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Selective flotation separation of andalusite and quartz and its mechanism

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Abstract: The separation of andalusite and quartz was investigated in the sodium oleate flotation system, and its mechanism was studied by solution chemical calculation, zeta-potential tests, Fourier transform infrared spectroscopic (FTIR), and X-ray photoelectron spectroscopic (XPS). The flotation tests results show that $FeCl_3·6H_2O$ has a strong activation effect on andalusite and quartz and citric acid has a strong inhibitory effect on activated quartz, thus increasing the floatability difference between quartz and andalusite when the pulp pH is approximately 8. The FTIR, Zeta potential, and XPS analyses combined with the chemical calculation of flotation reagent solutions demonstrate that Fe forms hydroxide precipitates on the surface of andalusite and quartz and that oleate anions and metal ions adsorb onto the surface of the minerals. The elements Al and Fe can be chemically reacted. The anions in citric acid have different degrees of dissolution of Fe on the andalusite and quartz surfaces, thereby selectively eliminating the activation of the elemental Fe on andalusite and quartz and increasing the floatability of andalusite, leading to a better separation effect between andalusite and quartz.

Keywords: andalusite; quartz; flotation mechanism; zeta potential; Fourier infrared spectrum analysis; X-ray photoelectron energy spectrum analysis

1. Introduction

The chemical composition and theoretical contents of andalusite, which is one of the island-structure silicate minerals, are 62.92wt% Al_2O_3 and 37.08wt% SiO_2 [1]. Andalusite is widely used in metallurgy, building materials, ceramics, and other industrial sectors. It can be directly used as an energy-saving refractory raw material without calcination [2]. It can also be used to prepare silicon–aluminum alloys and metal fibers. These materials can be used in the manufacture of special parts for cars, spacecraft, and radar devices [3].

China's andalusite resources are abundant in reserves and high in yield; they are mainly distributed in Xixia county of Henan province, Korla city of Xinjiang Uygur Autonomous Region, and Fengcheng city of Liaoning province, China [4]. Most of the Chinese andalusite ores are of medium or low grade, with a content less than 25wt%, and the associated minerals are complex. Among them, biotite, garnet, and metal minerals can be removed through conventional magnetic separation or gravimetric concentration methods. Because the differences in the specific gravity and specific magnetic susceptibility between quartz and andalusite are slight, these minerals are difficult to separate by physical methods. According to the analysis and statistics [5–7], quartz is the most important associated mineral of andalusite, and the associated content is generally between 30wt% and 50wt%. The presence of quartz will reduce the quality of fine-grained andalusite products. In this paper, the flotation mechanism of andalusite and quartz is studied in depth, providing a theoretical basis for the flotation separation of andalusite and quartz.

2. Experimental

2.1. Materials and equipment

The andalusite single mineral was collected from Na-

Corresponding author: Wan-zhong Yin E-mail: yinwanzhong@mail.neu.edu.cn nyang city, Henan province, China and the pure quartz mineral was collected from Luanping county, Hebei province, China. The lump ores with high crystallinity and high purity were selected and crushed to less than 2 mm with a jaw crusher and ground with an agate ball mill. The 45–106 μm fraction of the ore was sieved out, and the magnetic materials in the ore were removed using a high-intensity magnetic separator. The heavy minerals were removed by manual panning to obtain the pure minerals of andalusite and quartz. The results of the chemical composition analysis are shown in Table 1. The X-ray diffraction (XRD) patterns of the andalusite and quartz are shown in Fig. 1.

According to the results of the chemical and XRD analyses, the purity of the andalusite single mineral was greater than 96wt% and that of the quartz single mineral was greater than 99wt%, which satisfies the requirement for sample purity in single-mineral flotation tests.

Table 1. Chemical compositions of andalusite and quartz wt%

Mineral	SiO_2	Al_2O_3	TFe	MgO	CaO	TiO_2	Mn	LOI
Andalusite	35.49	60.30	0.17	0.13	—	0.023	—	1.08
Quartz	99.32	—	0.07	—	—	—	—	—

Note: LOI— Loss on ignition.

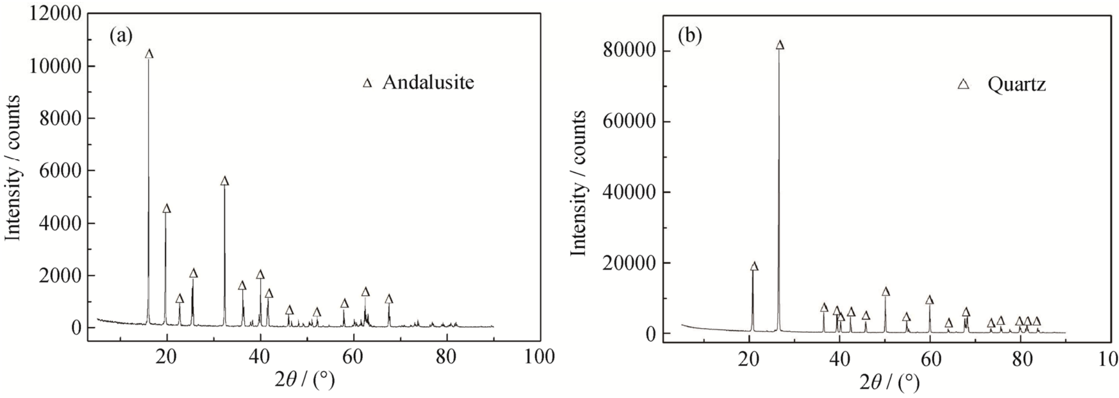

Fig. 1. XRD patterns of (a) andalusite and (b) quartz single minerals.

