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Comparison of the Effects of Sodium Oleate and Benzohydroxamic Acid on Fine Scheelite and Cassiterite Hydrophobic Flocculation

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Abstract: Sodium oleate (NaOL) and benzohydroxamic acid (BHA) are commonly used scheelite and cassiterite flotation collectors. Hydrophobic flocculation flotation of fine minerals has been extensively studied and reported under a NaOL system, but not under a BHA system. In this paper, the particle size distribution and flotation behaviour of fine scheelite ($-10\ \mu\text{m}$) and cassiterite ($-37 + 10$ and $-23\ \mu\text{m}$) after shear stirring in NaOL, BHA, and Pb^{2+} + BHA systems were studied by laser particle size analysis and flotation tests. The measured particle size distribution results revealed that the fine minerals could aggregate under a NaOL system, and the aggregate size increased with increasing stirring time and speed, with scheelite aggregating faster than cassiterite. BHA did not cause scheelite or cassiterite to form hydrophobic aggregates. At low stirrer speeds, the minerals could form small, weak, and easily broken aggregates when Pb^{2+} + BHA was added. The results of the flotation tests revealed that increasing the stirring time and speed increased the flotation rate and recovery when NaOL and BHA were added. When Pb^{2+} + BHA was added, however, the changes in flotation rate and recovery were not noticeable when the stirring conditions were changed.



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Keywords: fine minerals; shear flocculation; flotation; sodium oleate; benzohydroxamic acid

1. Introduction

Warren first proposed shear flocculation when hydrophobic ultrafine scheelite aggregated in turbulent flow [1,2]. After that, this method is widely used in flotation recovery of fine-grained ores, and it performs well in improving the recovery of fine minerals [3–5]. As a result, shear-flocculation can help with fine ore recovery to some extent, and many articles have studied the influencing factors that govern the aggregation process [4–6]. Zeta potential, hydrophobicity, the concentration and type of surfactant, stirrer speed, flocculation time, suspension concentration, and temperature are the factors, with zeta potential and hydrophobicity of mineral surface being the most important [1,4–6].

The type of surfactant is critical because it influences the hydrophobicity and zeta potential of minerals. When dodecylamine was added, fine hematite particles flocculated over a wide pH range, but only over a narrow pH range (2.5–3.5) when Aero 801 (a mixture of petroleum sulfonate and mineral oil) was added [4]. NaOL, sodium lauryl sulfate, and the Cyanamid reagent S3903 could induce shear-flocculation of fine cassiterite and tourmaline, but styrene phosphonic acid (SPA) did not, probably due to its short hydrocarbon chain and weak adsorption [7]. However, SPA is one of the best collectors for cassiterite flotation, with better selectivity and the ability to obtain higher grade tin concentrates at high recoveries [8,9]. These suggest that not all collectors can induce shear flocculation of minerals.

Cassiterite [10] and scheelite [11] are brittle and easily crushed to fine particles, causing difficulty in recovering the minerals, thus many fine particles are lost in the tailings [12–14]. Froth flotation is usually used to process finely grained scheelite [15]. As shear-flocculation

flotation is a good method to aggregate fine minerals and then the aggregates are recovered by flotation, articles have studied recovering fine cassiterite and scheelite by this method [3,7]. However, the widely used surfactants are NaOL and its derivatives, and this kind of surfactant lacks selectivity. For cassiterite, these collectors are suitable for simple ores largely containing quartz as gangue [8]. For scheelite, these collectors also recover calcium-bearing gangue minerals such as fluorite and calcite, which are difficult to separate from scheelite [16].

Benzohydroxamic acid (BHA, $C_6H_5CONHOH$) as an environmentally friendly reagent [17] is a widely used chelating collector in cassiterite [12,18] and scheelite [19] flotation and shows excellent selectivity [20]. BHA can float cassiterite well, calcite quite limitedly, and quartz not at all, but the presence of sodium hexametaphosphate can inhibit calcite flotation, allowing cassiterite to separate from calcite [18]. Cassiterite in a tailing slime from the Datun concentration plant was effectively recovered with a reagent regime of BHA as the collector, lead nitrate as the activator, and pine oil as a frother [12]. When BHA is used as a collector, Pb^{2+} is usually added as an activator, and the activation mechanism has been extensively explored [21–23]. However, no research has been performed on shear flocculation of fine minerals using BHA or BHA + Pb^{2+} . Therefore, the main purpose of this paper is to study the shear-flocculation behaviour of fine cassiterite and scheelite using BHA and BHA + Pb^{2+} and compare it with the flocculation behaviour using NaOL.

2. Materials and Methods

2.1. Mineral Samples and Reagents

The cassiterite sample with a particle size of $-23\ \mu m$ is the same as the sample in [24] but with a different particle size. The cassiterite sample with a particle size of $-37 + 10\ \mu m$ was obtained from Xintian Plant, Yunnan Province, China. Chemical analysis of the sample shows that it contains 94.95% SnO_2 , 0.78% SiO_2 , and 0.93% Fe. The scheelite sample was selected from a crushing feeding belt of a plant in China. After being handpicked and crushed, the solid sample was selected by a shaking table, and then the concentrate was ground in a laboratory ceramic mill. After that, the sample was sieved to obtain the $-10\ \mu m$ fraction. Chemical analysis of the sample shows that it contains 75.54% WO_3 , 22.25% CaO, and 0.70% CaF_2 .

In the single mineral flotation tests, NaOL and BHA were used as collectors, and lead nitrate was used as the activator. NaOL and lead nitrate were purchased from Tianjin Kermil Chemical Reagents Development Centre, and BHA (>98.0%) was purchased from TCI Shanghai Chemical Industrial Development Co., Ltd. NaOH and HCl were used as pH regulators. In the single mineral flotation tests, all reagents except BHA were of analytic grade, and deionized water was used.

The actual ore was taken from the fine cassiterite flotation feed of the Xintian Concentration Plant of Yunnan Zinc & Indium Stock CO., Ltd., Wenshan, Yunnan, China. The main gangue minerals of the sample are chlorite, quartz, calcite, dolomite, phlogopite, and hornblende. The results of particle size analysis by sieve and elutriation are shown in Table 1.

Table 1. Size analysis results of actual ore samples.

Size Range (μm)	Weight (%)	Assay (% Sn)	Distribution (% Sn)	Cumulative Oversize (%)	Cumulative Distribution (% Sn)
+74	4.18	0.08	1.40	4.18	1.40
−74 + 38	34.07	0.17	23.02	38.25	24.42
−38 + 19	48.93	0.30	59.06	87.18	83.48
−19 + 10	8.69	0.31	10.66	95.87	94.14
−10 + 5	2.60	0.50	5.17	98.47	99.31
−5	1.53	0.11	0.69		
	100.00	0.25	100.00		

In the actual ore flotation tests, Na_2CO_3 (200 g/t) was used as the regulator. KT-51 (300 g/t) was used as the activator, and its main component is $\text{Pb}(\text{NO}_3)_2$. Tributyl phosphate (TBP, 38 g/t) was used as an auxiliary collector. The main components of the collector are BHA and arsonic acid and the dosage was 1000 g/t. Terpeneol oil (35 g/t) was used as a frother. In the actual ore flotation tests, all reagents were industrial products, and tap water was used.

