293 K. This result indicates that EDEA is a satisfactory low temperature resistant collector for removing quartz from iron ores.

(4) The results of zeta potential and contact angle analyses demonstrated that EDEA possessed greater capacity to adsorb on quartz surface than oleic acid. Zeta potential and FTIR spectra analyses indicated that the interaction between EDEA and quartz surface included both electrostatic interaction and hydrogen bonds.

(5) The neighbouring EDEA⁻ molecules coating on quartz surfaces could form intermolecular hydrogen bonds by peroxide hydroxyl groups ($-OOH$), resulting in a closer alignment of EDEA on quartz surface. Therefore, the floatability of quartz could be significantly promoted in the presence of EDEA.

Acknowledgements

References

DE OLIVEIRA, P., MANSUR, H., MANUSR, A., DA SILVA, G., CLARK, A.E.C., 2019. *Apatite flotation using pataua palm tree oil as collector*. J. Mater. Res. Technol. 8, 4612–4619.

DESTA, M., MOLLA, A., YUSUF, Z., 2020. *Characterization of physico-chemical properties and antioxidant activity of oil from seed, leaf and stem of purslane (Portulaca oleracea L.).* Biotechnol. Reports 27, e00512.

FENG, Q.M., FENG, B., LU, Y.P., 2013. *Influence of copper ions and calcium ions on adsorption of CMC on chlorite.* Trans. Nonferrous Met. Soc. China 23, 237–242.

FILIPPOV, L.O., SEVEROV, V. V, FILIPPOVA, I. V, 2014. *An overview of the beneficiation of iron ores via reverse cationic flotation.* Int. J. Miner. Process. 127, 62–69.

FLETCHER, B., CHIMONYO, W., PENG, Y., 2020. *A comparison of native starch, oxidized starch and CMC as copper-activated pyrite depressants.* Miner. Eng. 156, 106532.

FOCA, G., FERRARI, C., ULRICI, A., IELO, M.C., MINELLI, G., LO FIEGO, D.P., 2016. I*odine Value and Fatty Acids Determination on Pig Fat Samples by FT-NIR Spectroscopy: Benefits of Variable Selection in the Perspective of Industrial Applications.* Food Anal. Methods 9, 2791–2806.

FUERSTENAU, D.W., PRADIP, 2005. *Zeta potentials in the flotation of oxide and silicate minerals.* Adv. Colloid Interface Sci. 114–115, 9–26.

GONG, G., WU, S., WU, X., 2019. *Effects of storage time and temperature on toxic aldehydes and polycyclic aromatic hydrocarbons in flavouring oil gravy during storage.* Lwt 116, 108510.

GUO, W., HAN, Y., ZHU, Y., LI, Y., TANG, Z., 2020a. *Effect of amide group on the flotation performance of lauric acid.* Appl. Surf. Sci. 505, N.PAG-N.PAG.

GUO, W., ZHU, Y., HAN, Y., LI, Y., YUAN, S., 2020b. *Flotation performance and adsorption mechanism of a new collector 2-(carbamoylamino) lauric acid on quartz surface.* Miner. Eng. 153, 106343.

HAN, Y.X., GUO, W.D., ZHU, Y.M., WEI, Y.H., GU, X.T., 2018. *Flotation behavior and separation mechanism of quartz and iron minerals in alpha-bromolauric acid reverse flotation system.* Physicochem. Probl. Miner. Process. 54, 992–1003.

HILP, M., 2002. *Determination of iodine values according to Hanuš using 1,3-dibromo-5,5-dimethylhydantoin (DBH): Analytical methods of pharmacopeias with DBH: Part 7.* J. Pharm. Biomed. Anal. 28, 81–86.

HUANG, Z.G., ZHONG, H., WANG, S., XIA, L.Y., ZOU, W.B., LIU, G.Y., 2014. *Investigations on reverse cationic*

flotation of iron ore by using a Gemini surfactant: Ethane-1,2-bis(dimethyl-dodecyl-ammonium bromide). Chem. Eng. J. 257, 218–228.

