Home

Paper No. 145

FLOTATION SEPARATION OF SCHEELITE FROM FLUORITE AND CALCITE

X Qiu[1], X Zhou[1], H Hu[1] and G Q Fu[1]

ABSTRACT

Ca-containing gangue minerals such as Fluorite, Calcite have same surface activity point--calcium ions and approximate floatability with scheelite, it is difficult to achieve good dressing index of rough concentrate of scheelite. Mono-mineral experiments and ore tests indicate that, according to mineral composition, gangue minerals can be inhibited selectively by adopting suitable regulators, then the separation of scheelite from gangue minerals can be realized effectively. Mechanism analysis was taken by zeta potentials measurements and FTIR tests. Good dressing indexes are also obtained in practical ore tests and industrial tests.

Keywords: scheelite, fluorite, calcite, regulator, flotation separation

INTRODUCTION

In scheelite flotation, gangue minerals such as Fluorite and Calcite have the same surface-active cation (Ca^{2+}) with scheelite minerals and strong binding capacity with the fatty acid collectors. So the floatability of scheelite is close with that of Fluorite and Calcite and it is difficult to get good scheelite rough concentrate indexes. It is necessary to research regulators with high selectivity to achieve good indexes for scheelite concentrate.

THE FLOATABILITY TESTS AND DISCUSSION

Preparation of samples and conditions

The mono minerals were taken respectively from the rich ore of scheelite, Fluorite and Calcite by crushing, grinding and purification. The content of scheelite in the mono mineral is 91.45%, the content of fluorite is 99.90% and the content of calcite 99.90%. Finally, one part of the pure samples was treated to -0.074 mm by grinding and another part was treated to -0.002mm for zeta potentials measurements and FTIR tests.

The reagent NaOH, which was used as a regulator in the flotation tests for mono minerals, was analytical reagent. The other reagents such as Na_2SiO_3, the new fatty acids collector TAB-3, common collectors sodium oleate and oxidized paraffin soap (733, 731) were all industrial products. As X Zhou (2010) showed that the new fatty acids collector TAB-3 have strong adsorption ability on scheelite and weak adsorption ability on the calcium minerals.

All the flotation tests were done at the temperature of 30℃ in a 35ml flotation machine, and3.0 g sample is used in each test. After adding pH regulator, Na_2SiO_3 and collector sequently and the conditioning time is 2 min, 3 min and 4 min respectively. After flotation for 4 minutes, the concentrate is achieved and weighted to calculate the recovery.

The zeta potentials of minerals is measured by Zetaplus Zeta analyzer and every sample is measured three times and averaged. The infrared spectral analysis results are produced by FTIR tests.

1. Guangzhou Research Institute of Nonferrous Metals, Guangzhou, Guangdong PRC, 510650. Email: qxyysy66@163.com

The mono-mineral tests

Effect of pH on the floatability of minerals

The effect of pH on flotation performance of Scheelite, Fluorite and Calcite is shown in Figure 1 while the dosage of the reagent TAB-3 is 50mg/L and using NaOH as the regulator. Figure 1 shows that the floatability of Fluorite is better than that of Calcite. When pH > 6, the recovery of scheelite is higher than 90%. The floatability of scheelite is better when pH = 8.5 and is remarkably weakened when pH > 10.