Major reagents: The pH regulators were HCl and NaOH solutions, the flotation activator was $FeCl_3·6H_2O$, the flotation depressant was citric acid, and the flotation collector was sodium oleate, all of which were of analytical grade. The test water was distilled water.

Major equipment: An XFG flotation machine from Changchun Prospecting Machinery Factory (China), a Nano-ZS90 zeta potentiometer from Malvern Co. (United Kingdom), an IS-10 Fourier transform infrared (FTIR) spectrometer from Nicolet Co. (USA), a VG Multilab 2000 X-ray photoelectron spectrometer from Thermo Electron Co. (USA), and a pH25 pH meter from Shanghai Weiye Instrument Factory were used.

2.2. Test methods

2.2.1. Single-mineral flotation tests

Single-mineral flotation tests were carried out on the XFG flotation machine. A 2.0 g sample of the ore was weighed each time, and 40 mL of deionized water was added. After the mixture was stirred for 1 min, its pH was adjusted with HCl or NaOH. The regulator was added first, the pulp was stirred for 2 min, and then the collector was added. The flotation test was started and continued for 6 min. The froth product and the product in the flotation cell were separately dried and weighed to calculate the recovery of the concentrate.

2.2.2. Zeta potential tests

The single-mineral sample was ground to a particle size of less than 5 μm. For each test, 0.02 g of the ground sample was weighed and placed in a beaker to which 40 mL of deionized water was added. The pH of the mixture was adjusted with HCl or NaOH followed by the addition of regulators under stirring on a magnetic stirrer. A small amount of the suspension was used for measurement of the zeta potential of the mineral sample with a Nano ZS-90 zeta analyzer.

2.2.3. FTIR spectroscopic analysis

In the flotation cell, the ore sample and the flotation reagents were sequentially added according to the test conditions. The ore sample was collected after the mixture was stirred for a corresponding period of time, subjected to solid–liquid separation, and naturally dried. The dried sample to be tested was uniformly mixed with potassium bromide with a mass ratio of 1:100, and the mixture was pressed into a small wafer using a press machine. The FTIR spectra of the mineral samples were collected over the wavenumber range 4000–400 cm^{-1} at a resolution of 4.00 cm^{-1}.

2.2.4. XPS analysis

The samples for X-ray photoelectron spectroscopy (XPS) analysis were directly collected from the flotation slurry, subjected to solid–liquid separation, repeatedly washed with deionized water to remove the soluble impurities, and naturally dried. The XPS spectra were collected using monochromated Al K_α X-rays with an energy of 300 W. The full-spectrum scan range for each sample analysis was 0–1100 eV, the pass-through energy was 100 eV, and the scan step size was 1.0 eV. The sample unit fine-scan pass-through energy was 25 eV, and the scan step size was 50 meV.

3. Results and discussion

3.1. Single-mineral flotation tests

In the actual mineral beneficiation process, because of the influences of the crushing and grinding equipment and the flotation water quality, Fe^{3+} ions are inevitable in the pulp. Therefore, the influence of Fe^{3+} ions in the pulp on the flotation of andalusite and quartz was investigated. The results are listed in Fig. 2, in which the pulp pH and sodium oleate concentration were approximately 8 and 150 mg/L, respectively. When $FeCl_3 \cdot 6H_2O$ with a concentration of 20 mg/L was added, the floatability of andalusite and quartz was relatively good. Then, we investigated the effect of adding citric acid as a method to suppress the flotation of quartz, as also seen in Fig. 2. When the pH, sodium oleate concentration, and $FeCl_3 \cdot 6H_2O$ concentration were approximately 8, 150 mg/L, and 20 mg/L, respectively, and the concentration of added citric acid reached 5 mg/L, the floatability of andalusite and quartz differed substantially. By comparing the results of the flotation behavior tests of andalusite and quartz single minerals in Fig. 2, it can be seen that, under condition A, the floatability difference of andalusite and quartz in 150 mg/L sodium oleate solution was large: the flotation recovery of andalusite was approximately 60%, whereas that of quartz was less than 10%. Under condition A + B, where 20 mg/L $FeCl_3 \cdot 6H_2O$ was added, the flotation recovery of andalusite and quartz in 150 mg/L sodium oleate solution was greatly increased and the floatability difference between the two became smaller: the flotation recovery of andalusite was greater than 95% and that of quartz reached 70%. Thus, $FeCl_3 \cdot 6H_2O$ had a strong activation effect on andalusite and quartz. Under condition A + B + C, where 20 mg/L $FeCl_3 \cdot 6H_2O$ and 5 mg/L citric acid were added, the difference in floatability between andalusite and quartz in 150 mg/L sodium oleate solution increased: the flotation recovery of andalusite was greater than 90%, whereas that of quartz was less than 15%. These results indicate that citric acid has a strong depressing effect on quartz activated by $FeCl_3 \cdot 6H_2O$ and a weaker depressing effect on andalusite, which increased the difference in floatability between andalusite and quartz.

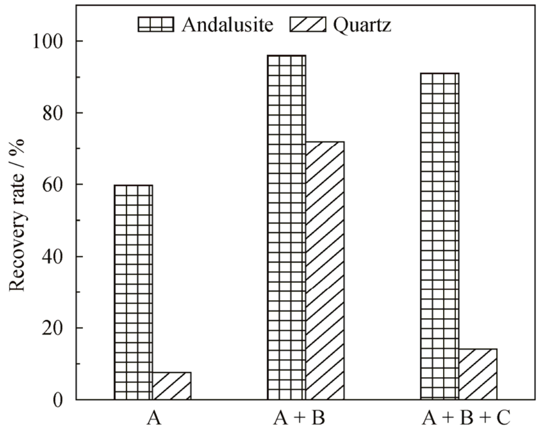

Fig. 2. Comparative study on the flotation behavior of andalusite and quartz (A—150 mg/L sodium oleate; A + B—150 mg/L sodium oleate + 20 mg/L $FeCl_3 \cdot 6H_2O$; A + B + C—150 mg/L sodium oleate + 20 mg/L $FeCl_3 \cdot 6H_2O$ + 5 mg/L citric acid).