IMMING, P., GERMERSHAUS, O., 2002. P*roducts of the determination of the iodine value with iodine monobromide. Arch. Pharm. (Weinheim).* 335, 449–451.

JOHNSON, R., DANIELS, R., 2000. *Carboxylic Acids, Manufacture.* John Wiley & Sons, New York.

KIRPLUKS, M., VANAGS, E., ABOLINS, A., FRIDRIHSONE, A., CABULIS, U., 2019. *Chemo-enzymatic oxidation of tall oil fatty acids as a precursor for further polyol production.* J. Clean. Prod. 215, 390–398.

KOU, J., XU, S., SUN, T., SUN, C., GUO, Y., WANG, C., 2016. *A study of sodium oleate adsorption on Ca2+ activated quartz surface using quartz crystal microbalance with dissipation.* Int. J. Miner. Process. 154, 24–34.

KYRIAKIDIS, N.B., KATSILOULIS, T., 2000. *Calculation of iodine value from measurements of fatty acid methyl esters of some oils: Comparison with the relevant American Oil Chemists Society method.* J. Am. Oil Chem. Soc. 77, 1235–1238.

LI, D., YIN, W.Z., XUE, J.W., YAO, J., FU, Y.F., LIU, Q., 2017. *Solution chemistry of carbonate minerals and its effects on the flotation of hematite with sodium oleate.* Int. J. Miner. Metall. Mater. 24, 736–744.

LI, H.C., DE BRUYN, P.L., 1966. *Electrokinetic and adsorption studies on quartz.* Surf. Sci. 5, 203–220.

LIN, X., LU, P., CHEN, R., CHEN, J., MA, X., LIN, B., 1993. *Preparation and application of a new type of efficient collector RA-315.* Min. Metall. Eng. 13, 31–35.

LIU, C., ZHU, G., SONG, S., LI, H., 2019. Flotation separation of smithsonite from quartz using calcium lignosulphonate as a depressant and sodium oleate as a collector. Miner. Eng. 131, 385–391.

LUO, B.B., ZHU, Y.M., SUN, C.Y., LI, Y.J., HAN, Y.X., 2018. *The flotation behavior and adsorption mechanisms of 2-((2-(decyloxy)ethyl) amino)lauric acid on quartz surface.* Miner. Eng. 117, 121–126.

LUO, B.B., ZHU, Y.M., SUN, C.Y., LI, Y.J., HAN, Y.X., 2015. *Flotation and adsorption of a new collector alpha-Bromodecanoic acid on quartz surface.* Miner. Eng. 77, 86–92.

MA, X., MARQUES, M., GONTIJO, C., 2011. *Comparative studies of reverse cationic/anionic flotation of Vale iron ore.* Int. J. Miner. Process. 100, 179–183.

MEI, J., HE, R., YANG, W., 2009. *Design, synthesis and application of KS-II flotation reagents for iron ores.* Min. Eng. 7, 26–28.

MUNIYAPPAN, V.K., TAMILMANI, E., DESIKAN, R., RANGAGATHAN, U., 2019. *Influence of groundnut seed viability on biodiesel feedstock quality.* Ind. Crops Prod. 140.

NAKHAEI, F., IRANNAJAD, M., 2018. *Reagents types in flotation of iron oxide minerals: A review.* Miner. Process. Extr. Metall. Rev. 39, 89–124.

NAN, N., ZHU, Y., HAN, Y., 2019. F*lotation performance and mechanism of a-Bromolauric acid on separation of hematite and fluorapatite.* Miner. Eng. 132, 162–168.

OGATA, Y., SUGIMOTO, T., INAISHI, M., 1979. *a-Chlorination of Long-chain Aliphatic Acids.* Bull. Chem. Soc. Japan 52, 255–256.

OZKAN, A., UCBEYIAY, H., DUZYOL, S., 2009. *Comparison of stages in oil agglomeration process of quartz with sodium oleate in the presence of Ca(II) and Mg(II) ions.* J. Colloid Interface Sci. 329, 81–88.