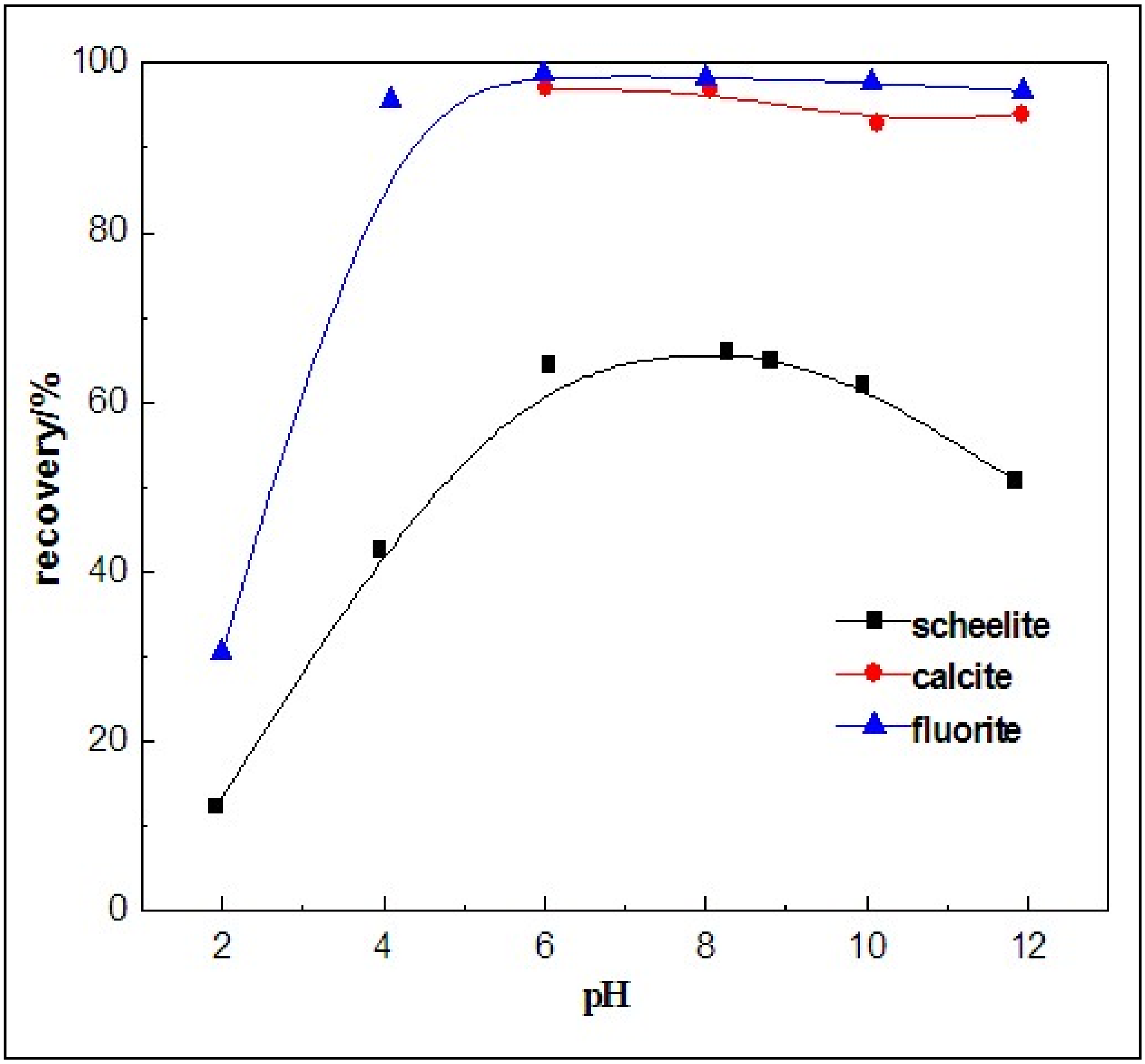

Figure 1. Effect of pH on flotation performance of Scheelite, Fluorite, and Calcite

Effect of TAB-3 dosage on the floatability of minerals

The effect of TAB-3 dosage on flotation performance of Scheelite, Fluorite and Calcite was studied at the condition of pH 8.5 and only the reagent TAB-3 is added. The results are shown in Figure 2. From Figure 2, the recovery of Scheelite increases visibly with the increase of the TAB-3 dosage.

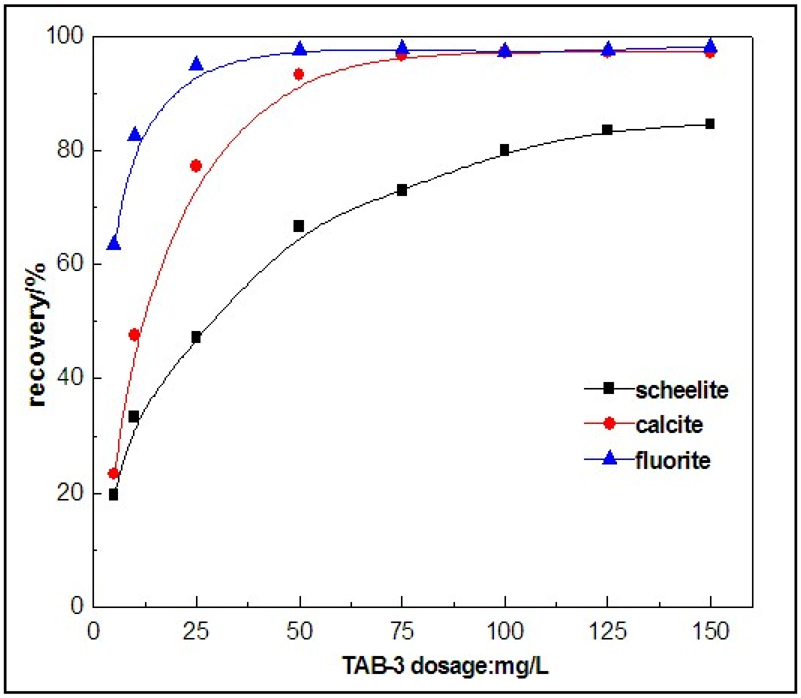

Figure 2. Effect of TAB-3 dosage on flotation performance of minerals when pH is 8.5

Effect of pH on the floatability of minerals when using Na_2SiO_3

The effect of pH on flotation performance of Scheelite, Fluorite and Calcite is shown in Figure 3 while the dosage of the reagent Na_2SiO_3 is 400 mg/L and using NaOH as the regulator. From Figure 3, the recovery of Fluorite and Calcite reduces obviously when $8.0<pH<11.0$. When $pH\geq 11.0$, the recovery of Fluorite reduces sharply with the increase of pH, but the recovery of calcite increases obviously.