The activation with $FeCl_3 \cdot 6H_2O$ and subsequent deactivation with citric acid can selectively increase the flotation difference between andalusite and quartz and, in particular, can greatly improve the flotation of andalusite. Focusing on this key test result, we studied the flotation mechanism of andalusite and quartz in depth.

3.2. Solution chemical analysis of flotation reagents

To study the mechanism of action of the flotation reagents, according to the chemical calculation results for the flotation solution [8–9], flotation tests were conducted with 150 mg/L sodium oleate ($C_{17}H_{33}COONa$), 20 mg/L $FeCl_3 \cdot 6H_2O$, and 5 mg/L citric acid. The lg*C*–pH diagrams (*C* is the concentration) of the components in the investigated flotation reagent solutions are shown in Fig. 3. When the pH of the slurry is approximately 8, the sodium oleate solution contains oleate ion and oleate ion dimer as the major components, whereas the $FeCl_3 \cdot 6H_2O$ solution mainly contains hydroxide precipitates. Citric acid under weak alkaline conditions contains predominantly citrate ion L^{3-} with superior chelating ability, which can form stable soluble substances with metal cations and metal hydroxides on the mineral surfaces.

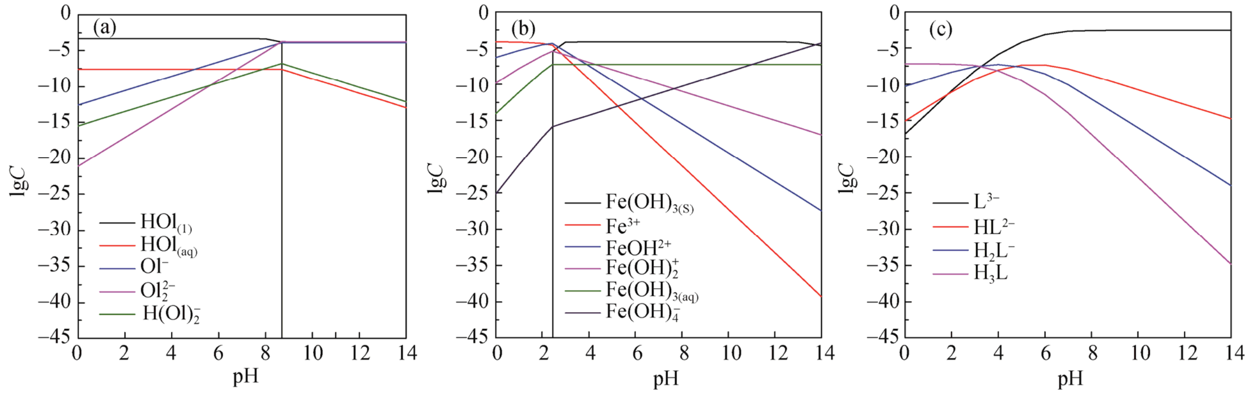

Fig. 3. lg*C*–pH diagrams of components in flotation reagent solutions: (a) sodium oleate solution ($C_T = 4.93 \times 10^{-4}$ mol/L); (b) $FeCl_3·6H_2O$ solution ($C_T = 7.40 \times 10^{-5}$ mol/L); (c) citric acid solution ($C_T = 2.60 \times 10^{-5}$ mol/L). C_T—Initial concentration of reagents.

3.3. Zeta-potential analysis of minerals

The zeta potentials of andalusite and quartz single minerals in deionized water, 150 mg/L sodium oleate solution (A), 20 mg/L $FeCl_3·6H_2O$ solution (B), and 150 mg/L sodium oleate mixed solution and 20 mg/L $FeCl_3·6H_2O$ (A + B) were determined at different pH levels; the results are shown in Fig. 4.

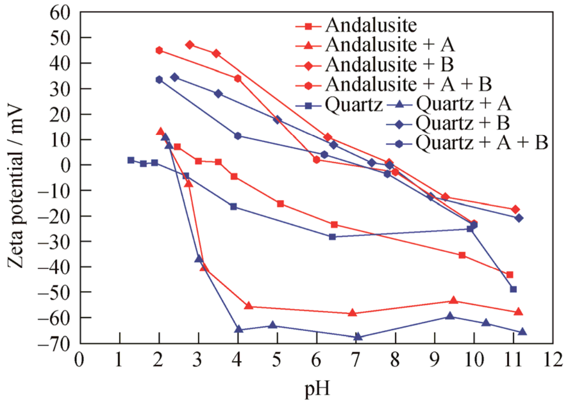

Fig. 4. Zeta potentials of andalusite and quartz single minerals in different flotation reagent solutions (A—150 mg/L sodium oleate; B—20 mg/L $FeCl_3·6H_2O$).