2.2. Microflotation Tests

Microflotation tests were carried out using an inflatable hanging slot flotation apparatus (XFGC II), and the impeller rotation speed was fixed at 1900 r/min. 2.0 g of mineral sample was added into a 40 mL cell for each test. The collector was stirred for 3 min, and flotation was performed for a total of 3 min.

A part of the sample after hydrophobic flocculation in Section 2.3 was taken into a 100-mL cell for the flotation test at a rotation speed of 1500 r/min and the total flotation time was 8 min. Incremental concentration samples were collected, dried, and weighed to plot the recovery–time curves. The first order rate equation was used to describe the flotation activity, which is usually expressed as:

$$R = R_{\max} (1 - e^{-kt}) \quad (1)$$

where R is the cumulative recovery after time t , k is the rate constant, t is the cumulative time, and $R_{\max}$ is their flotation recovery at an infinite time.

2.3. Hydrophobic Flocculation Tests and Particle Size Measurements

A 7-cm-diameter cylinder container fitted with four baffles and a four-impeller paddle stirrer were used to stir the mineral suspension. The baffle width is 0.8 cm, the width of the impeller is 1 cm, and the diameter of the impeller is 4 cm. In the stirring process, the weight of the mineral was 10 g, and the total volume of pulp was 200 mL. First, the suspension was stirred at a given speed for a given time. Then, some samples were moved for particle size measurement and optical microscopy observation, and the remaining samples were used for flotation tests to plot the recovery–time curve.

2.4. Laser-Based Particle Size Analysis

A Mastersizer2000 (Malvern Instruments, Malvern, Worcestershire, UK) was used to measure the size distribution of the stirred suspension. The impeller's stirring speed was set at 1200 r/min. The sample was gently shaken to ensure that it was evenly mixed, then pipetted into a beaker filled with 1 L of water. Ultrasonic was not used on the suspensions in all tests to protect aggregates from undermining during the measuring process. The particle size distribution was determined using the standard instrument software.

2.5. Optical Microscopy Observation of Aggregate Structures

Particle and aggregate structures were observed using a Leica DM RE microscope equipped with a DFC 480 digital camera. One drop of diluted mineral suspension was pipetted onto a glass slide and fixed gently with a thin coverslip on the top. The images of the prepared samples were viewed and captured immediately. The photos were recoloured and converted to black and white using the picture processing tool in Word program. The mineral slurry was prepared following the procedure described previously in Section 2.3.

3. Results

3.1. Conventional Froth Flotation of Single Minerals

To determine collector (NaOL and BHA) concentrations in shear-flocculation tests, microflotation tests were carried out by varying the collector concentration. Additionally, the results of scheelite ($-10 \mu\text{m}$) and cassiterite ($-37 + 10$ and $-23 \mu\text{m}$) are shown in Figures 1–3. The figures indicate that the flotation recovery of scheelite and cassi-

terite increased with increasing NaOL and BHA concentrations. The addition of Pb^{2+} increased the flotation recovery of the minerals when BHA was used as the collector. When 1×10^{-5} mol/L NaOL or 5×10^{-4} mol/L BHA was added, the recovery of $-23 \mu\text{m}$ cassiterite was approximately 80% and that of $-37 + 10 \mu\text{m}$ cassiterite was less than 20%. This indicates that the floatability of $-23 \mu\text{m}$ cassiterite was better than that of $-37 + 10 \mu\text{m}$ cassiterite in conventional flotation. In the flotation tests of Wang et al., the recovery of $-10 \mu\text{m}$ cassiterite was approximately 20% higher than that of $-20 + 10 \mu\text{m}$ cassiterite in the presence of 10 mg/L NaOL [25].

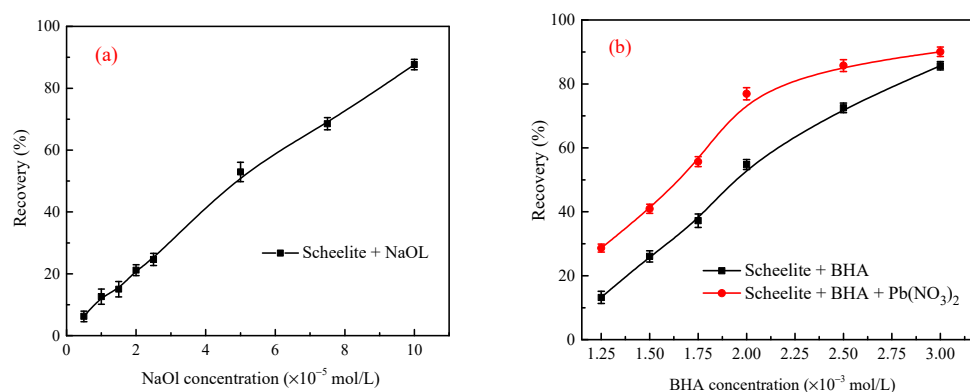


Figure 1. Effect of NaOL (a) and BHA (b) concentrations on the flotation recovery of scheelite (pH = 8.5).

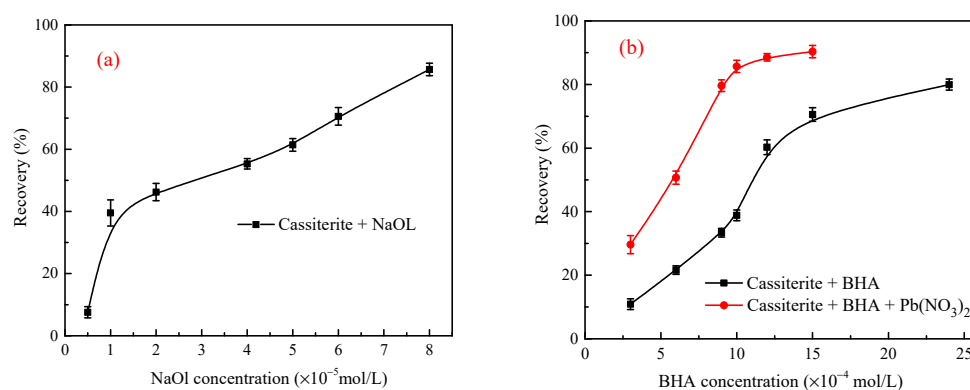


Figure 2. Effect of NaOL (a) and BHA (b) concentrations on the flotation recovery of $-37 + 10 \mu\text{m}$ cassiterite (pH = 8.5).