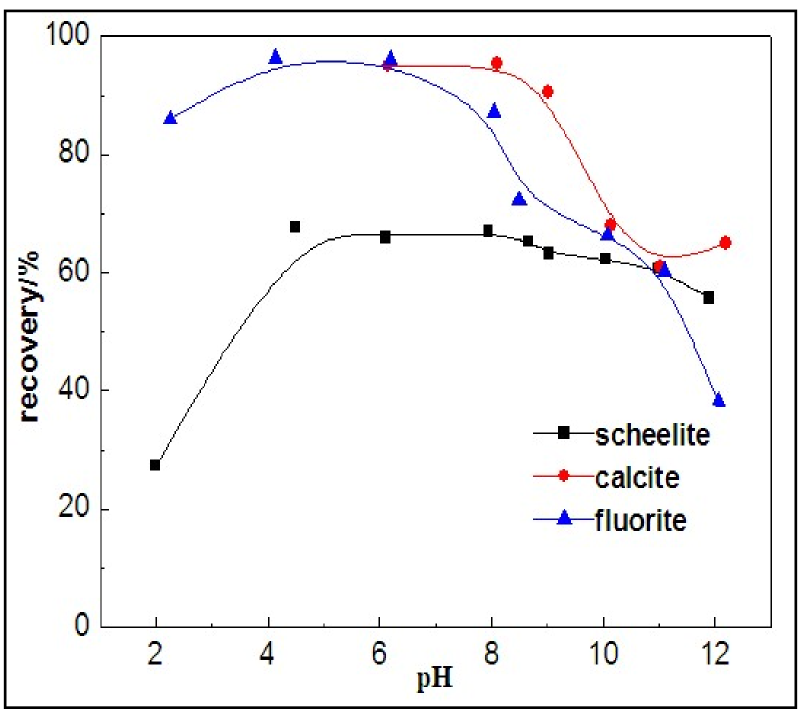

Figure 3. Effect of pH on flotation performance of scheelite, fluorite and calcite when using Na2SiO3

Effect of Na_2SiO_3 dosage on the floatability of minerals

While the dosage of the reagent TAB-3 is 100 mg/L, pH=10 and using NaOH or Na_2CO_3 as the regulator, the effect of pH on flotation performance of Scheelite, Fluorite and Calcite is shown in Figure 4.

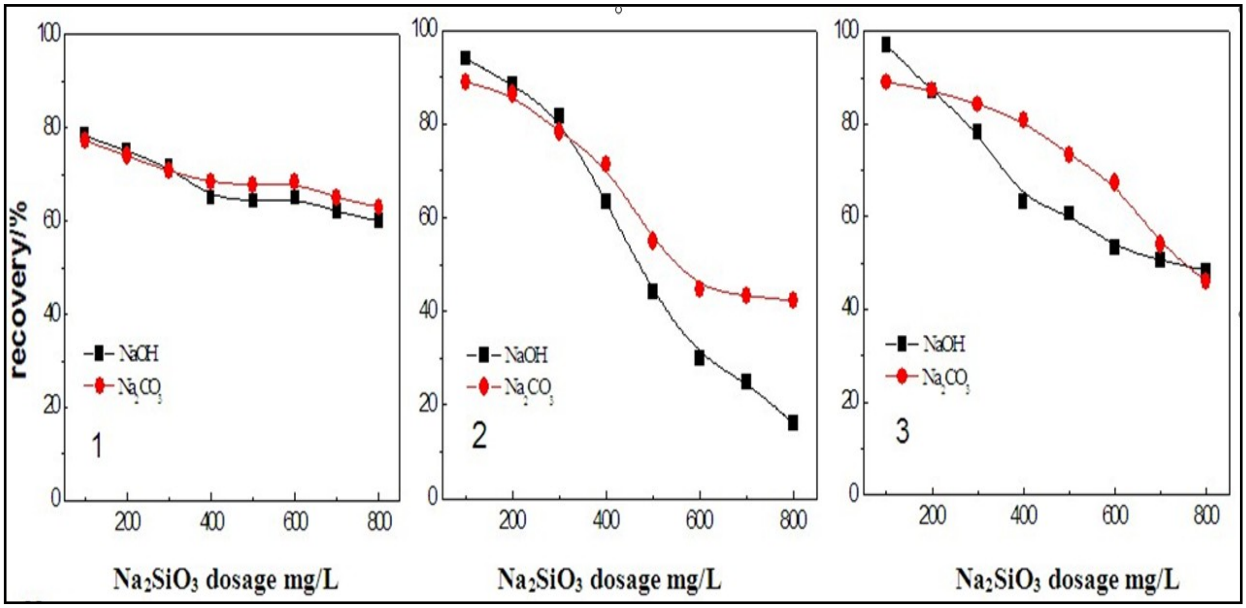

Figure 4. Effect of TAB-3 dosage on flotation performance of minerals when using Na2CO3 or NaOH as pulp regulators respectively

From Figure 4, the floatability of Scheelite, Fluorite and Calcite is better when using Na_2CO_3 as the regulator. However, when using NaOH as the regulator, the Na_2SiO_3 can depress Fluorite obviously when the dosage is above 400 mg/L.

The surface potential results of minerals and discuss

Effect of pH on the surface potential of minerals

While using NaOH as the regulator and undergoing a reaction with the reagents, the relation between pH and the surface potential of Scheelite, Fluorite and Calcite is shown in Figure 5.

