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Flotation separation of andalusite from quartz using sodium petroleum sulfonate as collector

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Abstract: The floatability of andalusite and quartz was studied using sodium petroleum sulfonate as collector, being successfully applied in the real ore separation. The collecting performance on minerals was interpreted by means of zeta potential measurement and infrared spectroscopic analysis. The single mineral experiments showed that andalusite got good floatability in acidic pH region while quartz exhibited very poor floatability in the whole pH range. At pH 3, the presence of Fe^{3+} obviously activated quartz, causing the identical flotation behavior of the two minerals, and calcium lignosulphonate exhibited good selective inhibition to quartz. The real ore test results showed that andalusite concentrate with 53.46% Al_2O_3 and quartz concentrate with 92.74% SiO_2 were obtained. The zeta potential and infrared spectroscopic analysis results indicated that chemical adsorption occurred between sodium petroleum sulfonate and andalusite.

Key words: flotation separation; andalusite; quartz; sodium petroleum sulfonate

1 Introduction

Andalusite is a kind of aluminosilicate minerals, which belongs to three different forms of kyanite minerals together with kyanite and sillimanite. After being heated to 1350 °C at normal pressure, andalusite begins to transform to acicular mullite in parallel with the original crystal and form a strong mullite network, thereby, it has good characteristics such as strong fire resistance and slag resistance, high mechanical strength and chemical stability [1,2]. Consequently, andalusite is a superior material to produce refractory materials, and it has been widely used in spaceflight, metallurgy, ship and other industrial circles [3,4]. Andalusite to be used in the refractory industry should be separated from impurities such as Fe_2O_3, TiO_2, CaO, MgO, Na_2O and K_2O as much as possible. The content of Al_2O_3 is required to be above 60% in high-grade andalusite, and 52%−54% in low-grade andalusite. So, concentration process is necessary for industrial needs.

There are many methods for andalusite beneficiation such as hand sorting, gravity separation, magnetic separation and flotation. And the suitable method is adopted based on the mineral properties. For andalusite ore containing larger single crystals, process of gravity separation−magnetic separation can be used to obtain coarse concentrate. Flotation is the most common and effective method for fine andalusite flotation. Prior to andalusite flotation, adequate desliming and iron removal are necessary in order to decrease reagent consumption and improve flotation results. In addition, cationic collectors are used for flotation of gangue minerals such as micas, kaolinite and garnet which are easy to float and influence the concentrate grade due to good floatability. Then, andalusite is separated from the gangue minerals, mainly quartz.

The flotation process mainly includes alkaline process and acid process, which is related to the mineral surface potential and reagent system. In alkaline process, the optimum pH is 8−10, which is adjusted by NaOH or Na_2CO_3, and the carboxylic acid and its salt are used as collectors. However, the optimum pH 3−4 is mainly adjusted by H_2SO_4, and the sulfonate type collector is employed for the flotation of andalusite in acid process. Sodium silicate, lactic acid, citric acid, carboxymethocel and their combinations can be used for depressing gangue minerals.

There are many successful practices of andalusite beneficiation. YANG et al [5] studied the separation of coarse andalusite (0.5−1 mm) using *d*150 mm heavy medium cyclones, and an acceptable coarse concentrate

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with a grade of 58.78% Al_2O_3 and a recovery of 29.7% was obtained. LI and LI [6] presented the research achievements and application of DMG electromagnetic pulsating high gradient magnetic separator in iron removal from andalusite. ZHOU and ZHANG [7] found that a pre-treatment by desliming and pre-floating (to remove carbonaceous species) followed by flotation produced a concentrate assaying 56.5% Al_2O_3 at an aluminum recovery of 65.7%.

In this work, the separation of andalusite from quartz using sodium petroleum sulfonate as collector was investigated. In the molecular structure of sodium petroleum sulfonate, a highly-hydrophilic sulfo-group is connected with alkyl, the structural formula is RSO_3Na, R is a linear aliphatic alkyl with an average of 14−18 carbon atoms.

2 Experimental

2.1 Materials

The pure andalusite and quartz samples were taken from Xinjiang Uyghui Autonomous Region, China. The samples were handpicked, ground in porcelain mill and then sieved to collect 0.038−0.074 mm fraction for the flotation tests. The chemical analyses showed that the grade of Al_2O_3 was 59%, the purity of andalusite was above 95%, and the main impurity was quartz. The purity of quartz was 99.8%, the sample was immersed in diluted hydrochloric acid (around 10%) due to the presence of iron, then washed repeatedly with distilled water, and dried for later use.