The results in Fig. 4 show that, in deionized water, the absolute values of the zeta potentials of andalusite and quartz increase with increasing pH and the isoelectric points of quartz and andalusite are 2.0 (quartz) and 3.6 (andalusite), respectively. In the 150 mg/L sodium oleate solution, the absolute values of the zeta potentials of andalusite and quartz increase sharply with increasing pH and then tend to become stable; in addition, the isoelectric point of andalusite decreases to 2.5, whereas the isoelectric point of quartz changes to a smaller extent. Combined with the chemical analysis of the sodium oleate solution, these results suggest that the oleate anion adsorbs onto the surface of the minerals, which greatly reduces their zeta potentials, and that sodium oleate is more strongly absorbed onto the surface of andalusite than that onto the surface of quartz. In the 20 mg/L $FeCl_3·6H_2O$ solution, the zeta-potential curves of andalusite and quartz display substantial positive shifts: the isoelectric point of andalusite increases to 7.9 and that of quartz increases to 7.8. This behavior might be explained by specific adsorption onto the surfaces of the minerals of the positively charged Fe species through the formation of hydroxide precipitates. In the mixed solution of 20 mg/L $FeCl_3·6H_2O$ and 150 mg/L sodium oleate, the overall trend of the zeta-potential curves of andalusite and quartz shifted in a negative direction compared with that in 20 mg/L $FeCl_3·6H_2O$ solution. The isoelectric point of quartz and andalusite decreased to 7.0 and 6.9, respectively.

The effect of citric acid on the zeta potential of andalusite and quartz in 20 mg/L $FeCl_3·6H_2O$ solution with a pH of approximately 8 was studied. When 5 mg/L citric acid was added, the zeta potential of andalusite and quartz increased substantially in the negative charge direction, as shown in Table 2. Combined with the lg*C*–pH diagram of the hydrolyzed components in citric acid solution, these results show that, under weak alkaline conditions, the citric acid solution contains a large amount of L^{3-} ions; these negatively charged ions are adsorbed onto the surface of the minerals, thereby greatly reducing the zeta potential of the minerals. This phenomenon enhances the strength and hydrophilicity of the mineral surface hydration layer, which can not only disperse the mineral particles but also form stable soluble substances with metal cations and metal hydroxides on the mineral surfaces, thereby removing the metal ions from mineral surfaces.

Table 2. Effect of citric acid on the zeta potential of andalusite and quartz

Citric acid concentration / ($mg·L^{-1}$)	Andalusite zeta potential / mV	Quartz zeta potential / mV
0	−1.82	−9.42
5	−20.13	−15.92

3.4. FTIR spectroscopic analysis

FTIR spectroscopy can be used to analyze and subsequently explore the interaction mechanism between flotation reagents and mineral surfaces. The infrared spectroscopic analysis results for the interaction of andalusite and quartz with flotation reagents are shown in Figs. 5 and 6.

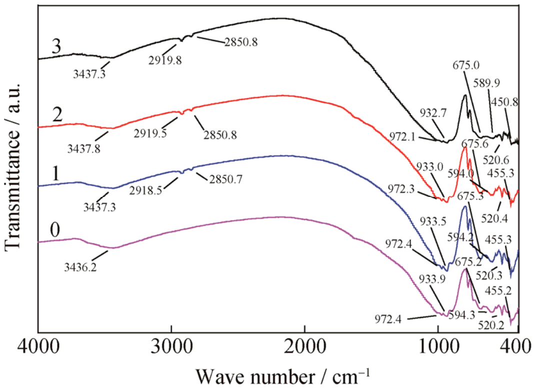

Fig. 5. Infrared spectroscopic analysis of the interaction between andalusite and flotation reagents (0—andalusite; 1—andalusite + sodium oleate; 2—andalusite + $FeCl_3·6H_2O$ + sodium oleate; 3—andalusite + $FeCl_3·6H_2O$ + citric acid + sodium oleate).

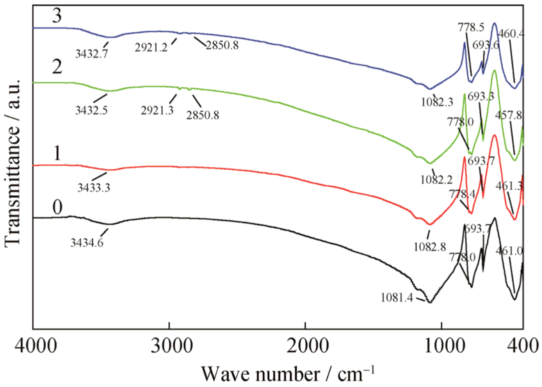

Fig. 6. Infrared spectroscopic analysis of the interaction between quartz and flotation reagents (0—quartz; 1—quartz + sodium oleate; 2—quartz + $FeCl_3·6H_2O$ + sodium oleate; 3—quartz + $FeCl_3·6H_2O$ + citric acid + sodium oleate).

3.4.1. Analysis of the interaction between andalusite and flotation reagents

The FTIR spectroscopic analysis of the interaction between andalusite and the flotation reagent is shown in Fig. 5. In the FTIR spectrum of the andalusite single mineral in Fig. 5 (spectrum No. 0), the absorption peaks at 933.9 and 972.4 cm^{-1} are the characteristic peaks of the asymmetric stretching vibration of the siloxane tetrahedron and the absorption peak at 675.2 cm^{-1} is a characteristic peak of the bending vibration of the siloxane tetrahedron. The absorption peaks at 520.2 and 594.3 cm^{-1} are the characteristic peaks of the vibration of the aluminum octahedron. The absorption peak at 455.2 cm^{-1} corresponds to the vibration of the aluminoxy hexahedron with a coordination number of 5 [10]. The absorption peak at 3436.2 cm^{-1} is attributed to the stretching vibration of the hydroxyl group formed on the andalusite surface.

