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Effects of citric acid on separation of sillimanite from quartz^①

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[Abstract] Quartz is the main gangue mineral of sillimanite. The results show that Al^{3+} and Fe^{3+} ion can activate the floatation of quartz and make the separation of quartz and sillimanite difficult when anion collector is used, and citric acid can inhibit the quartz activated by metallic ion and have slight influence on the sillimanite. X-ray photoelectronic energy spectrum analysis indicates that there are obvious electronic energy peaks on the surface of the quartz before citric acid is added into the ore pulp in presence of Al^{3+} and Fe^{3+} , and after citric acid is added, the energy peak vanished. So citric acid can make Al^{3+} and Fe^{3+} on the surface of quartz solve and decrease the active points on the surface of quartz which can adsorb anion collector.

[Key words] sillimanite; quartz; citric acid; interaction mechanism

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1 INTRODUCTION

Sillimanite($\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$) is a kind of silicate mineral. It is the main material of excellent refractory in industry production, such as metallurgy, glass work, ceramics and so on^[1, 2]. As the sillimanite in structure is acicular, has similar specific gravity to associated mineral, and has no magnetism, it is very difficult to separate sillimanite from associated minerals by gravity separation or magnetism separation solely. Furthermore, the major associated mineral quartz is not a kind of silicate but a kind of oxide^[3, 4], intergrowth relationship is complex, and all kinds of ions in the ore pulp can decrease the differences in the surface character^[5, 6], so it is very difficult to separate sillimanite from quartz in floatation^[7, 8]. The authors have investigated different depressants used to increase the selectivity of floatation and developed a new floatation circuits. This paper focuses on effects of citric acid on the floatation separation of sillimanite from quartz.

2 EXPERIMENTAL

Sillimanite was taken from some sillimanite mine in Hubei Province, P. R. China; its chemical composition is shown in Table 1.

Table 1 Chemical compositions of sillimanite ores(%)

Al_2O_3	SiO_2	Fe_2O_3	K_2O
36.72	44.4	8.05	5.00
Na_2O	CaO	MgO	Loss on ignition
1.38	1.30	0.15	1.16

Preparation of pure sillimanite: original ore was

crushed and screened into the sample ore of 0.074~0.150 mm, then the magnetite and other gangue mineral in it was removed by shaking table. Sillimanite concentrate was further concentrated as following processes.

1) Sillimanite concentrate $\xrightarrow{\text{heavy liquid separation}}$ heavy liquid is the mixture of KI and HgI_2 , specific gravity 3.0 $\xrightarrow{\text{pure sillimanite}}$ pure sillimanite.

2) The pure sillimanite was washed by distilled water repeatedly and dried in low temperature. This kind of sample had purity of 93% and was applied in floatation experiment. The sample in size range from 0.038 to 0.074 mm was applied in adsorption and X-ray photoelectron energy spectrum test.

The content of SiO_2 in the quartz was 99.95% and the agents were analytically pure in this experiment and the water was distilled water.

3 RESULTS AND DISCUSSION

3.1 Floatation experiment of pure mineral

Fig. 1 shows the relationship of pH of ore pulp and the recovery of sillimanite floatation in the condition that NaOL was used as collector. When pH is from 7 to 9, the floatability of sillimanite is very good, its recovery is above 90%, but in this range quartz can't be floated.

When pH is from 7 to 8, the effect of the content of NaOL on the floatability of sole mineral is shown in Fig. 2.