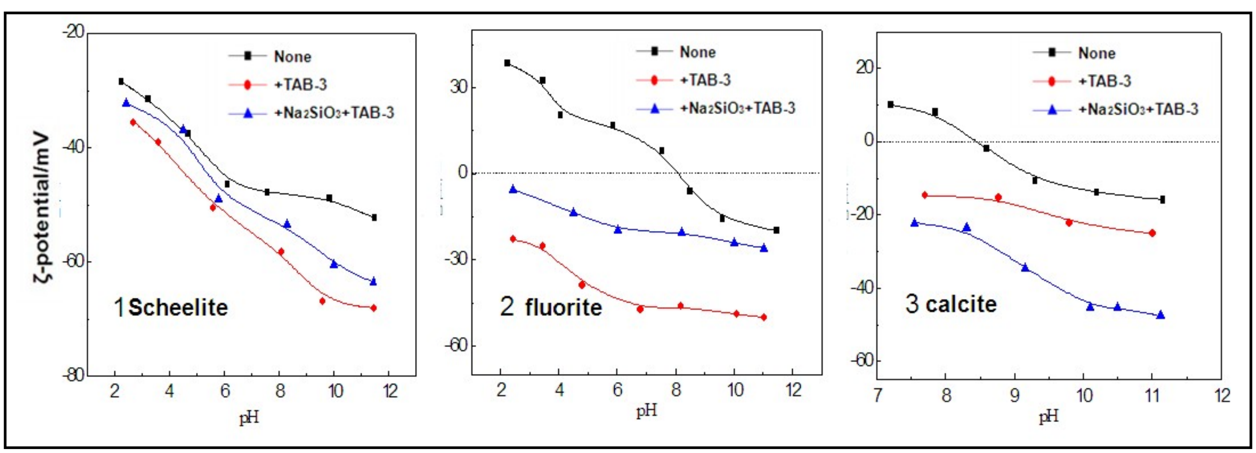

Figure 5. The relation between pH and the surface potential of scheelite, fluorite and calcite （$C_{Na2SiO3}$＝400mg/L，C_{TAB-3}＝100mg/L；1.scheelite；2.fluorite；3.calcite）

From Figure 5, when using the reagent TAB-3 and Na_2SiO_3, the surface potential of scheelite shifts slightly and the surface potential is closely with that, only when the reagent TAB-3 is used, the surface potential of fluorite shifts a bit further and is different from that of only using the reagent TAB-3; the surface potential of calcite shifts the farthest.

Effect of Na2SiO3 dosage on the surface potential of minerals

While the dosage of the reagent TAB-3 is 100 mg/L, pH=10 and using NaOH or Na_2CO_3 as the regulator, the relation between the dosage of Na_2SiO_3 and the surface potential is shown in Figure 6.

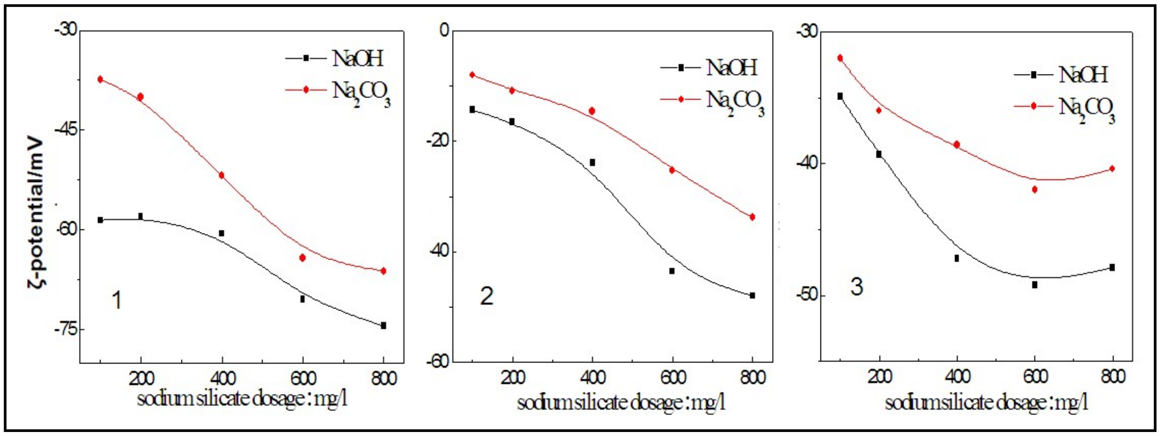

Figure 6. Effect of Na_2SiO_3 dosage on the surface potential of minerals when using Na_2CO_3 or NaOH as pulp regulators respectively （CNa_2SiO_3＝400mg/L，CTAB-3＝100mg/L；1.scheelite；2.fluorite；3.calcite）

From Figure 6, the surface potential of Scheelite, Fluorite and Calcite in Na_2CO_3 is higher than that in NaOH. The order of the surface potential difference extent between the two solution mediums is scheelite<fluorite<calcite.

The IR results of the reagent TAB-3 and minerals

IR of the reagent TAB-3

Figure 7 shows the infrared spectrum of the reagent TAB-3. In the infrared spectrum, the peak at 2921.6 cm^{-1} wave number was assigned to C-H asymmetric stretching vibration in $-CH_3$ bond and the peak at 2854.1 cm^{-1} wave number was assigned to C-H symmetric stretching vibration in $-CH_2$ - bond. The peak of C-O stretching vibration in carboxyl group is around 1560.1cm^{-1}.

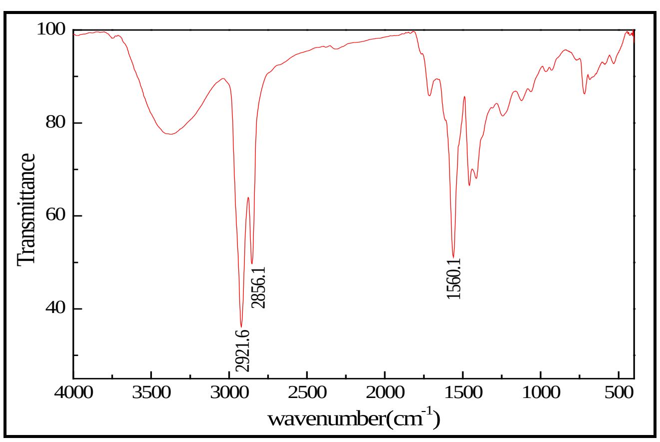

Figure 7. Infrared spectrum of the reagent TAB-3

IR of minerals after using the reagents

Figure 8 shows the infrared spectrum of Scheelite, Fluorite and Calcite treated with Na_2SiO_3 and TAB-3.