The products after the reaction between the reagents and andalusite were also analyzed by FTIR spectroscopy. After the interaction between sodium oleate and andalusite, strong absorption peaks appeared at 2850.7 and 2918.5 cm^{-1} (spectrum No. 1), which correspond to the symmetric and asymmetric stretching vibrations of the methylene ($–CH_2–$) groups of sodium oleate [11]; thus, sodium oleate strongly adsorbed onto the surface of the andalusite. After the interaction among $FeCl_3·6H_2O$, sodium oleate, and andalusite, strong absorption peaks appeared at 2850.8 and 2919.5 cm^{-1} (spectrum No. 2). These absorption peaks are stronger than those in spectrum No. 1, indicating that the $FeCl_3·6H_2O$ activates the adsorption of sodium oleate onto the andalusite surface. After the reaction between $FeCl_3·6H_2O$, citric acid, sodium oleate, and andalusite, the peaks at 2850.8 and 2919.8 cm^{-1} (spectrum No. 3) were still observed. These strong absorption peaks indicate that sodium oleate still adsorbed onto the surface of andalusite after the addition of citric acid.

3.4.2. Analysis of the interaction between quartz and flotation reagents

The infrared spectroscopic analysis of the interaction between quartz and flotation reagents is shown in Fig. 6. In the infrared spectrum of the quartz single mineral in Fig. 6 (spectrum No. 0), the absorption peaks at 778.0 and 461.0 cm^{-1} are the characteristic peaks of the symmetrical stretching vibration of the siloxane tetrahedron and the absorption peak at 693.7 cm^{-1} is ascribed to the bending vibration of the siloxane tetrahedron. The absorption peak at 1081.4 cm^{-1} is the characteristic peak of the asymmetric stretching vibration of the siloxane tetrahedron, and the absorption peak at 3434.6 cm^{-1} is attributed to the stretching vibration of the hydroxyl group formed on the quartz surface [12].

After the interaction between sodium oleate and quartz (spectrum No. 1), no obvious characteristic peak of sodium oleate was found in the spectrum of the product, indicating that sodium oleate did not strongly adsorb onto the surface of the quartz. After the interaction among $FeCl_3·6H_2O$, sodium oleate, and quartz, strong sodium oleate absorption peaks appeared at 2850.8 and 2921.3 cm^{-1}, indicating that $FeCl_3·6H_2O$ activated the quartz surface for the adsorption of sodium oleate. After the interaction among $FeCl_3·6H_2O$, citric acid, sodium oleate, and quartz (spectrum No. 3), the peaks at 2850.8 and 2921.2 cm^{-1} were substantially weakened, which, combined with the results of the flotation test, indicated that the addition of citric acid likely weakened the activation action of $FeCl_3·6H_2O$ for the sodium oleate adsorption on the quartz surface [12].

3.5. XPS analysis

To further investigate the interaction mechanism of flotation reagents with andalusite and quartz, XPS analyses of the products before and after the interaction between the flotation agents and andalusite and quartz were carried out. XPS analysis technology is a surface analysis technique used to study the elemental composition and ionic state of materials. XPS was used to analyze the mineral surface elements before and after the action of the reagents. According to the change of the surface electron binding energy, the mode of interaction between the reagents and the minerals could be determined. Because the maximum systematic error of the XPS test in this study did not exceed 0.4 eV, a measured chemical shift (change in binding energy) greater than 0.4 eV indicated that the chemical environment of the element had substantially changed (i.e., a chemical reaction occurred); otherwise, it was a physical reaction. At the same time, the amount of the reagent adsorbed was determined according to the change in the relative content of the surface elements [13–14].

3.5.1. XPS analysis of the interaction between andalusite and flotation reagents

The full XPS spectra of the products of the interaction between andalusite and flotation reagents are shown in Fig. 7. Spectrum No. 0 in Fig. 7 shows that the single mineral of andalusite contains four elements: Al, Si, O, and C; among these elements, C is derived from hydrocarbon contaminants. The carbon produced by this pollution can be used to correct the concentrations of the other elements [15]. The characteristic peak of each element on the surface of the product after the action of the reagent changes somewhat compared with that of the single mineral, wherein the element C is derived from the hydrocarbon contaminant and the adsorbed reagent. The XPS spectrum was analyzed in detail to determine the relative content and electron binding energy of each element on the mineral surface. Combined with Fig. 8, the analysis results are shown in Tables 3 and 4.

After the reaction between sodium oleate and andalusite (spectrum No. 1), the relative content of C on the surface of andalusite is greatly increased compared with that before the reaction, whereas the relative contents of Al, Si, and O are greatly reduced. This result is attributed to sodium oleate adsorbing onto the surface of andalusite. The chemical shift

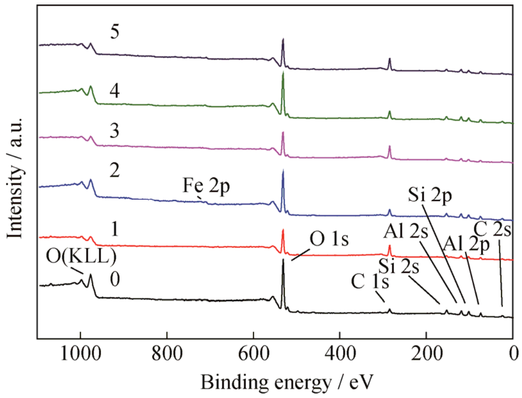

Fig. 7. Full XPS spectra of andalusite with flotation reagents (0—andalusite; 1—andalusite + sodium oleate; 2—andalusite + $FeCl_3·6H_2O$; 3—andalusite + $FeCl_3·6H_2O$ + sodium oleate; 4—andalusite + $FeCl_3·6H_2O$ + citric acid; 5—andalusite + $FeCl_3·6H_2O$ + citric acid + sodium oleate).