According to Fig. 2, when the concentration of NaOL is low, with the increasing of concentration the adsorption on the surface of sillimanite and the recovery of sillimanite floatation increase. When the content of NaOL arrives at $2.3 \times 10^{-4} \text{ mol/L}$, the sill-

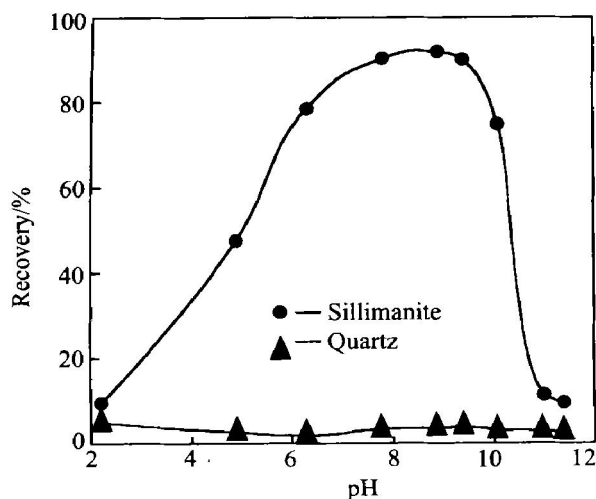


Fig. 1 Relationship between pH and floatation recovery of sillimanite and quartz

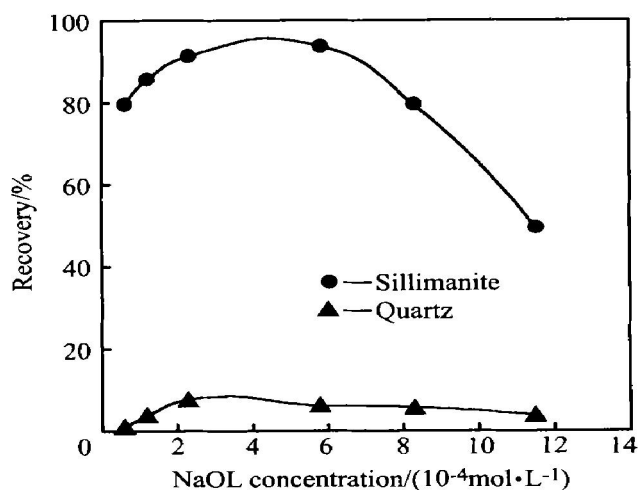


Fig. 2 Relationship between the concentration of NaOL and floatation recovery of sillimanite and quartz

manite will be floated. But when its content arrives at critical micellar concentration (CMC is 2.1×10^{-3} mol/L), the floatability of sillimanite becomes poor. So experiment proves that sillimanite can be floated if NaOL covers 10% of the surface area in the mineral^[9], but quartz still can't be floated with the increasing of the concentration. This result proves that the quartz in the ore pulp can't be floated when the anion collector is used.

3.2 Effect of Al^{3+} and Fe^{3+} on floatation of sillimanite and quartz

Fig. 3 shows the effect of pH on the floatation of sillimanite and quartz, when the concentration of NaOL is 2.3×10^{-4} mol/L, of FeCl_3 is 6.4×10^{-5} mol/L. The result shows that because of the existence of Fe^{3+} . When pH is in the range from 3 to 7, the floatation of quartz becomes easier. This pH range is closed to the optimum pH of sillimanite floatation. So Fe^{3+} is one of the main factors that af-

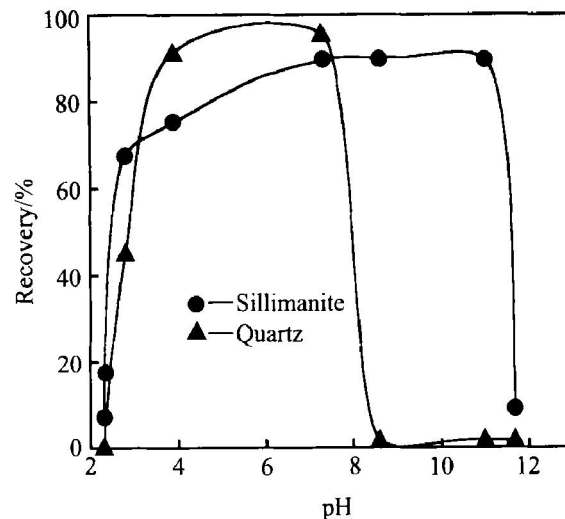


Fig. 3 Relationship between recovery and pH in presence of Fe^{3+} (6.36×10^{-5} mol/L)

fect the floatation. This result is in accordance with the report of Ref. [10] in which pH is in the range from 2.7 to 7.3.