The multi-element analysis results and the aluminum phase analysis results of the real ore sample are shown in Tables 1 and 2, respectively.

Table 1 Multi-element analysis results of real ore sample

Composition	Al_2O_3	TiO_2	SiO_2	TFe	Mg
Mass fraction/%	18.47	0.65	68.28	2.80	0.085
Composition	Ca	Mn	S	P	Ignition loss
Mass fraction/%	0.315	0.017	0.71	0.76	2.76

Table 2 Aluminum phase analysis results of real ore samples

Phase	Mass fraction of content/%	Occupancy/%
Al_2O_3 in andalusite	12.21	66.11
Al_2O_3 in other minerals	6.26	33.89
Total Al_2O_3	18.47	100.00

It can be seen that the main chemical compositions of the real ore samples are SiO_2 and Al_2O_3, followed by Fe, and a little TiO_2. Aluminum in the ore is not all distributed in andalusite, and the Al_2O_3 content in andalusite is 12.21%, accounting for 66.11%.

2.2 Flotation tests

Flotation tests of single minerals were performed on a 40 mL flotation machine at a constant impeller speed of 1650 r/min. Experiments were carried out at varying pH and reagent concentrations. For each test, 2 g mineral samples were placed into the flotation cell, decent amount of distilled water was added and stirred for 2 min. Then, reagents were successively added to the pulp with each conditioning time of 3 min according to the experiment requirements, and the flotation was performed for 4 min. The floating and non-floating fractions were separately dewatered, dried and weighed for assessment.

Flotation tests on the real ore sample were carried out in a series of 0.5−1.5 L flotation machine. For each test, 500 g samples were used. A desirable sulfuric acid, calcium lignosulphonate and sodium petroleum sulfonate were added and stirred for 3 min, respectively. The concentrate and tailing were separately dried, weighed and sampled to analyze the contents of Al_2O_3 and SiO_2 to calculate the yield and recovery.

2.3 Zeta potential measurement

Zeta potential was measured with a zeta potential analyzer (DELSA−440SX, USA). The mineral suspensions with 0.01% solid of size less than 3 μm were dispersed in a beaker by ultrasonic cleaning, and transferred to the rectangular capillary cell of the instrument after treatment with relevant reagents.

2.4 Infrared spectroscopic analysis

To investigate the mechanism between collector and minerals, the infrared spectra were obtained with a Fourier transform infrared spectrophotometer (740−FTIR, USA). The mineral samples of size less than 2 μm were treated with reagents in high concentration, dewatered, and washed 3 times using distilled water with the same pH value, and then dried in air. After that, the samples were pressed into flake in a specialized mould, and the flaky samples were placed in sample stand to be analyzed.

3 Results and discussion

3.1 Flotation behavior of single mineral

3.1.1 Effect of collector

The effect of pH on the flotation recovery of andalusite and quartz using sodium petroleum sulfonate as collector is shown in Fig. 1. It is shown that the andalusite exhibits good floatability at acidic pH values and the flotation recovery decreases with the increase of pH value. By contrast, quartz keeps very low flotation recovery at pH values of 2–12.

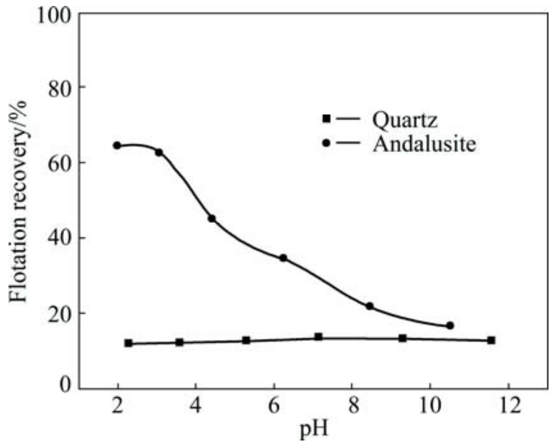

Fig. 1 Effect of pH value on flotation recoveries of andalusite and quartz at 1.2 g/L sodium petroleum sulfonate

The effect of collector concentration on the flotation recoveries of andalusite and quartz at pH 3 is shown in Fig. 2. With the increase of collector concentration, the flotation recovery of andalusite is gradually improved, and essentially unchanged when the concentration is higher than 1.2 g/L. However, quartz shows poor floatability as the flotation recovery is no more than 20%. The floatability of the two minerals demonstrates that sodium petroleum sulfonate is a selective collector for andalusite flotation, and the separation of andalusite from quartz is expected to be achieved at 1.2 g/L sodium petroleum sulfonate and around pH 3.