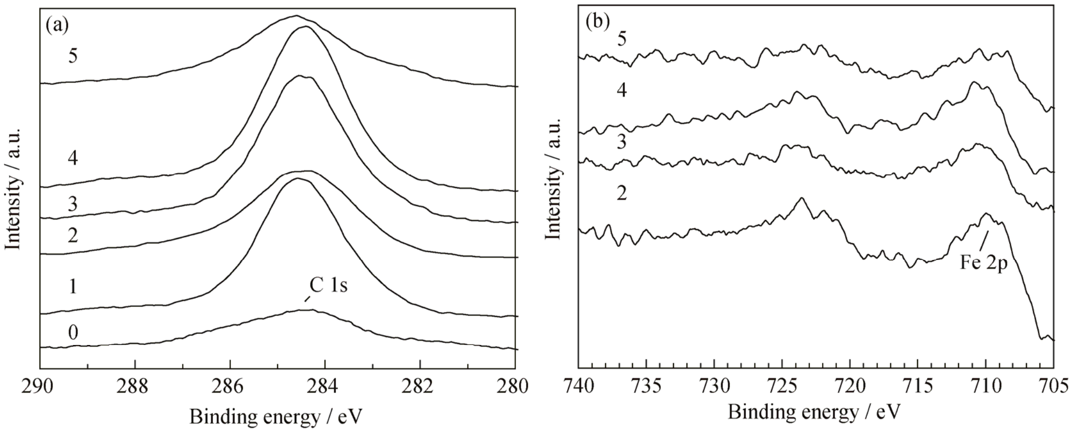

Fig. 8. High-resolution XPS scan of C (a) and Fe (b) on the andalusite surface under different conditions (0—andalusite; 1—andalusite + sodium oleate; 2—andalusite + $FeCl_3·6H_2O$; 3—andalusite + $FeCl_3·6H_2O$ + sodium oleate; 4—andalusite + $FeCl_3·6H_2O$ + citric acid; 5—andalusite + $FeCl_3·6H_2O$ + citric acid + sodium oleate).

Table 3. Relative contents of elements on andalusite surface before and after reaction with reagents

No.	Reagent	Relative content / wt%					(Al + Fe)/O mass ratio
		C	O	Si	Al	Fe	
0	None	14.09	56.34	14.51	15.06	—	0.27
1	Sodium oleate	46.60	35.76	8.28	9.36	—	0.26
2	$FeCl_3·6H_2O$	23.43	49.66	11.18	14.06	1.68	0.32
3	$FeCl_3·6H_2O$ + Sodium oleate	48.30	33.36	8.46	8.84	1.04	0.30
4	$FeCl_3·6H_2O$ + Citric acid	24.78	49.13	11.38	13.92	0.80	0.30
5	$FeCl_3·6H_2O$ + Citric acid + Sodium oleate	41.17	38.49	9.46	10.11	0.76	0.28

Table 4. Binding energy of elements on andalusite surface before and after reaction with reagents eV

No.	Reagent	C 1s	O 1s	Si 2p	Al 2p	Fe 2p
0	None	284.60	530.96	101.73	73.91	—
1	Sodium oleate	284.60	531.32	102.07	74.35	—
2	$FeCl_3·6H_2O$	284.62	531.26	101.99	74.57	709.49
3	$FeCl_3·6H_2O$ + Sodium oleate	284.60	531.36	102.08	74.56	710.29
4	$FeCl_3·6H_2O$ + Citric acid	284.61	531.26	101.84	74.29	710.19
5	$FeCl_3·6H_2O$ + Citric acid + Sodium oleate	284.60	531.31	102.00	74.53	708.77

of Al was 0.44 eV, and the chemical shifts of the other elements were less than 0.4 eV, indicating that the chemical environment of Al on the andalusite surface changed substantially after sodium oleate adsorption. Combined with the chemical analysis results for the sodium oleate solution, these results suggest that the oleate anions have reacted with the elemental Al on the surface of andalusite.

After the reaction between $FeCl_3·6H_2O$ and andalusite (spectrum No. 2), elemental Fe appeared on the surface of the andalusite and the metal-cations-to-oxygen ((Al + Fe)/O) mass ratio increased from 0.27 to 0.32. These results indicate that the element Fe adsorbed onto the surface of andalusite and increased the active sites on the surface of andalusite. At this time, the chemical shift of Al was 0.66 eV. Combined with the chemical analysis of the Fe solution, these results indicate that, when the pH is approximately 8, Fe is mainly adsorbed onto the surface of andalusite in the form of a hydroxide precipitate, which causes a substantial change in the chemical environment of Al on the mineral surface.

After the reaction of $FeCl_3·6H_2O$ and sodium oleate with andalusite (spectrum No. 3), the increased relative content of C and the decreased relative contents of Al, Si, and O on andalusite surface are both greater than those in spectrum No. 1. Thus, the presence of Fe increased the amount of sodium oleate adsorbed onto the surface of andalusite. Compared with the case in spectrum No. 2, the relative content of elemental Fe was greatly reduced and the (Al + Fe)/O mass ratio was reduced from 0.32 to 0.30, indicating that sodium oleate adsorbs onto the active sites on the mineral surface, decreasing the activity of the metal. The chemical shift of Fe relative to that in spectrum No. 2 is 0.80 eV, and the chemical shift of Al relative to the single mineral andalusite is 0.65 eV; the chemical shifts of the remaining elements do not exceed 0.4 eV. Combined with the chemical analysis of the solution, these results suggest that the oleate anion reacts with the Fe and Al on the surface of andalusite. The Fe activates the adsorption of sodium oleate onto andalusite surface.