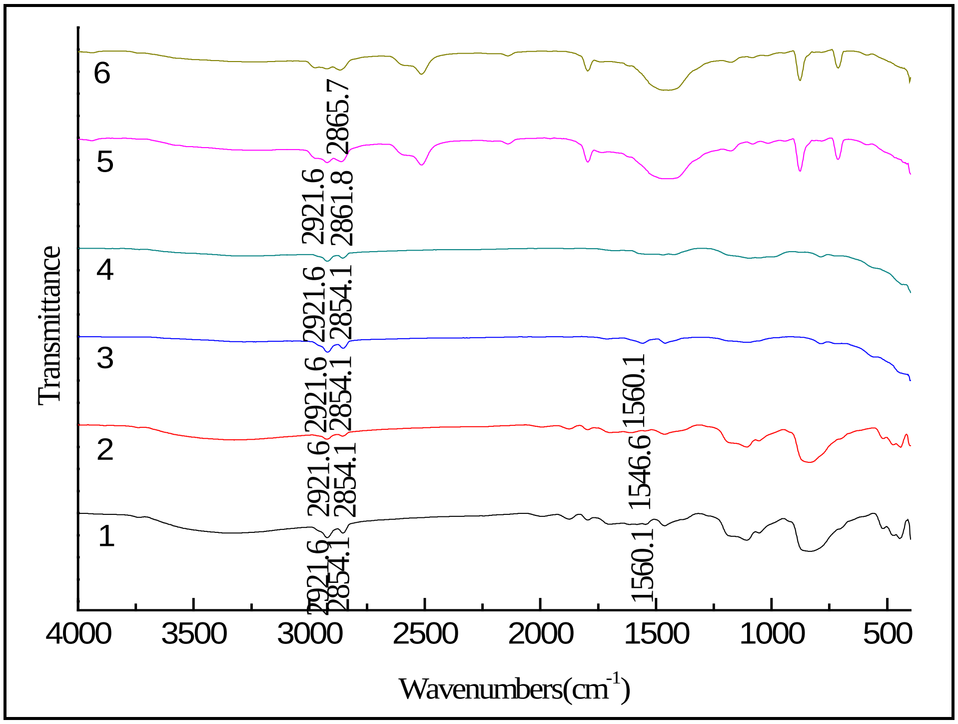

Figure 8. Infrared spectrum of scheelite, fluorite and calcite after treatment with sodium silicate and TAB-3 1.Scheelite + TAB-3; 2.Scheelite + sodium silicate + TAB-3; 3.Fluorite + TAB-3; 4.Fluorite + sodium silicate + TAB-3; 5.Calcite + TAB-3; 6.Calcite + sodium silicate + TAB-3

From Figure 8, it shows as follows: Firstly, the peak of C-O stretching vibration in carboxyl group around 1546.6cm-1 is found in Scheelite, and as Guoxi Zheng (1983) showed, the peak around 1546.6cm-1 is the dominant peak in calcium acid. Secondly, the peaks of C-H asymmetric stretching vibration in -CH3 bond around 2921.6cm-1 and C-H symmetric stretching vibration in -CH2- bond around 2854.1cm-1 are found in Fluorite, but no peak of associating O-H stretching vibration is found. Thirdly, the peak of C-H asymmetric stretching vibration in -CH3 bond around 2921.6cm-1 is not found in calcite.

DISCUSSION AND ANALYSIS OF THE RESULTS

Through the solution chemistry of Na_2SiO_3 in flotation, analysis on the Zeta-potential and infrared spectrometry of the mineral surface and the reagent TAB-3, the influence mechanism of regulators on the floatability of Scheelite, Fluorite and Calcite is studied and discovered.

Discussion of the solution chemistry of Na_2SiO_3 in flotation

As Dianzuo Wang(1988) showed, through the solution chemistry calculation of Na_2SiO_3 in flotation, the relation between distribution coefficient of Na_2SiO_3 component and pH is obtained and shown in Figure 9.