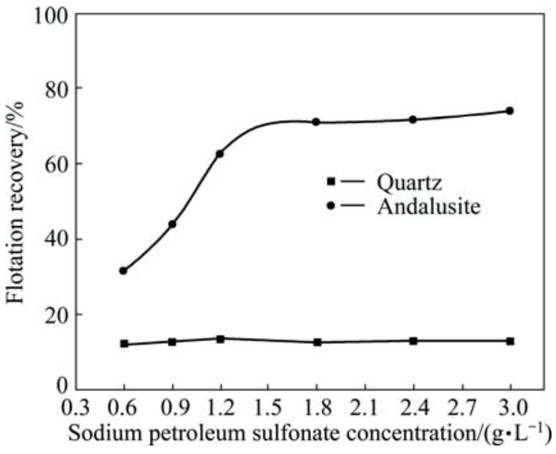

Fig. 2 Effect of sodium petroleum sulfonate concentration on flotation recoveries of andalusite and quartz

3.1.2 Effect of metal ions

In fact, there usually exist various kinds of inevitable ions in the real ore flotation pulp, especially some multivalent metal ions such as Al^{3+}, Fe^{3+}, Ca^{2+} and Mg^{2+} which may activate quartz and deteriorate the flotation selectivity.

Figures 3 and 4 demonstrate the flotation response of andalusite and quartz as a function of metal ion concentration at 1.2 g/L sodium petroleum sulfonate and pH 3, respectively. With the increase of Al^{3+} concentration, the flotation recoveries of andalusite and quartz decrease with no effect on their flotation separation in a certain concentration range, so it is needed to decrease the Al^{3+} concentration in the real ore flotation pulp so as to decrease its effect on the floatability of andalusite. Fe^{3+} activates andalusite and quartz distinctly, leading to the flotation without selectivity, and seriously influencing the flotation separation between andalusite and quartz. While Ca^{2+} and Mg^{2+} have little effect on the floatability of andalusite and quartz.

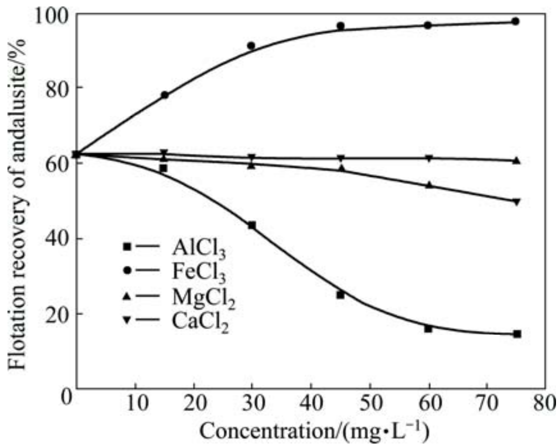

Fig. 3 Flotation response of andalusite as function of metal ion concentration at 1.2 g/L sodium petroleum sulfonate and pH 3

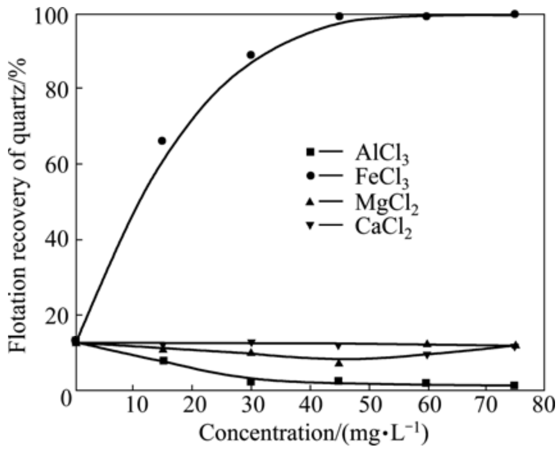

Fig. 4 Flotation response of quartz as function of metal ion concentration at 1.2 g/L sodium petroleum sulfonate and pH 3

3.1.3 Effect of depressant

From the above tests, it can be seen that it is difficult to separate andalusite from quartz by using sodium petroleum sulfonate as collector at pH 3 in the presence of Fe^{3+} in the pulp. The effect of calcium lignosulphonate concentration on the flotation recovery of andalusite and quartz activated by Fe^{3+} is shown in Fig. 5. With the increase of calcium lignosulphonate concentration, the flotation recovery of quartz decreases more obviously than that of andalusite, and calcium lignosulphonate presents a great difference in the floatability of andalusite and quartz at pH 3, so it is possible to achieve their flotation separation with calcium lignosulphonate as depressant.