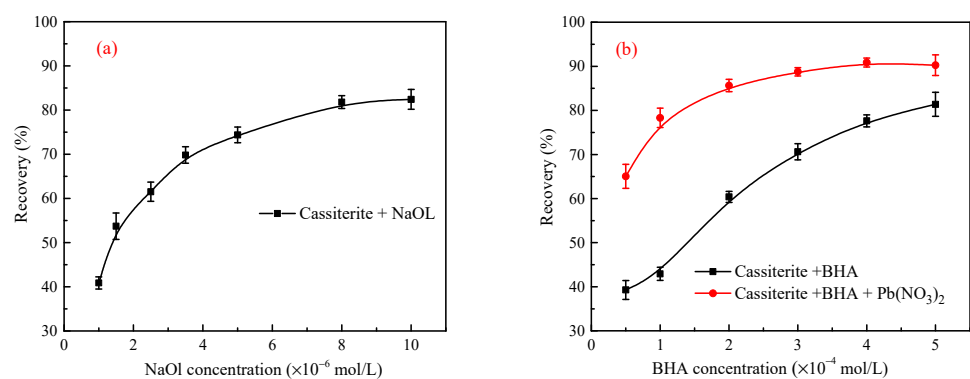


Figure 3. Effect of NaOL (a) and BHA (b) concentrations on the flotation recovery of $-23 \mu\text{m}$ cassiterite (pH = 8.5).

3.2. Shear-Flocculation of Single Minerals Stirred Suspension

3.2.1. Scheelite

The size distribution curves of scheelite suspensions under different reagent conditions after stirring at a given speed for a given time are shown in Figure 4a–d, and the vol. weighted mean particle sizes are shown in Figure 4e. In the presence of NaOL, with increasing stirring time (T) or stirring speed (N), the particle size at the $-2\ \mu\text{m}$ part decreased, while the size at the $+15\ \mu\text{m}$ part increased significantly, indicating that increasing T and N was conducive to the formation of fine scheelite aggregates. Figure 4e also indicates that in the presence of NaOL, the average size of scheelite particles increased with increasing T or N . In the presence of BHA, the size distribution of scheelite suspensions under different stirring conditions and BHA concentrations are shown in Figure 4b,c, respectively. Combining with the mean particle sizes in Figure 4e, it can be seen that scheelite did not aggregate either by changing the stirring conditions or increasing the BHA concentration. Conversely, scheelite suspensions were more dispersed after adding BHA. Figure 4d indicates that in the presence of Pb^{2+} and BHA, the particle size at the $+10\ \mu\text{m}$ part increased slightly, that at the $-10 + 1\ \mu\text{m}$ part decreased, and that at the $-1\ \mu\text{m}$ part remained basically unchanged, indicating that in the presence of Pb^{2+} and BHA, small size aggregates were formed in scheelite suspensions. Figure 4e clearly shows that the average size of scheelite aggregates reached the maximum after stirring at 600 r/min for 10 min. With further increasing T and N , the average size decreased, indicating that the aggregates were unstable and easily broken.

Optical microscope-observed images of scheelite suspensions in the presence of BHA and NaOL are shown in Figure 5. In the presence of BHA, the images did not show significant aggregation. However, in the presence of NaOL, aggregates were observed. Aggregates of about $20\ \mu\text{m}$ were observed after stirring at 900 r/min for 10 min, and after stirring at 1300 r/min for 20 min a larger aggregate of approximately $100\ \mu\text{m}$ was observed.

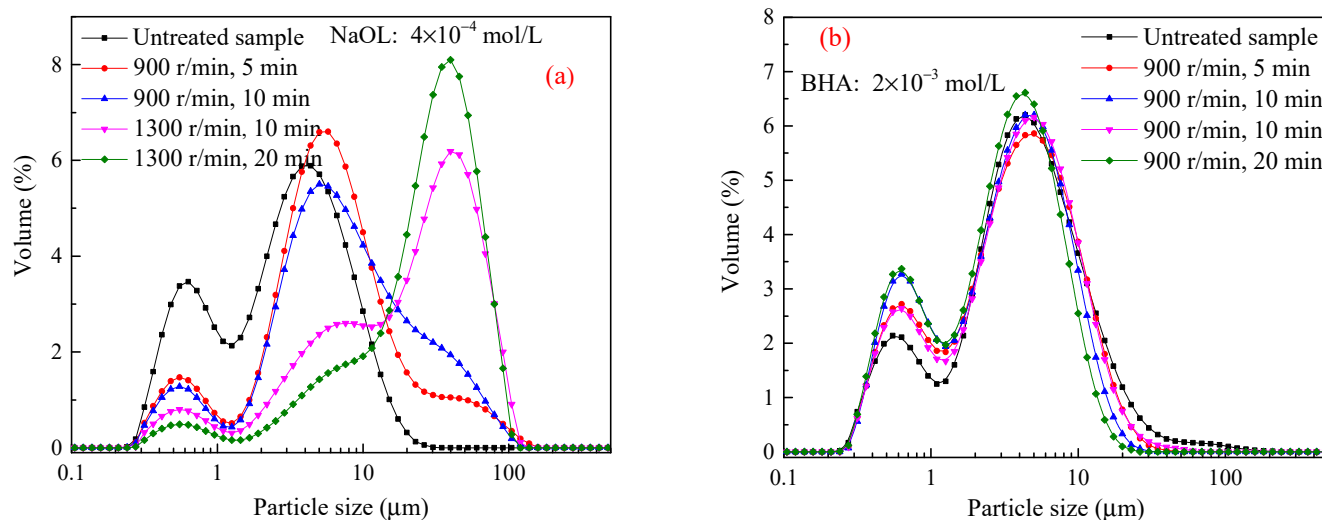


Figure 4. Cont.