After the reaction of $FeCl_3·6H_2O$ and citric acid with andalusite (spectrum No. 4), the relative content of elemental Fe was substantially reduced compared with that in spectrum No. 2, and the (Al + Fe)/O ratio decreased from 0.32 to 0.30. The chemical shift of Fe compared with that in spectrum No. 2 was 0.70 eV, and the chemical shifts of the remaining elements were all less than 0.4 eV. Combined with the chemical analysis of the solution, these results indicate that the anion in citric acid mainly dissolves the hydroxide of Fe precipitated on the surface of andalusite, decreasing the number of active sites of the metal.

After the reaction of $FeCl_3·6H_2O$, citric acid, and sodium oleate with andalusite (spectrum No. 5), the increased relative content of C and the decreased relative contents of Al, Si, and O on the andalusite surface were both lower than those in spectrum No. 3. Compared with the case in spectrum No. 2, the relative content of elemental Fe is greatly reduced and the (Al + Fe)/O ratio is reduced from 0.32 to 0.28. The chemical shift of Al relative to the single mineral of andalusite is 0.62 eV, the chemical shift of Fe relative to sample No. 2 is 0.72 eV, and the chemical shifts of the other elements are less than 0.4 eV. On the basis of the results of the chemical analysis of the solution, we speculate that, although citric acid dissolves most of the elemental Fe on the mineral surface and eliminates the activation of most of the elemental Fe on the mineral surface, the mineral surface element Al and the residual element Fe can still react with the oleate anions.

In summary, when the pH is approximately 8, the oleate anion reacts with Al on the surface of the single mineral of andalusite and the chemical adsorption of sodium oleate is activated by Fe on the surface of andalusite. Although citric acid can partially deactivate the andalusite surface activated by Fe, the elemental Al and the residual Fe on the surface after deactivation will still exhibit strong chemisorption interaction with oleate anions.

3.5.2. XPS analysis of the interaction between quartz and flotation reagents

The full XPS spectra of the products of the interaction between quartz and flotation reagents are shown in Fig. 9. Spectrum No. 0 in Fig. 9 shows that the quartz single mineral contains three elements of Si, O, and C, wherein element C is derived from hydrocarbon contaminants. Compared with the single mineral, the characteristic peak of each element on the surface of the products of interaction changed to some extent. The XPS spectra were analyzed in detail to determine the relative content and electron binding energy of each element on the mineral surface. Combined with Fig. 10, the analysis results are shown in Tables 5 and 6.

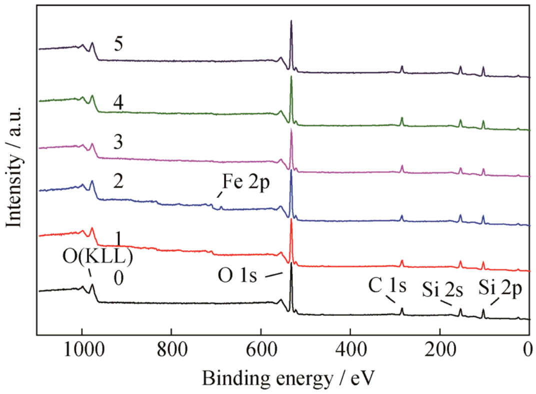

Fig. 9. XPS full spectra of quartz with flotation reagents (0—quartz; 1—quartz + sodium oleate; 2—quartz + $FeCl_3·6H_2O$; 3—quartz + $FeCl_3·6H_2O$ + sodium oleate; 4—quartz + $FeCl_3·6H_2O$ + citric acid; 5—quartz + $FeCl_3·6H_2O$ + citric acid + sodium oleate).

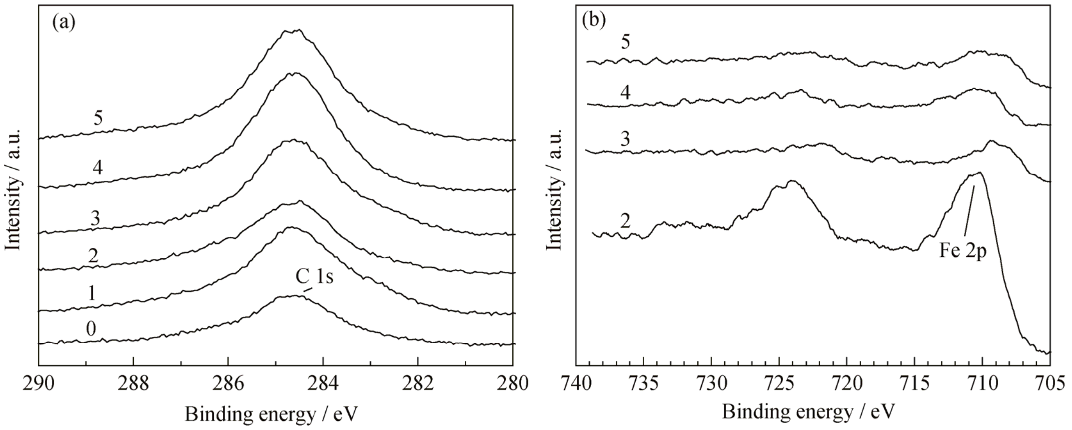

Fig. 10. High-resolution XPS scan of C (a) and Fe (b) on the quartz surface under different conditions (0—quartz; 1—quartz + sodium oleate; 2—quartz + $FeCl_3·6H_2O$; 3—quartz + $FeCl_3·6H_2O$ + sodium oleate; 4—quartz + $FeCl_3·6H_2O$ + citric acid; 5—quartz + $FeCl_3·6H_2O$ + citric acid + sodium oleate).