3.2 Flotation separation tests

Previous trial tests indicated that iron removal by magnetic separation, desliming and pre-floating to remove mica are necessary before andalusite flotation. The closed test of the whole flowsheet was conducted. The flowsheet is shown in Fig. 6, and the results are given in Table 3.

The andalusite concentrate with 53.46% Al_2O_3 and quartz concentrate with 92.74% SiO_2 are obtained.

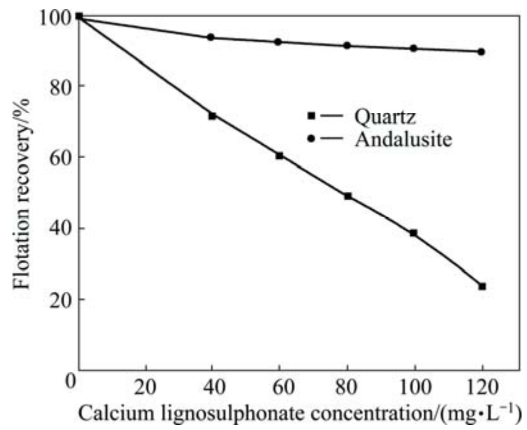

Fig. 5 Influence of calcium lignosulphonate concentration on floatability of andalusite and quartz at 45 mg/L $FeCl_3$, 1.2 g/L sodium petroleum sulfonate and pH 3