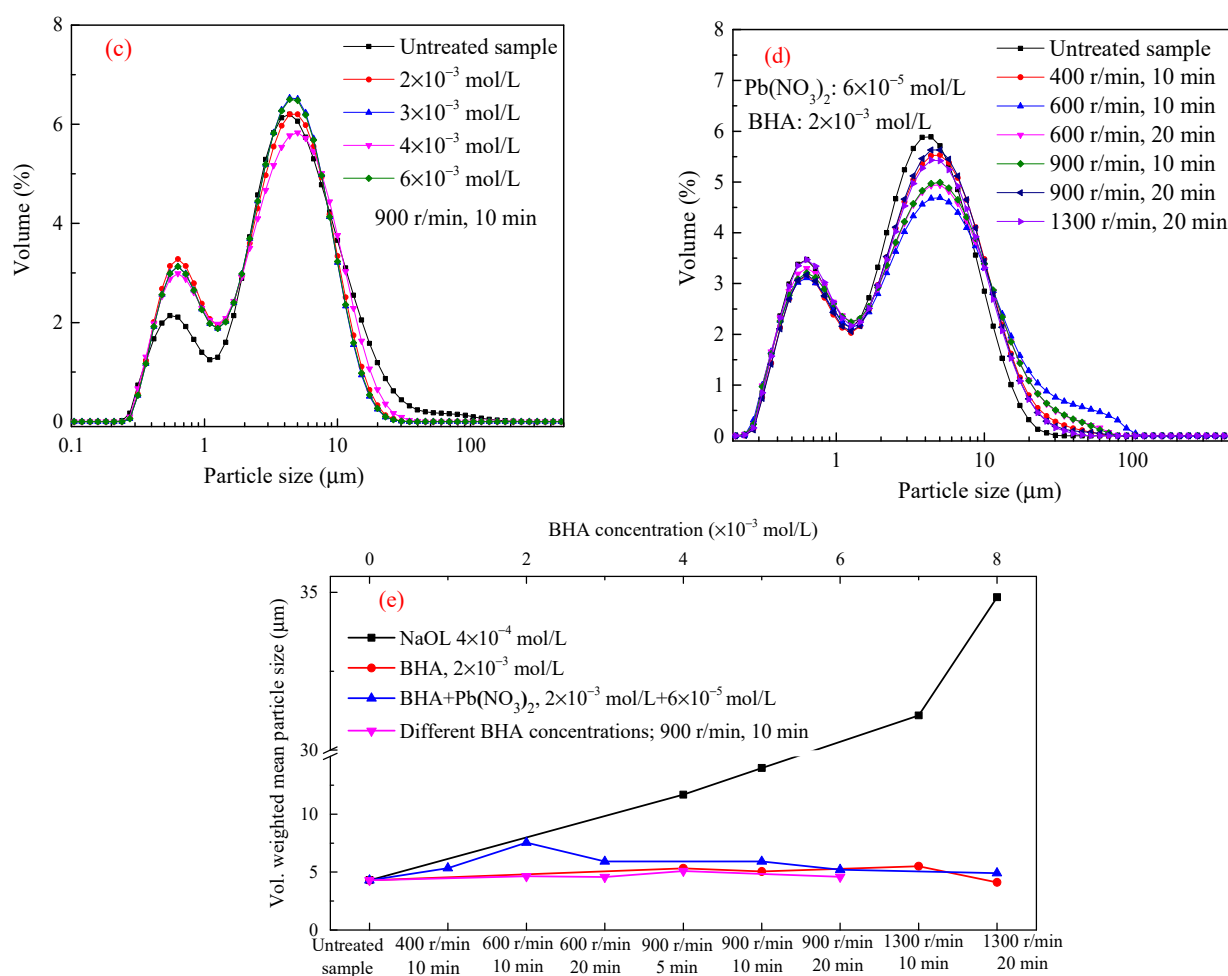


Figure 4. The particle size analysis results of $-10\ \mu\text{m}$ scheelite in the presence of NaOL (a), BHA (b,c), and BHA + Pb^{2+} (d) under different conditions, (e): vol. weighted mean particle size (pH = 8.5–9).

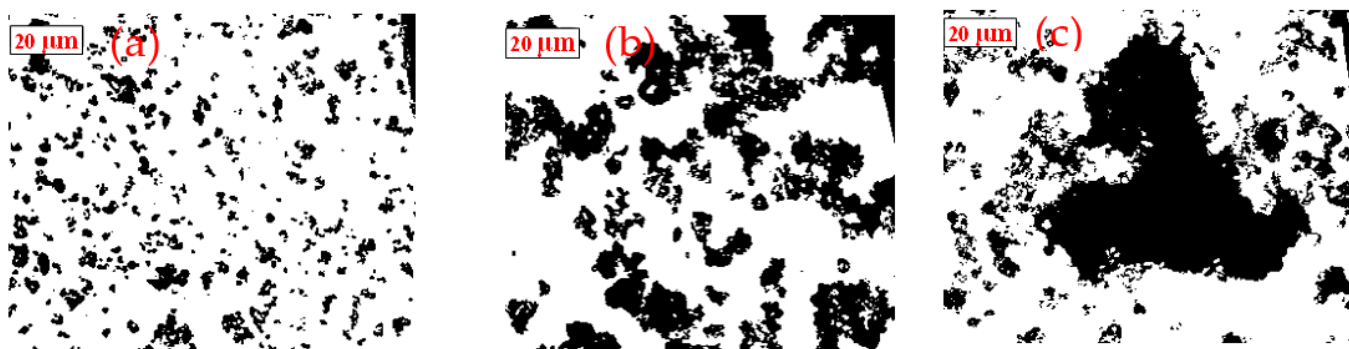


Figure 5. Optical microscope images of scheelite in the presence of BHA (a) and NaOL after stirring at 900 r/min for 10 min (b) and 1300 r/min for 20 min (c).

3.2.2. $-37 + 10\ \mu\text{m}$ Cassiterite

The size distribution curves of $-37 + 10\ \mu\text{m}$ cassiterite suspensions under different reagent conditions after stirring at a given speed for a given time are shown in Figure 6a–c, and the vol. weighted mean particle sizes are shown in Figure 6d. In the presence of NaOL, when $N > 900\ \text{r/min}$ and $T > 5\ \text{min}$ with increasing T or N , the particle size at the $-40\ \mu\text{m}$ part decreased, while the size at the $+40\ \mu\text{m}$ part increased significantly, indicating that increasing T and N was conducive to the formation of cassiterite aggregates. Figure 6d indicates that with increasing T or N , the average size of the cassiterite particles increased.

However, when $N = 900$ r/min and $T = 5$ min, the average size decreased. In the presence of BHA, combining the size distribution curves in Figure 6b with the mean particle sizes in Figure 6d, it can be seen that the cassiterite did not aggregate by increasing N or T . Conversely, the cassiterite suspensions were more dispersed after adding BHA. Figure 6c,d shows that in the presence of BHA and Pb^{2+} , when $N = 400$ r/min, the cassiterite did not aggregate, and the average particle size increased only when the stirring speed was 600 r/min, indicating that the aggregates were unstable and could be broken by high-speed shearing.