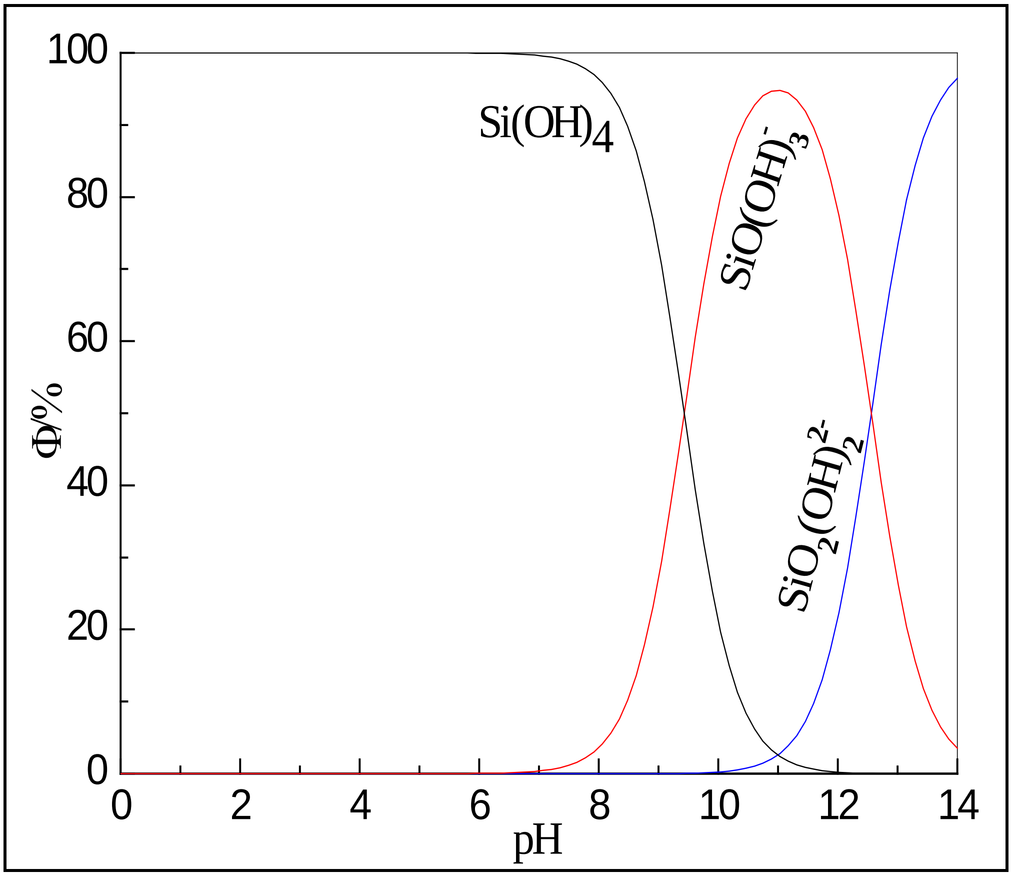

Figure 9. The relation between distribution coefficient of Na_2SiO_3 component and pH

From Figure 3 and Figure 9, the decline extent of the recovery of fluorite and calcite is higher when 8.0<pH<11.0. In addition, higher the pH is, the larger the $[Si(OH)_3^-]$ content becomes. It is because, the competitive adsorbability between $[Si(OH)_3^-]$ content and the reagent TAB-3 gradually strengthens and the adsorption of TAB-3 on the surface of Fluorite and Calcite gradually weakens, the floatability of Fluorite and Calcite also becomes weaker. When pH≥11.0, the recovery of fluorite drops sharply with the rise of pH, but the recovery of calcite evidently increases. It is because $[Si(OH)_3^-]$ content gradually decreases and $[Si(OH)_2^{2-}]$ content increases. Thus it can be seen that the $[Si(OH)_2^{2-}]$ content can depress fluorite strongly but depress calcite weakly, and the $[Si(OH)_3^-]$ content can both depress fluorite and calcite strongly. As stated previously, when pH=8~10, it is better to the flotation separation of Scheelite from Calcite; when pH=10~11, it is better to the flotation separation of scheelite from fluorite and calcite; When pH≥11, it is better to the flotation separation of Scheelite from Fluorite.

Discussion of the results of the surface potential

Effect of Na_2SiO_3 on the surface potential and floatability

When using the reagent TAB-3 and Na_2SiO_3, the surface potential of scheelite shifts slightly and the surface potential is close with that, only when the reagent TAB-3 is used, so it can be seen that the influence of adding Na_2SiO_3 on the adsorption of TAB-3 on the surface of scheelite is weak and the decline extent of the recovery of scheelite is minor. The surface potential of fluorite shifts a bit further and is different from that of only using the reagent TAB-3, so it can be seen that the influence of adding Na_2SiO_3 on the adsorption of TAB-3 on the surface of fluorite is larger and the decline extent of the recovery of scheelite is larger. The surface potential of calcite shifts the farthest, so it can be seen that the influence of adding Na_2SiO_3 on the adsorption of TAB-3 on the surface of Calcite is the largest and the decline extent of the recovery of scheelite is the largest. Thus this proves that adding Na_2SiO_3 is beneficial to the separation of scheelite from fluorite and more beneficial to the separation of scheelite from calcite.

Effect of Na_2SiO_3 dosage on the surface potential and floatability

From Figure 6, the surface potential of scheelite, fluorite and calcite in Na_2CO_3 is higher than that in NaOH, it is because the existence of [HCO_3^-] and [CO_3^{2-}] makes the adsorption of [$Si(OH)_3^-$] or [$Si(OH)_2^{2-}$] on Ca^{2+} weak. The order of the surface potential difference between the two solution mediums is scheelite<fluorite<calcite, so when using NaOH as the regulator, increasing the dosage of Na_2SiO_3 can depress fluorite strongly and is beneficial to the separation of scheelite from fluorite.

Analysis on the results of IR

From Figure 8, the peak of C-O stretching vibration in carboxyl group is found in scheelite, so the reagent TAB-3 form strong chemical adsorption on the surface of scheelite. The peak of C-O stretching vibration in carboxyl group is not obvious in fluorite, so the reagent TAB-3 only forms weak adsorption on the surface of fluorite. The peak of C-H asymmetric stretching vibration in -CH_3 bond is not obvious in calcite, so the reagent TAB-3 only forms weak adsorption on the surface of calcite. This proves, that using Na_2SiO_3 weakens the adsorption of TAB-3 on the surface of fluorite and calcite and improves the selective adsorption of TAB-3 on scheelite. Adding Na_2SiO_3 is beneficial to the separation of scheelite from Fluorite and Calcite.