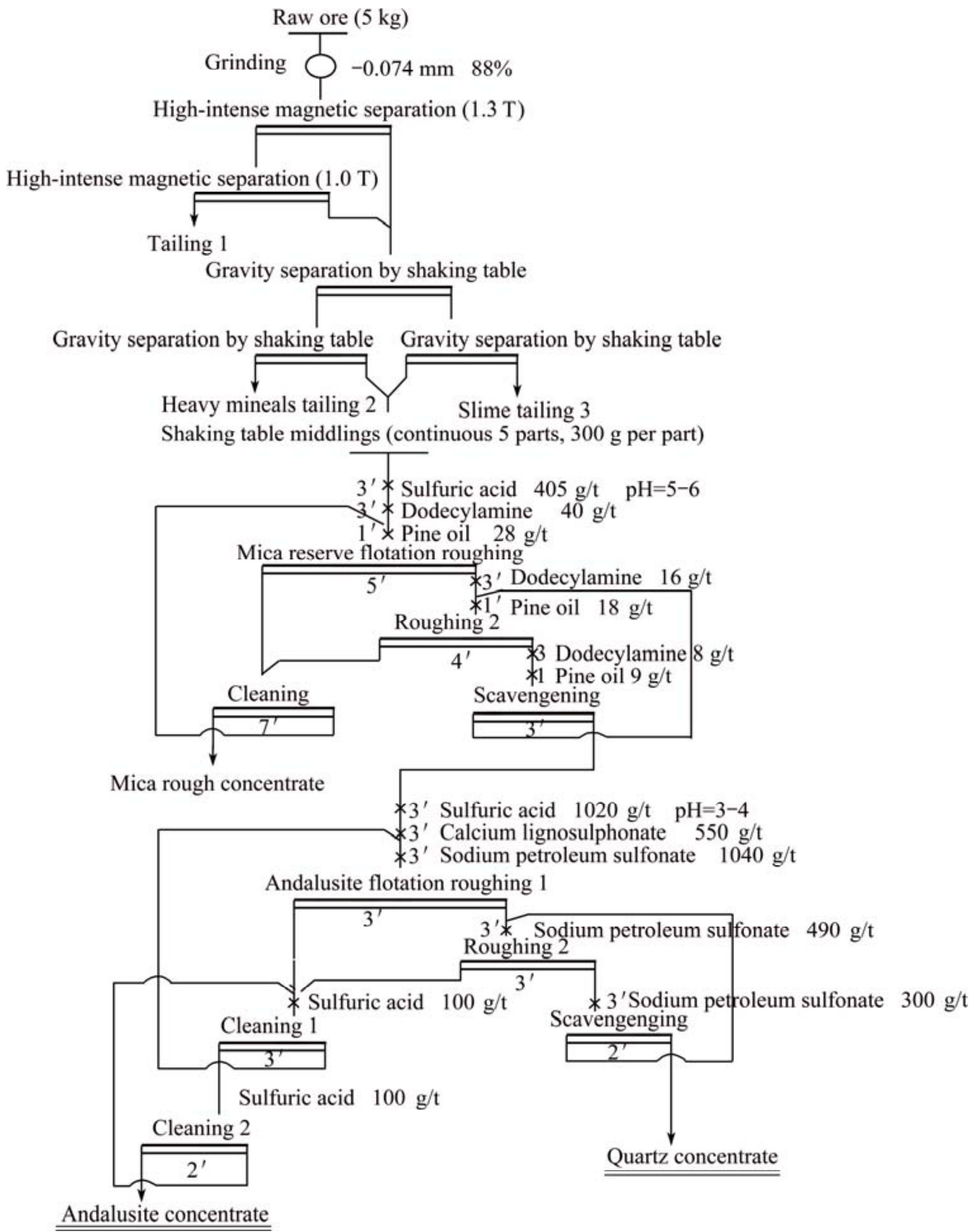

Fig. 6 Flotation flowsheet of closed circuit experiment

Table 3 Closed circuit experiment results of real ore

Product	Yield/%	Al_2O_3 grade/%	Al_2O_3 recovery/%	SiO_2 grade/%	SiO_2 recovery/%
Andalusite concentrate	13.80	53.46	39.94		
Quartz concentrate	30.95	4.28	7.17	92.74	42.04
Mica rough concentrate	16.25	19.16	16.86		
Slime tailing 3	30.16	16.20	26.44		
Heavy minerals tailing 2	1.95	8.81	0.93		
Tailing 1	6.89	23.21	8.66		
Raw ore	100.00	18.47	100.00		

According to the aluminum phase analysis results, the andalusite recovery of the concentrate is 60.41%, which is a fairly good index for this complex and refractory andalusite ore.

This depicts that the flotation separation of andalusite against quartz is accomplished using sodium petroleum sulfonate as collector and calcium lignosulphonate as depressant at pH 3. At the same time, the quartz concentrate is obtained, making the best use of the mineral resource.

3.3 Zeta potential measurement results

The effect of pH value on zeta potential of andalusite and quartz in distilled water is given in Fig. 7. It is seen that the isoelectric points of andalusite and quartz are about 4.5 and 2, respectively. At pH 3, the andalusite surface is positively charged while the quartz surface is negatively charged, so sodium petroleum sulfonate, an anionic collector, can adsorb and float andalusite by electrostatic force.

The effect of metal ion concentration on zeta potential of andalusite and quartz in distilled water at pH 3 is given in Figs. 8 and 9, respectively. Al^{3+}, Ca^{2+} and Mg^{2+} barely set influence on zeta potential of andalusite and quartz, playing a role in compressing the thickness of electric double layer. However, the effect of Fe^{3+} is extremely strong, with the increase of $FeCl_3$ concentration, zeta potentials of quartz and andalusite become more and more positive, which is enough to make zeta potential of quartz change to positive value at 15 mg/L $FeCl_3$, indicating that Fe^{3+} is adsorbed on the surface of andalusite and quartz, which is consistent with the previous researches [8].