Fig. 4 shows that the pH of ore pulp affects the floatation of sillimanite and quartz with the existence of AlCl_3 , when pH is close to the optimum value of sillimanite floatation that is from 7 to 9. So Al^{3+} is also one of the main factors that affect the floatation^[11]. This result is in accordance with the report in which pH is from 2.9 to 9.8.

3.3 Effect of citric acid on floatation of sillimanite and quartz

For eliminating the effect of Al^{3+} and Fe^{3+} on the floatation of sillimanite and quartz, the selection of proper floatation inhibitor is very important. It is found in the experiment that citric acid has strong inhibition on Al^{3+} and Fe^{3+} and the inhibition on the floatation of sillimanite is very weak. So the authors selected citric acid as the inhibitor. The results are shown in Fig. 5.

According to Fig. 5, when pH was from 7 to 8 and the concentration of citric acid was larger than

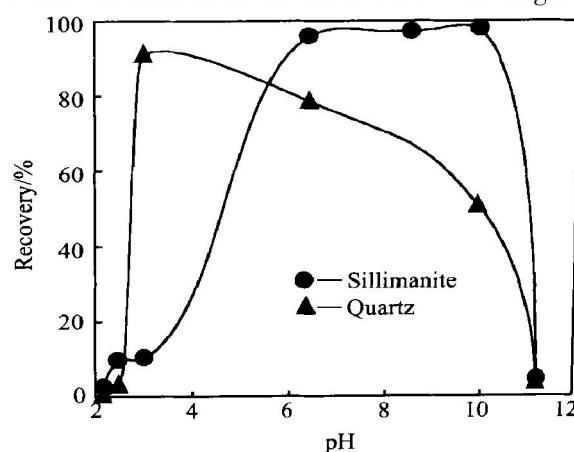


Fig. 4 Relationship between recovery and pH in presence of Al^{3+} (4.3×10^{-5} mol/L)

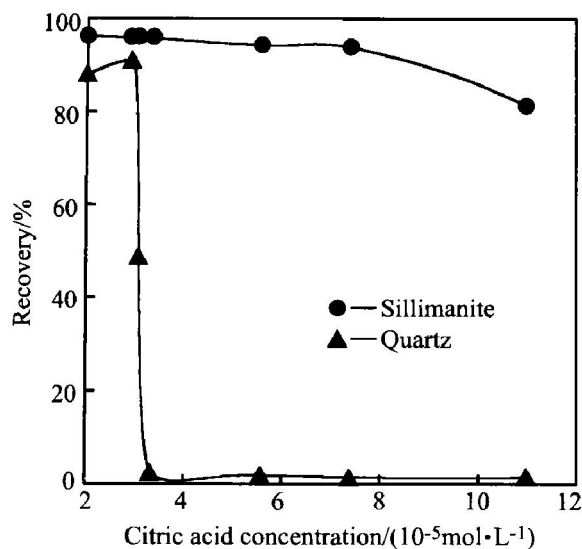


Fig. 5 Relationship between recovery and dosage of citric acid

6.67×10^{-5} mol/L, the inhibition of citric acid on Al^{3+} and Fe^{3+} was very strong, but when its concentration was smaller than 6.67×10^{-5} mol/L, the inhibition was weak, and its effect on sillimanite was weak. So citric acid can inhibit the floatation of sillimanite and quartz selectively.

3. 4 Interaction mechanism of citric acid on surface of sillimanite and quartz

To make out the interaction mechanism of citric acid on sillimanite and quartz with the existence of Al^{3+} and Fe^{3+} , the authors used XPS photoelectron energy spectrum to test the $\text{Al}2\text{p}$ and $\text{Fe}2\text{p}$ energy peak, the results are shown in Figs. 6 and 7.

According to Fig. 6, the electronic chemical displacement of sillimanite is 0.3 eV after citric acid is used. So the action of the citric acid on the surface of sillimanite is chemical interaction^[12].