THE LABORATORY TESTS AND INDUSTRIAL APPLICATIONS

The main scheelite ore types are the scheelite-fluorite type and scheelite-calcite type. Therefore, it is very important to research on separating scheelite from the calcium minerals of the two ore types.

Scheelite-fluorite type ore tests

The raw ore of a tungsten ore in Hunan assays 0.26% WO_3, 19.27% CaF_2 and 9.42% $CaCO_3$, The main tungsten minerals in the raw ore are Scheelite, Wolframite and Tungstite and their proportion is 82.69%, 13.85% and 3.46% respectively. The scheelite in the raw ore assays 0.26% WO_3. The raw ore in Hunan belongs to scheelite-fluorite type.

Table 1 shows the results of regulator tests when the dosage of the fatty acid collector TAB-3 is 0.24 kg/t. Adopting the combination of NaOH and Na_2SiO_3 as regulators can get higher grade and recovery.

Figure 10 shows the results of NaOH dosage test when the dosage of Na_2SiO_3 is 3 kg/t and the dosage of TAB-3 is 0.64 kg/t. When the dosage of Na_2CO_3 is 0.4 kg/t and pH is 11,the concentrate with higher grade and recovery can be achieved.

Table 1. The results of regulator tests when the TAB-3 dosage is 0.24 kg/t %

Regulator Type and Dosage kg/t	Pulp pH	Feeding Grade WO_3	Concentrate	
			Grade WO_3	WO_3 Recovery
NaOH 0. 1 Na_2SiO_3 3.0	10.0	0.26	2.20	62.02
NaOH 0.1 Na_2SiO_3 2.0	9.5	0.26	0.97	74.95
NaOH 0.2 Na_2SiO_3 3.0	11.0	0.26	3.10	60.28
Na_2CO_3 0.2 Na_2SiO_3 3.0	8.0	0.26	0.96	42.46
Na_2CO_3 0.5 Na_2SiO_3 3.0	8.5	0.26	0.78	73.16

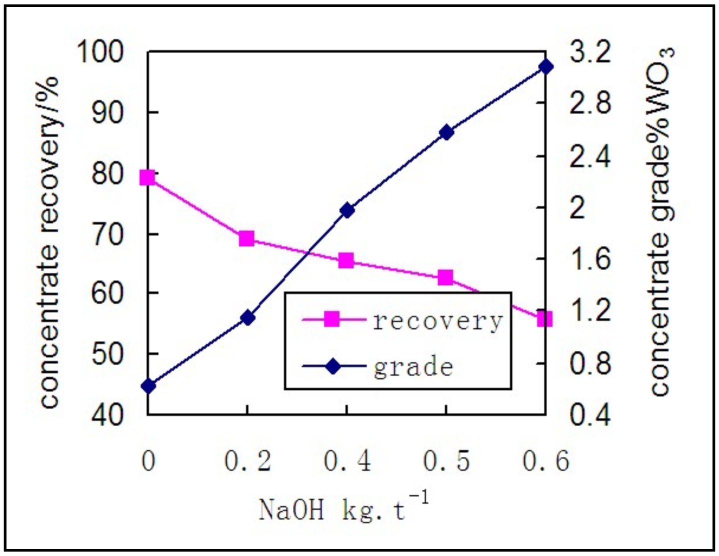

Figure 10. Influence of NaOH dosage on the scheelite flotation

The reagents NaOH, Na_2SiO_3 and TAB-3 are used in scheelite flotation. Through the closed-circuit test of scheelite flotation including one roughing, three cleanings and three scavengings, the scheelite rough concentrate assaying 11.70% WO_3 with its stage recovery being 75.69% and the tailing assaying 0.065% WO_3 are obtained. Then the scheelite rough concentrate is treated by heating concentration and the scheelite concentrate assaying 74.57% WO_3 with the WO_3 recovery of 69.47% is achieved. The total recovery of scheelite is 84.01%.

During the industrial trial production, which ran for one month, the average degree of the raw ore is 0.44% WO_3 and 21.65%CaF_2. The percentage of scheelite and wolframite in the raw ore are 59.52% and 40.48% respectively. After scheelite flotation, the scheelite rough concentrate assaying 4.423%WO_3 with the WO3 recovery of 65.18% is got. Then the scheelite rough concentrate is treated by heating concentration and the scheelite concentrate assaying 68.20%WO_3 with the WO_3 recovery of 55.32% is achieved. The total recovery of scheelite is 92.94%.

Scheelite-Calcite Type Ore Tests

The raw ore of a tungsten ore in Anhui assays 0.19% WO_3, 16.42% $CaCO_3$ and 1.58% CaF_2, The main tungsten minerals in the raw ore are Scheelite, Wolframite and Tungstite and their proportion is 91.55%, 5.92% and 2.53% respectively. The raw ore in Anhui belongs to scheelite-calcite type.

Table 2 shows the results of regulator tests when the dosage of TA-3 is 0.18 kg/t. Adopting the combination of Na_2CO_3 and Na_2SiO_3 as regulators can get higher grade and recovery.