POULENAT, G., SENTENAC, S., MOULOUNGUI, Z., 2003. *Fourier-Transform Infrared Spectra of Fatty Acid Salts - Kinetics of High-Oleic Sunflower Oil Saponification.* J. Surfactants Deterg. 6, 305–310.

QUAST, K., 2006. *Flotation of hematite using C6-C18 saturated fatty acids.* Miner. Eng. 19, 582–597.

SAHOO, H., RATH, S.S., DAS, B., MISHRA, B.K., 2016. *Flotation of quartz using ionic liquid collectors with different functional groups and varying chain lengths.* Miner. Eng. 95, 107–112.

SAHOO, H., RATH, S.S., JENA, S.K., MISHRA, B.K., DAS, B., 2015. *Aliquat-336 as a novel collector for quartz flotation.* Adv. Powder Technol. 26, 511–518.

SHI, Q., ZHANG, G.F., FENG, Q.M., DENG, H., 2013. *Effect of solution chemistry on the flotation system of smithsonite and calcite.* Int. J. Miner. Process. 119, 34–39.

SIS, H., CHANDER, S., 2003. *Reagents used in the flotation of phosphate ores: a critical review.* Miner. Eng. 16, 577–585.

SOARES, S., ROCHA, F.R.P., 2018. *Fast Spectrophotometric Determination of Iodine Value in Biodiesel and Vegetable Oils.* J. Braz. Chem. Soc. 29, 1701–1706.

SONG, R., 2010. *Research on LKD New-type Anionic Reverse Flotation Collector.* Met. Mine 3, 57–61.

UWADIALE, G.G.O.O., 1992. *Flotation of Iron Oxides and Quartz – A Review.* Miner. Process. Extr. Metall. Rev. 11, 129–161.

VIELRA, A.M., PERES, A.E.C., 2007. *The effect of amine type, pH, and size range in the flotation of quartz.* Miner. Eng. 20, 1008–1013.

WANG, L., SUN, W., HU, Y.H., XU, L.H., 2014. *Adsorption mechanism of mixed anionic/cationic collectors in Muscovite*

- Quartz flotation system. Miner. Eng. 64, 44–50.

YU, X., WANG, L., LIU, C., HU, L., WEI, X., HUANG, Z., HE, G., 2018. *Utilization of benzyl aminopropyl dimethoxymethylsilane as collector for the reverse flotation of silicate minerals from magnetite*. Miner. Eng. 129, 106–111.

ZHANG, Z., LIU, G., 2003. *Study on lab test and commercial test of anion collector LKY*. China Min. Mag. 12, 43–44.

ZHAO, X., MENG, Q., YUAN, Z., ZHANG, Y., LI, L., 2019. *Effect of sodium silicate on the magnetic separation of ilmenite from titanaugite by magnetite selective coating*. Powder Technol. 344, 233–241.

ZHOU, D., ZHI, Q., PAN, J., LIU, M., LONG, Y., GE, F., 2019. *Effectively improve the quality of camellia oil by the combination of supercritical fluid extraction and molecular distillation (SFE-MD)*. Lwt 110, 175–181.

ZHU, T.W., ZHANG, X., ZONG, M.H., LINHARDT, R.J., WU, H., LI, B., 2020. *Storage stability studies on interesterified blend-based fast-frozen special fats for oxidative stability, crystallization characteristics and physical properties*. Food Chem 306, 125563.

ZHU, Y., JIANLEI, R., ZHAO, N., LI, Y., 2012. *Reverse flotation of the mixed magnetic concentrate of Qidashan dressing plant in Anshan by a novel anion collector DZN-1*. China Min. Mag. 74–77.

ZHU, Y., LUO, B., SUN, C., LI, Y., HAN, Y., 2015. *Influence of bromine modification on collecting property of lauric acid*. Miner. Eng. 79, 24–30.