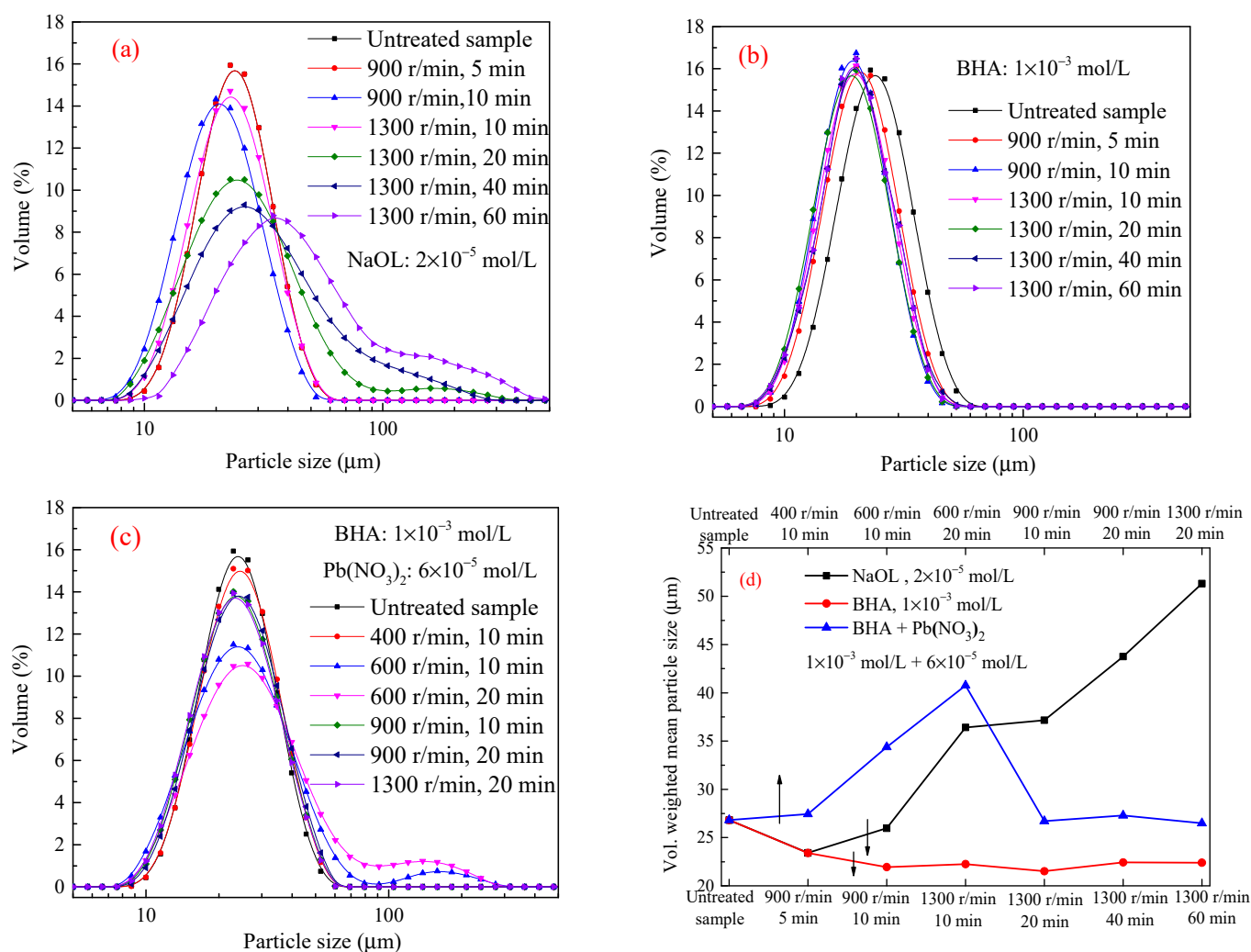


Figure 6. The particle size analysis results of $-37 + 10 \mu m$ cassiterite in the presence of NaOL (a), BHA (b), and BHA + Pb^{2+} (c) under different stirring conditions, (d): vol. weighted mean particle size (pH = 8.5–9).

Optical microscope-observed images of $-37 + 10 \mu m$ cassiterite in the presence of BHA and NaOL are shown in Figure 7. In the presence of BHA, no aggregates were observed. In the presence of NaOL, irregularly shaped aggregates of about 50–150 μm were observed after stirring at 1300 r/min for 20 min, and an elongated aggregate with a width of about 200 μm was observed after stirring for 60 min. Obviously, the aggregates stirred for 60 min were larger than those stirred for 20 min.

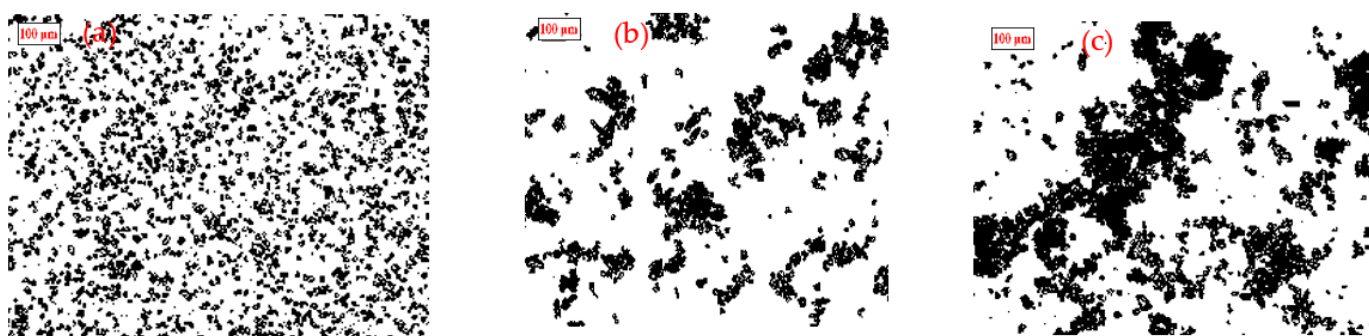


Figure 7. Optical microscope image of $-37 + 10 \mu\text{m}$ cassiterite in the presence of BHA (a) and NaOL after stirring at 1300 r/min for 20 min (b) and 60 min (c).

3.2.3. $-23 \mu\text{m}$ Cassiterite

The size distribution curves of $-23 \mu\text{m}$ cassiterite suspensions under different reagent conditions after stirring at a given speed for a given time are shown in Figure 8a–c, and the vol. weighted mean particle sizes are shown in Figure 8d. Cassiterite particles did not aggregate at $5 \times 10^{-6} \text{ mol/L}$ NaOL but aggregated when the NaOL concentration increased to $5 \times 10^{-5} \text{ mol/L}$. Figure 8d indicates that when T increased from 20 min to 60 min, the mean particle size increased slightly. In the presence of BHA, combining the size distribution curves in Figure 8b with the mean particle sizes in Figure 8d, it can be seen that cassiterite particles did not aggregate by increasing N or T . Figure 8c,d indicates that, in the presence of Pb^{2+} and BHA, the mean particle sizes increased slightly, and the mean size of scheelite aggregates reached the maximum after stirring at 600 r/min for 20 min.