Table 2. The results of regulator tests when the TA-3 dosage is 0.18 kg/t %

Regulator Type and Dosage kg/t	Pulp pH	Feeding Grade WO_3	Concentrate	
			Grade WO_3	WO_3 Recovery
Na_2CO_3 0. 4 Na_2SiO_3 2.0	8.0	0.19	1.75	90.06
Na_2CO_3 0. 4 Na_2SiO_3 3.0	8.5	0.19	2.23	84.68
Na_2CO_3 1.0 Na_2SiO_3 3.0	9.0	0.19	1.88	79.67
Na_2CO_3 1.0 NaOH 0.1 Na_2SiO_3 3.0	10	0.19	2.03	77.40
NaOH 0.4 Na_2SiO_3 3.0	11	0.19	1.78	79.96

Figure 11 shows the results of Na_2CO_3 dosage test when the dosage of Na_2SiO_3 is 2.6 kg/t and the dosage of TA-3 is 0.16 kg/t. When the dosage of Na_2CO_3 is 0.5 kg/t and pH is between 8 and 10,the concentrate with higher grade and recovery can be achieved.

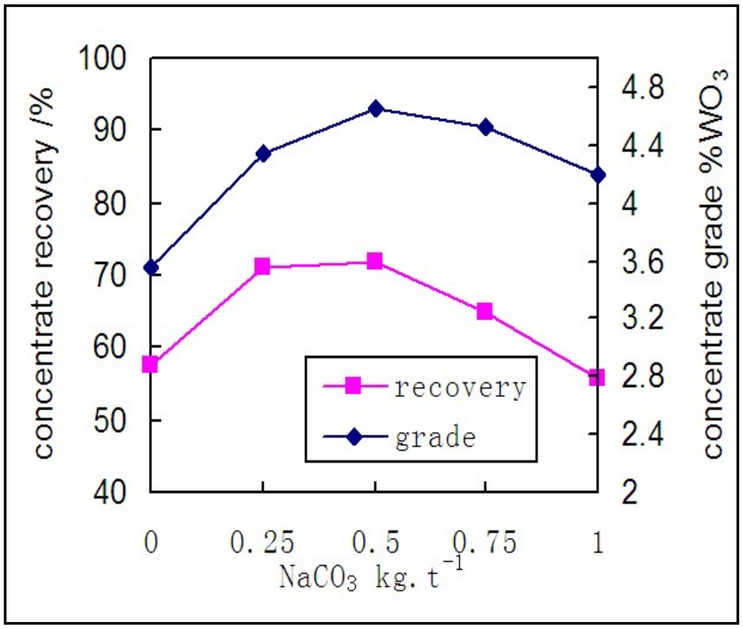

Figure 11. Influence of Na_2CO_3 dosage on the scheelite flotation

The reagents Na_2CO_3, Na_2SiO_3 and TA-3 are used in scheelite flotation. Through the closed-circuit test of scheelite flotation including one roughing, three cleanings and two scavengings, the scheelite rough concentrate assaying 7.52% WO_3 with its stage recovery being 91.59% and the tailing assaying 0.016% WO_3 is obtained. Then the scheelite rough concentrate is treated by heating concentration and the scheelite concentrate assaying 65.62% WO_3 with the WO_3 recovery of 87.47% is achieved. The total recovery of scheelite is 95.55%.

During the industrial trial production, which ran for 3 months, the average degree of the raw ore is 0.31% WO_3. The percentage of Scheelite and Wolframite in the raw ore are 90.32% and 5.63% respectively. After scheelite flotation, the scheelite rough concentrate assaying 4.45%WO_3 with the WO_3 recovery of 80.63% is achieved. Then the scheelite rough concentrate is treated by heating concentration and the scheelite concentrate assaying 62.61%WO_3 with the WO_3 recovery of 77.77% is achieved. The total recovery of scheelite is 86.10%.

CONCLUSIONS

In pulp solution, $[Si(OH)_3^-]$ component in Na_2SiO_3 can depress fluorite and calcite strongly; the $[Si(OH)_2^{2-}]$ component can depress fluorite strongly but calcite weakly. The floatability of Scheelite, Fluorite and Calcite is better in Na_2CO_3 solution medium, so using NaOH solution medium is more beneficial to the separation of scheelite from Fluorite. When pH =8~10 and using the combined regulator of Na_2CO_3 and Na_2SiO_3 is beneficial to the separation of scheelite from calcite; when the raw ore is 0.17%WO_3, the scheelite concentrate assaying 65.62% WO_3 is achieved and the total recovery of scheelite is 95.55%.When pH≥11 and using the combined regulator of NaOH and Na_2SiO_3 is beneficial to the separation of scheelite from fluorite; when the raw ore is 0.21%WO_3, the scheelite concentrate assaying 74.57% WO_3 is achieved and the total recovery of scheelite is 84.01%.

The results of the surface potential of minerals and the infrared spectrophotometry indicate that, after adding Na_2SiO_3, the reagent TAB-3 can form strong chemical adsorption on the surface of scheelite and the surface potential of scheelite shifts slightly; using Na_2SiO_3 weakens the adsorption of TAB-3 on the surface of fluorite and calcite. Thus it can be seen that adding Na_2SiO_3 is beneficial to the flotation separation of scheelite from fluorite and is more beneficial to the flotation separation of scheelite from calcite.

REFERENCES

Dianzuo Wang, Yuehua Hu, 1988. Solution Chemistry of Flotation, pp:23-24(Hunan Science and Technology Press: Changsha).

Guoxi Zheng, Fangru Jia, 1983. IR Spectra Studies of Phosphorite with Sodium Oleate, Industrial Minerals and Processing, (3):35-38.

X Zhou, X Li, L Deng, W Huang, T Guan and A Zhai, 2010. The New Technology of Enrichment of a Fine Low-grade Tungsten from Complex Multi-metallic Ore, in XXV International Mineral Processing Congress 2010, pp 2711-2718 (The Australasian Institute of Mining and Metallurgy: Brisbane).