According to Fig. 7, on the surface of the quartz activated by Al^{3+} , there is obvious $\text{Al}2\text{p}$ electronic peak and the binding energy is 74.25 eV. After citric

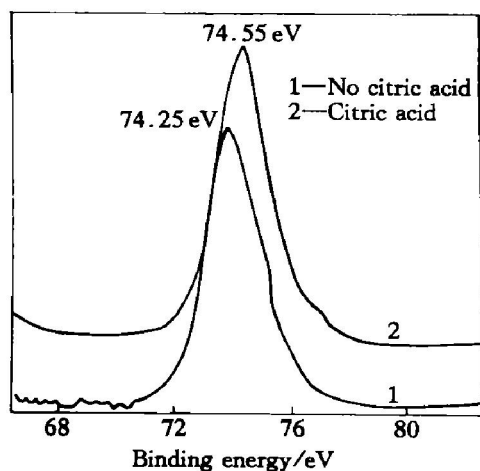


Fig. 6 XPS photoelectron spectra of $\text{Al}2\text{p}$ on sillimanite surface before and after treatment with citric acid

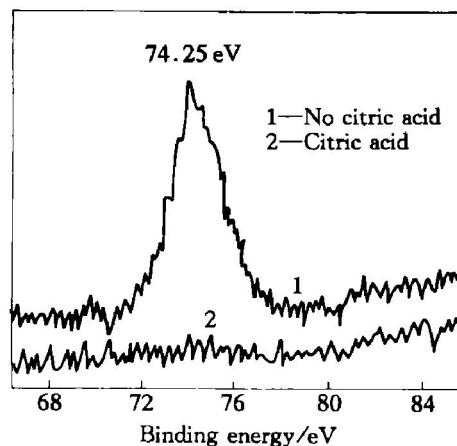


Fig. 7 XPS photoelectron spectra of $\text{Al}2\text{p}$ on Al^{3+} activated quartz surface before and after treatment with citric acid

acid is used, the peak vanishes. This result shows that after the citric acid is used, the adsorbed Al^{3+} is solved and the citric acid makes chemical interaction on the surface of the quartz.

According to Fig. 8, the same chemical interaction is made by the citric acid on the surface of quartz. Fe^{3+} is solved and the citric acid is adsorbed on the surface of the quartz. The energy peak vanishes after the citric acid is used. All these results show that the citric acid decreases the action points that can adsorb the collector on the surface of quartz so that makes the quartz inhibited.

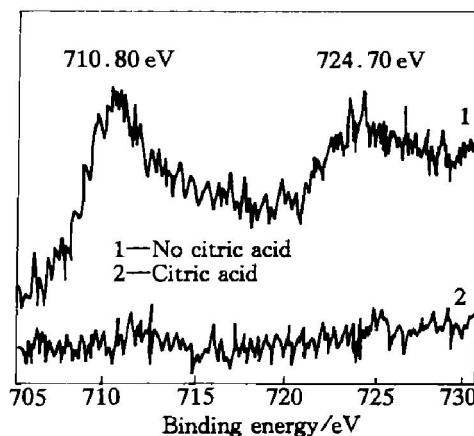


Fig. 8 XPS photoelectron spectra of $\text{Fe}2\text{p}$ on Fe^{3+} activate quartz surface before and after treatment with citric acid

4 CONCLUSIONS

1) When the NaOL is used as collector, the pure sillimanite can be floated and the floatation of the quartz is difficult.

2) When the NaOL is used as collector, the Al^{3+} and Fe^{3+} in the ore pulp can activate the floatation of the quartz. In the pH range from 3 to 10, Al^{3+} can activate the quartz; In the pH range from 3

to 7, Fe^{3+} can activate the quartz. So the separation of the quartz and the sillimanite is difficult.

3) Citric acid can inhibit the quartz activated by the metallic ions strongly, but its inhibition on the sillimanite is weak. So it is an effective depressant on quartz in sillimanite flotation.

4) Citric acid can solve the Al^{3+} and Fe^{3+} and decrease the active points on the surface of quartz which can adsorb anion collector.

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