3.4 Infrared spectroscopic analysis results

The infrared spectra of sodium petroleum sulfonate,

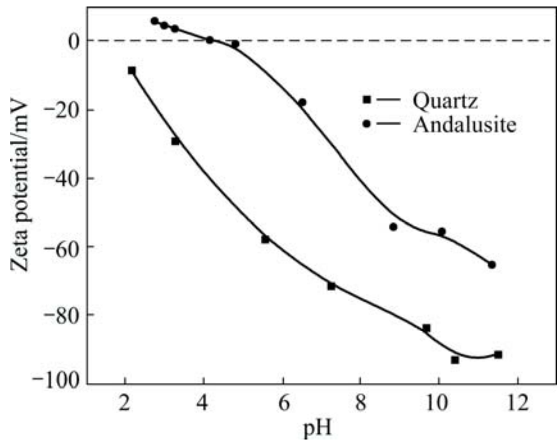

Fig. 7 Zeta potentials of andalusite and quartz as function of pH

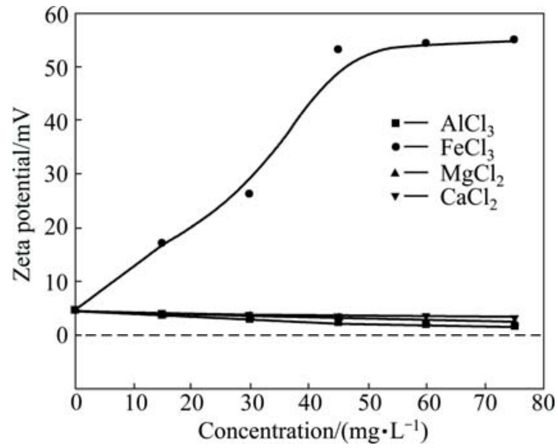

Fig. 8 Effect of metal ion concentration on zeta potential of andalusite at pH 3

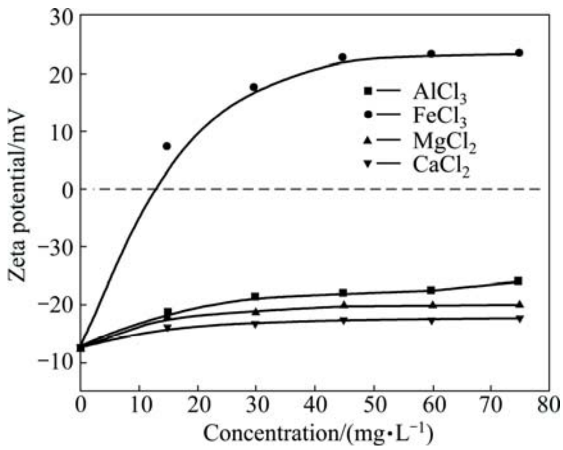

Fig. 9 Effect of metal ion concentration on zeta potential of quartz at pH 3

andalusite with or without being conditioned in the reagent solutions at pH 3 are given in Fig. 10. The spectrum (Fig. 10(a)) for untreated andalusite exhibits intense absorption bands at 900−1100 cm^{-1} due to the symmetrical and asymmetrical vibration of silica tetrahedron and 400−750 cm^{-1}, possibly owing to the deformation vibration of silica tetrahedron and the vibration of aluminium−oxygen octahedron [9]. The peaks at 1058 and 1198.8 cm^{-1}, characteristic of sulfo-group along with the peak at 826.5 and 891.6 cm^{-1} (S—O—C stretching), 2922.8 and 2725.6 cm^{-1} (C—H stretching), and 1457.6 and 1375.3 cm^{-1} (C—H bending) are observed on the spectrum (Fig. 10(b)) for sodium petroleum sulfonate. The infrared spectra of andalusite treated with reagents (Figs. 10(c), (d) and (e)) show the distinct peak of sulfo-group and the peak of C—H stretching, while the absorption band at 400−750 cm^{-1} is reduced, suggesting that there exists chemical adsorption by ionic bonding or donor-recipient bonding with Al atom of unsaturated valence or coordinate valence in andalusite lattice, and sodium petroleum sulfonate can adsorb on the surface of andalusite whether $FeCl_3$ and calcium lignosulphonate exist or not, which is consistent with flotation results.

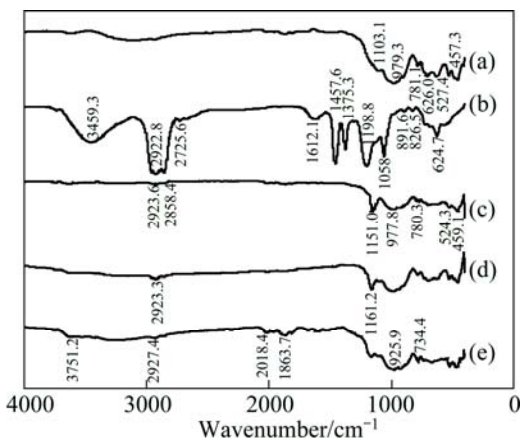

Fig. 10 Infrared spectra of andalusite (a), sodium petroleum sulfonate (b), andalusite + sodium petroleum sulfonate (c), andalusite + $FeCl_3$ + sodium petroleum sulfonate (d) and andalusite + $FeCl_3$ + calcium lignosulphonate + sodium petroleum sulfonate (e)