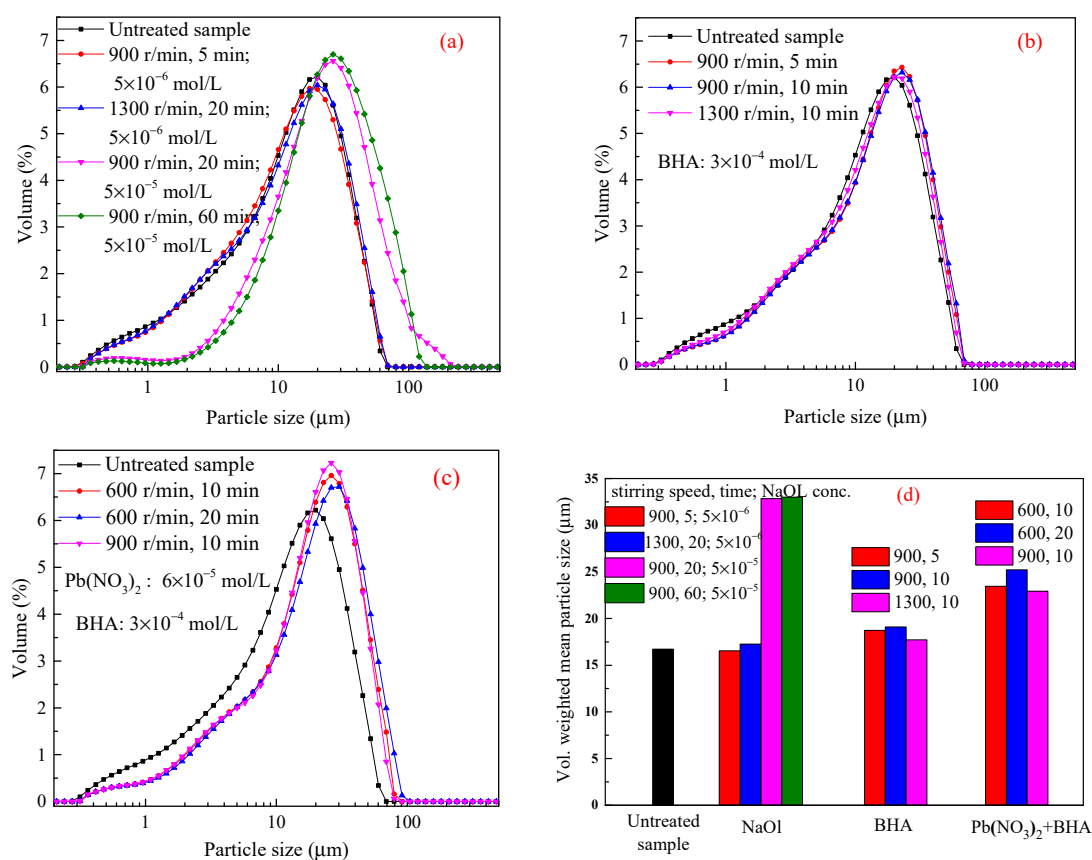


Figure 8. The particle size analysis results of $-23 \mu\text{m}$ cassiterite in the presence of NaOL (a), BHA (b), and $\text{Pb}^{2+} + \text{BHA}$ (c) under different stirring conditions, (d): vol. weighted mean particle size (pH = 8.5–9).

Optical microscope-observed images of $-23\ \mu\text{m}$ cassiterite in the presence of BHA and NaOL are shown in Figure 9. In the presence of BHA, no significant aggregates were observed. However, in the presence of NaOL, large aggregates were observed.

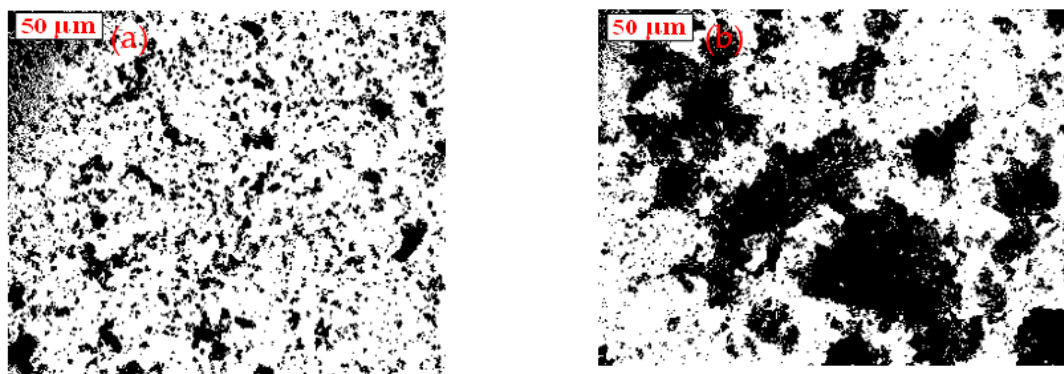


Figure 9. Optical microscope image of $-23\ \mu\text{m}$ cassiterite in the presence of BHA (a) and $5 \times 10^{-5}\ \text{mol/L}$ NaOL after stirring at 900 r/min for 60 min (b).

3.3. Flotation Tests of the Stirred Mineral Suspensions

Flotation tests were carried out to plot the recovery–time curves, and the curves were fitted by the first-order rate equation to obtain rate constants (k) and flotation recoveries at an infinite time (R_{max}). The fitted results of scheelite in the presence of different reagents and different BHA concentrations are shown in Figure 10, and the results of -23 and $-37 + 10\ \mu\text{m}$ cassiterite in the presence of different reagents are shown in Figures 11 and 12, respectively. In the presence of NaOL and BHA, the k and R_{max} of the minerals increased with increasing T or N . In the presence of different BHA concentrations, the k and R_{max} of scheelite increased with increasing BHA concentration. However, in the presence of $\text{Pb}^{2+} + \text{BHA}$, the rule of changes of k and R_{max} for the mineral samples was not obvious with the changes of the stirring conditions.

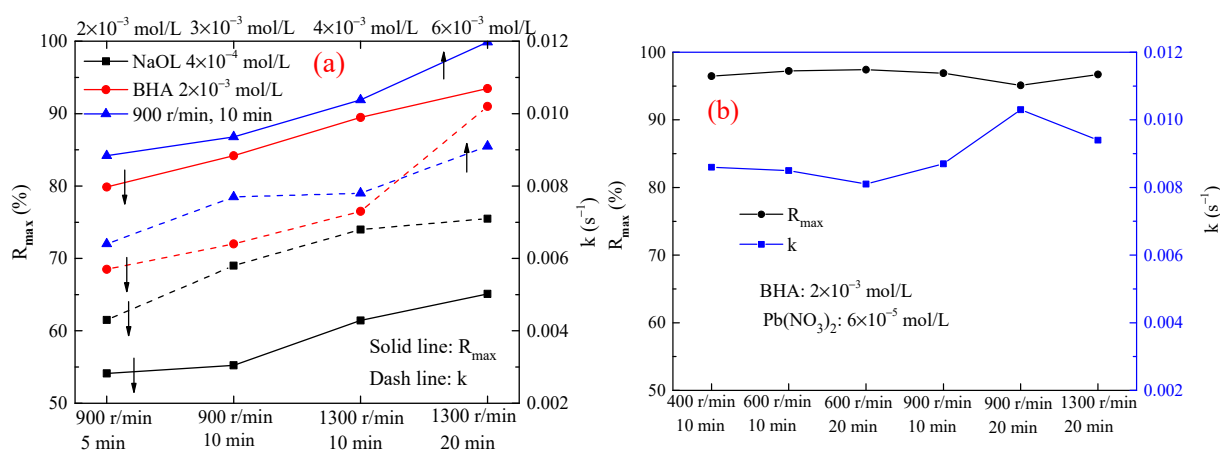


Figure 10. Fitting results of scheelite flotation rate experiments in the presence of NaOL and BHA under different stirring conditions and different BHA concentrations after stirring at 900 r/min for 10 min (a) and in the presence of $\text{Pb}^{2+} + \text{BHA}$ under different stirring conditions (b).