Table 5. Relative contents of elements on quartz surface before and after the reaction with reagents

No.	Reagent	Relative content / wt%				Fe/O mass ratio
		C	O	Si	Fe	
0	None	22.22	49.47	28.31	—	—
1	Sodium oleate	23.64	50.80	25.56	—	—
2	$FeCl_3·6H_2O$	18.34	52.67	26.97	2.02	0.04
3	$FeCl_3·6H_2O$ + Sodium oleate	25.72	47.68	25.87	0.74	0.02
4	$FeCl_3·6H_2O$ + Citric acid	25.31	47.02	27.00	0.68	0.01
5	$FeCl_3·6H_2O$ + Citric acid + Sodium oleate	24.56	47.89	26.97	0.58	0.01

Table 6. Binding energies of elements on quartz surface before and after reaction with reagents eV

No.	Reagent	C 1s	O 1s	Si 2p	Fe 2p
0	None	284.63	532.27	103.19	—
1	Sodium oleate	284.60	532.14	103.05	—
2	$FeCl_3·6H_2O$	284.62	532.09	103.00	710.44
3	$FeCl_3·6H_2O$ + Sodium oleate	284.61	532.08	103.01	708.79
4	$FeCl_3·6H_2O$ + Citric acid	284.61	532.07	102.96	709.51
5	$FeCl_3·6H_2O$ + Citric acid + Sodium oleate	284.62	532.09	102.98	710.09

The test results in Tables 5 and 6 show that, after the reaction between sodium oleate and quartz (spectrum No. 1), the relative content of each element changed little and the chemical shift of the element was less than 0.4 eV, indicating that sodium oleate did not substantially adsorb onto the quartz surface. After the reaction between $FeCl_3·6H_2O$ and quartz (spectrum No. 2), Fe appeared on the surface of the product, indicating that Fe adsorbed onto the quartz surface. After the reaction of quartz with $FeCl_3·6H_2O$ and sodium oleate (spectrum No. 3), the increased relative content of C on the quartz surface was higher than that in spectrum No. 1. The relative contents of Si and O decreased greatly, and the relative content of Fe was also greatly reduced compared with that in spectrum No. 2. The chemical shift of Fe relative to the sample in spectrum No. 2 was 1.65 eV, and the chemical shifts of other elements were less than 0.4 eV, indicating that the chemical environment of Fe on the surface of the quartz changed substantially after the adsorption of sodium oleate. Combined with the chemical analysis of the solution, these results suggest that the oleate anion reacts chemically with the Fe on the quartz surface. After the reaction of quartz with $FeCl_3·6H_2O$ and citric acid (spectrum No. 4), the relative content of Fe on the quartz surface was greatly reduced compared with that in spectrum No. 2, the chemical shift was 0.93 eV, and the Fe/O mass ratio was reduced from 0.04 to 0.01, and According to the analysis, we considered that the anion in citric acid mainly dissolves the hydroxide of Fe precipitated on the quartz surface and that fewer active sites of the metal on the surface were available. After the reaction of quartz with $FeCl_3·6H_2O$, citric acid, and sodium oleate (spectrum No. 5), the relative content of Fe decreased substantially compared with that in spectrum No. 2 and the Fe/O mass ratio decreased from 0.04 to 0.01, indicating that citric acid had dissolved elemental Fe on the quartz surface and reduced the activation effect of elemental Fe on the quartz surface. Combined with the infrared spectroscopic analysis, these results indicated that sodium oleate had obviously not adsorbed onto the quartz surface under this condition.

In summary, when the pH is approximately 8, sodium oleate does not adsorb onto quartz. The elemental Fe can activate the adsorption of sodium oleate onto quartz. Citric acid can eliminate the activation of quartz by Fe and, after the deactivation by citric acid, sodium oleate will not adsorb onto quartz surface largely.

4. Conclusions

(1) Flotation tests indicated that the difference in floatability between andalusite and quartz in 150 mg/L sodium oleate solution at pH 8 after the addition of 20 mg/L $FeCl_3·6H_2O$ and 5 mg/L citric acid was increased. The flotation recovery of andalusite was greater than 90%, whereas that of quartz was approximately 15%.

(2) Chemical analysis of the flotation reagent solutions and zeta-potential measurements of the minerals showed that, when the pH is approximately 8, in the mixed solution of 20 mg/L $FeCl_3·6H_2O$ and 150 mg/L sodium oleate, sodium oleate adsorbs more strongly onto andalusite and quartz compared with the case in deionized water, indicating that Fe is a major activator of minerals in the sodium oleate system. Under weak alkaline conditions, citric acid contains a large amount of L^{3-} species, which can form stable soluble substances with metal cations or metal hydroxides on the mineral surfaces, thereby reducing the activation or depression of minerals by metal cations or metal hydroxides.

(3) Infrared spectroscopy and XPS studies on the mechanism of interaction between the flotation reagents and the mineral surfaces demonstrated that, when the pH was approximately 8, oleate anions reacted with Al on the andalusite surface and Fe activated the chemical adsorption of sodium oleate onto the andalusite. Citric acid reduced the activation of Fe on the andalusite; however, the Al ions and residual Fe ions on the surface of the andalusite still exhibited strong chemisorption with sodium oleate. When the pH was approximately 8, sodium oleate did not adsorb onto the quartz. Elemental Fe activated the adsorption of sodium oleate onto quartz. Citric acid reduced the activation of

quartz by Fe and deactivated the adsorption of sodium oleate onto quartz. Therefore, under the sodium oleate flotation system, citric acid can effectively depress the flotation of quartz, thereby creating a selective separation between andalusite and quartz.

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