3.5 Discussion

Andalusite is a type of silicate mineral with island structure. According to its structural features, the liberation of andalusite generally occurs on the Al^{3+} dominant surface with the breaking of Al—O bond, while the Si—O bond is seldom broken. Therefore, the ion exposed on andalusite surface is Al^{3+} which can make the surface adsorb anionic collectors easily [8].

At present, the common collectors used in andalusite flotation are mainly oleic acid [10], sodium oleate [11], hydroximic acid [12], sulfonate [13] and other anionic collectors. In addition, the combined collectors are also extensively used [14,15]. Due to the high selectivity to andalusite, there are many practices using alkyl sulfonate as collector in China and foreign countries. The adsorption between andalusite surface and alkyl sulfonate is only physical adsorption when alkyl sulfonate has a smaller molecular mass, while both physical adsorption and chemical adsorption occur with larger relative molecular mass, and physical adsorption makes more contributions to flotation [16]. Research has shown that sodium dodecyl sulfate (SDS) shows better favorable flotation performance than dodecylamine and sodium oleate in micro-flotation of pure mineral sample, and successfully applies to the real ore flotation [17]. The FTIR results show that the interaction between andalusite and sodium dodecyl benzene sulfonate (SDBS) contains not only physical adsorption but also chemical adsorption [9,18].

Moreover, many researches have been conducted on quartz activated by metal ions in anionic collector system. Scholars point out that the pH range of metal ions activating quartz is 2.8−7.8 for Fe^{3+}, 3.4−9.0 for Al^{3+}, 11.6−13.2 for Ca^{2+} and 9.4−12.0 for Mg^{2+} [19]. So, only Fe^{3+} can activate quartz at pH 3, which accords with the flotation results in this work. There are two opinions on the activation mechanism, one considers that hydroxo-complex of metal ion is the effective component for the activation, the other advocates surface sediment of metal hydroxide. SUN and YIN [16] found that the adsorption on the mineral surface occurred in the hydroxide form for the metal ions with high electrovalence and small radius such as Fe^{3+} and Al^{3+}, and in the form of hydroxo-complex for metal ions with low electrovalence and large radius such as Fe^{2+} and Ca^{2+}. In addition, both forms occur for metal ions with medium electrovalence and radius such as Cu^{2+}, and it is related to pH value whether adsorption form dominates.

4 Conclusions

1) Sodium petroleum sulfonate is a selective collector for andalusite flotation at acidic pH values. While the floatability of quartz is close to that of andalusite in the presence of Fe^{3+}, and calcium lignosulphonate presents good selective inhibition to quartz, so it is possible to achieve their flotation separation with calcium lignosulphonate as depressant.

2) The real ore test results show that the flotation separation of andalusite from quartz is achieved, and the andalusite concentrate with 53.46% Al_2O_3 and quartz concentrate with 92.74% SiO_2 is obtained.

3) The zeta potential and FT-IR spectra show that sodium petroleum sulfonate can adsorb on the surface of andalusite, and chemical adsorption occurs.

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石油磺酸钠对红柱石和石英浮选分离的影响

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摘 要：采用石油磺酸钠作捕收剂研究红柱石和石英的可浮性，并成功应用于实际矿石的浮选分离，通过动电位测试以及红外光谱分析解释药剂对矿物的捕收性能。单矿物浮选试验结果表明，在酸性 pH 条件下红柱石有良好的可浮性，而石英在整个 pH 范围内可浮性均较差。当 pH=3 时，Fe^{3+}的存在明显活化了石英，从而导致两种矿物可浮性相似，木质素磺酸钙对石英具有良好的选择性抑制作用。实际矿石分离试验结果显示，最终获得 Al_2O_3 品位为 53.46%的红柱石精矿和 SiO_2 品位为 92.74%的普通石英砂精矿。动电位测试以及红外光谱分析结果表明，石油磺酸钠在红柱石表面发生了化学吸附。

关键词：浮选分离；红柱石；石英；石油磺酸钠

(Edited by Wei-ping CHEN)