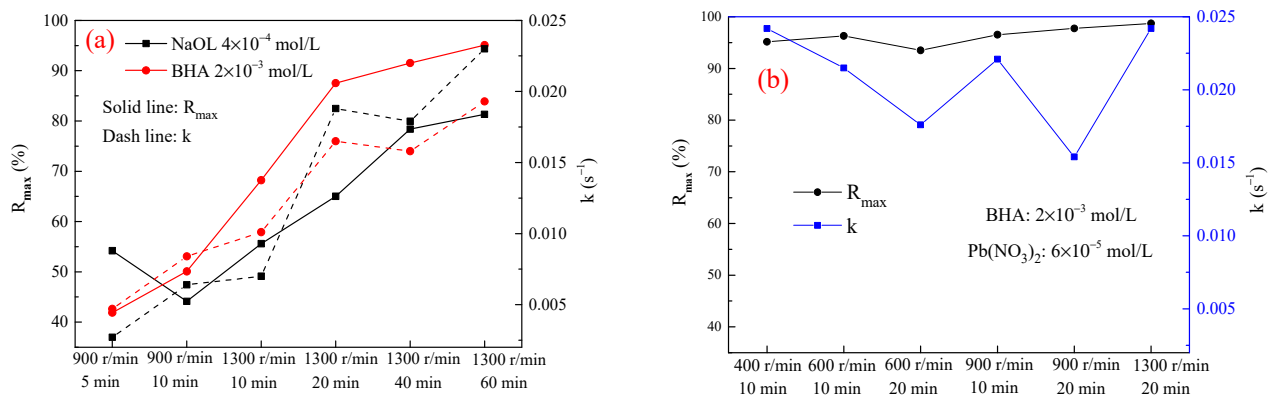


Figure 11. Fitting results of $-37 + 10 \mu\text{m}$ cassiterite flotation rate experiments in the presence of NaOL and BHA (a) and Pb^{2+} + BHA (b) under different stirring conditions.

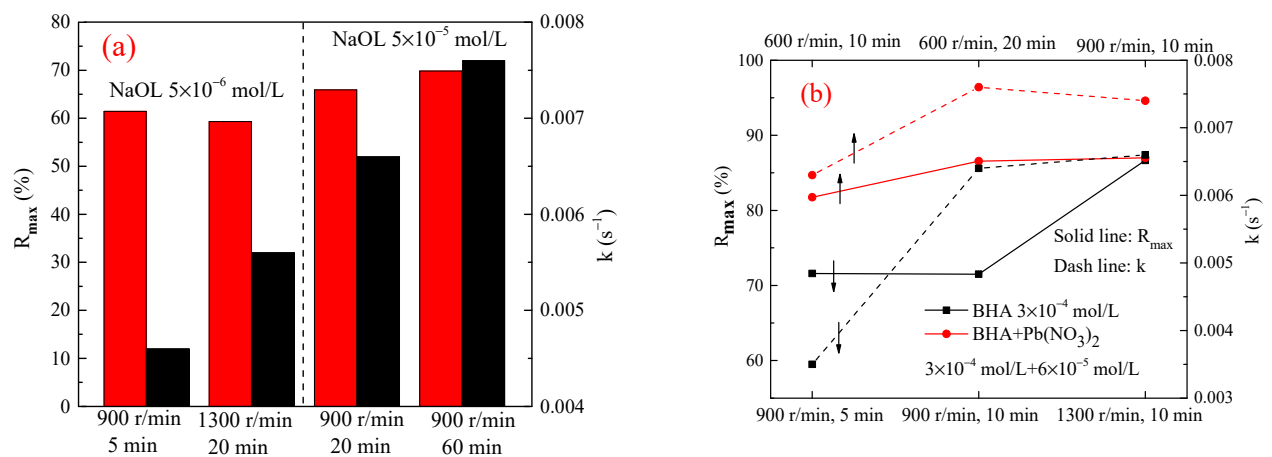


Figure 12. Fitting results of $-23 \mu\text{m}$ cassiterite flotation rate experiments in the presence of NaOL (a) and BHA and Pb^{2+} + BHA (b) under different stirring conditions.

3.4. The Influence of the Agitation Time of the Actual Ore Suspension on the Flotation Recovery of Cassiterite

Flotation tests were carried out on suspensions of the actual ore after stirring for different times at 1650 r/min and the results are shown in Table 2. The reagent regime of the tests is given in Section 2.1. The results indicated that, with increasing stirring time, the yield and recovery of Sn of the concentrate decreased. However, the Sn grade of the concentrate changed opposite to that of the recovery. This indicated that increasing stirring time was not conducive to the recovery of cassiterite, but to the improvement of the concentrate grade.

Table 2. Effect of stirring time on the flotation of Xintian $-37 \mu\text{m}$ cassiterite.

T (min)	Concentrate			Tailing		
	Yield (%)	Assay (%)	Recovery (%)	Yield (%)	Assay (%)	Recovery (%)
3	11.12	1.54	60.37	88.88	0.13	39.96
10	8.59	2.00	55.65	91.41	0.15	44.35
20	6.17	2.50	48.90	93.83	0.17	51.10
30	7.22	2.05	48.79	92.78	0.17	51.21
40	2.77	3.95	36.12	97.23	0.20	63.88

4. Discussion

In the presence of NaOL, stirred suspensions of scheelite and -23 and $-37 + 10 \mu\text{m}$ cassiterite were found to aggregate, and the mean particle size of the aggregates increased with increasing N and T . However, the aggregation rate and relative increment of aggregate particle size (RI) of scheelite were larger than those of cassiterite. To quantitatively compare the aggregation rate and RI of the three mineral samples, the RI and relative growth rate of aggregates (R, s^{-1}) can be calculated by the following formulas:

$$RI = \frac{\alpha_{D[4,3]} - \beta_{D[4,3]}}{\alpha_{D[4,3]}} \quad (2)$$

$$R = RI/T \quad (3)$$

where $\alpha_{D[4,3]}$ and $\beta_{D[4,3]}$ are the vol. weighted mean particle sizes of untreated mineral suspensions and stirred suspensions at a certain speed for a certain time in the presence of reagents, respectively, and T is stirring time. The RI and R of the mineral stirred suspensions are shown in Table 3.

Table 3. Relative increment of aggregate particle size (RI) and relative growth rate of aggregates (R) of the mineral stirred suspensions in the presence of NaOL at different stirrer speeds (N) and stirring times (T).

Sample	N (r/min), T (min)	RI	R (s^{-1})	Sample	N (r/min), T (min)	RI	R (s^{-1})
Scheelite	900, 5	1.72	0.34	$-37 + 10 \mu\text{m}$ cassiterite	900, 5	−0.13	−0.025
	900, 10	2.25	0.23		900, 10	−0.03	−0.003
	1300, 10	6.23	0.62		1300, 10	0.36	0.036
	1300, 20	7.10	0.36		1300, 20	0.39	0.019
$-23 \mu\text{m}$ cassiterite	900, 5 #	−0.01	−0.002		1300, 40	0.63	0.016
	1300, 20 #	0.03	0.002		1300, 60	0.91	0.015
	900, 20 *	0.96	0.048				
	900, 60 *	0.97	0.016				

5×10^{-6} mol/L NaOL; * 5×10^{-5} mol/L NaOL.

Table 3 shows that the RI s and R s of scheelite are larger than those of cassiterite, indicating that scheelite aggregated more easily and at a faster growth rate than cassiterite in the presence of NaOL. Generally, the rate of adsorption would be faster if the mineral has a certain degree of aqueous solubility [26,27]. Scheelite is a semi-soluble mineral [28,29], therefore the adsorption rate of NaOL on its surface would be faster. While cassiterite is a sparingly soluble mineral [27], the adsorption rate would be slow. Thus, NaOL was quickly adsorbed on the scheelite surfaces and aggregates were formed at a faster rate. NaOL was constantly adsorbed on the cassiterite surfaces with the stirring process, so the cassiterite aggregation rates were slow. This behaviour may be a reason for the slow aggregation of cassiterite compared to scheelite.

If the fluid flow can be considered the only dominant mechanism for transporting particles, the collision frequency (N_{ij}) can be written as [30,31]:

$$N_{ij} = \pi(R_i + R_j + H_m)^2 U_{ij} n(i) n(j) \quad (4)$$

where R_i and R_j are the particle and/or aggregate radii of i and j , respectively, $n(i)$ and $n(j)$ are the number concentrations of particles i and j , respectively, H_m is the separation distance between two particles at their energy barrier, and U_{ij} is the relative velocity at a separation distance of H_m . According to Equation (4), a large $n(i)n(j)$ yields a large N_{ij} . Equation (4) can be used to discuss the N_{ij} of the minerals in this study. Thus, the more particles there are in the system, the larger N_{ij} is. The minerals weigh the same, so the finer the particles are, the more particles there are in the system. The particle size of scheelite is

smaller than that of the two cassiterite samples; thus, scheelite particles collided with each other more frequently than the cassiterite, resulting in a faster R of scheelite, which may be another reason for the slow aggregation rate of cassiterite compared to scheelite. As the R of scheelite is faster than that of cassiterite, the RI of scheelite is also greater at the same stirring time.

Equation (4) also shows that N_{ij} is proportionate to U_{ij} ; thus, N_{ij} increases with increasing U_{ij} , and the greater the stirring speed is, the greater U_{ij} is. Therefore, the aggregate size increased with increasing N after stirring for the same time. The stirring conditions of 900 r/min for 5 or 10 min may be insufficient to achieve the number of collisions required for $-37 + 10\ \mu\text{m}$ cassiterite particles to form aggregates, so the cassiterite particles did not aggregate after stirring at 900 r/min for 5 or 10 min. When the N increased to 1300 r/min, after stirring for 10 min, the cassiterite particles aggregated. Additionally, with increasing N , the aggregate size increased; however, R decreased because, with the continuous formation of aggregates, the total number of particles in the system decreased, and the aggregates also fractured.

The roles of NaOL and BHA in mineral aggregation are to selectively hydrophobize the mineral surface, allowing mineral particles to aggregate via hydrophobic attraction. In addition, $-37 + 10\ \mu\text{m}$ cassiterite could aggregate in the range of NaOL dosages of conventional flotation (2×10^{-5} mol/L, about 50% recovery). However, $-23\ \mu\text{m}$ cassiterite did not aggregate in the range of NaOL dosages of conventional flotation (5×10^{-6} mol/L, about 75% recovery). When the NaOL dosage increased to 5×10^{-5} mol/L, cassiterite particles aggregated. This indicates that finer mineral particles require a higher reagent concentration to form aggregates. This is because the mineral with finer particles has a lower gravity and is therefore more likely to float with foam. Yoon and Luttrell suggested that the hydrophobic force between an air bubble and a hydrophobic surface is greater than the hydrophobic force between two hydrophobic solid surfaces [30]. Thus, when the concentration of NaOL was low, $-23\ \mu\text{m}$ cassiterite could adhere to bubbles via hydrophobic force, but the hydrophobic force between particles may be insufficient to cause them to aggregate. However, conventional flotation of $-37 + 10\ \mu\text{m}$ cassiterite required a stronger hydrophobic force to cause it to adhere to the surface of bubbles, so aggregate could be formed under the reagent conditions of conventional. In the presence of BHA, scheelite and cassiterite particles could not aggregate, probably due to the short hydrocarbon chain and weak adsorption of BHA and the high surface potential of the minerals after BHA adsorption. One benzene ring group corresponds to $3.5(-\text{CH}_2-)$ in the linear alkyl group. The zeta potential of cassiterite at pH 8.5–9 is higher than $-40\ \text{mV}$ [32].

In a BHA system, the presence of Pb^{2+} could promote the adsorption of BHA on cassiterite surfaces and reduce its surface potential [23], thus increasing hydrophobic attraction and reducing electrostatic repulsion between particles. Therefore, the presence of $\text{Pb}^{2+} + \text{BHA}$ induced hydrophobic aggregation of the minerals. However, the aggregates were obviously smaller than the NaOL-induced aggregates. Furthermore, the aggregate size decreased when the stirring speed and time increased, indicating that the aggregates were loose and easily broken.

After shear stirring, the flotation R_{max} and k of the minerals increased with increasing N and T in the NaOL and BHA systems. In the NaOL system, mineral particles aggregated, with a decrease in volume concentration of the $-10\ \mu\text{m}$ size fraction. With increasing N and T , the size of the aggregates increased, so R_{max} and k increased. Chen et al. also indicated that the flotation rate of fine scheelite is positively correlated with the flocculation degree [3]. However, in the BHA system, the mineral particles did not aggregate, and the reason for the increases in R_{max} and k may be that the agitation promoted the adsorption of BHA on the mineral surfaces. In the $\text{Pb}^{2+} + \text{BHA}$ system, the recovery and k were too large to obtain regular changes with changes in N and T .

Increasing the stirring time of the actual ore suspensions decreased the yield and recovery of the concentrate, while the Sn grade increased, which is not consistent with the single mineral experimental results. In the oil-assisted agglomeration flotation (OAF) study

of a fine cassiterite gravity separation tailing, it was found that after stirring, the Ca and Fe ion concentrations increased in the pulp, which affected the OFA results by decreasing cassiterite flotation recovery and grade [13]. The Ca and Fe ion concentrations of the actual ore pulp were measured after stirring at 2000 r/min for 3, 10, and 20 min and at 3000 r/min for 20 min, and the results are shown in Figure 13. At 2000 r/min, when the stirring time increased from 3 min to 20 min, the Ca and Fe ion concentrations increased from 48.77 and 0.91 mg/L to 55.62 and 1.32 mg/L, respectively, indicating that more ions were dissolved into the pulp. The dissolved ions may reduce the stability of the foam. In the tests, the stability of the foam weakened as the stirring time or speed increased, and the capacity of the foam carrying particles decreased. Thus, this led to decreases in the yield and recovery of Sn of the concentrate with increasing stirring time.

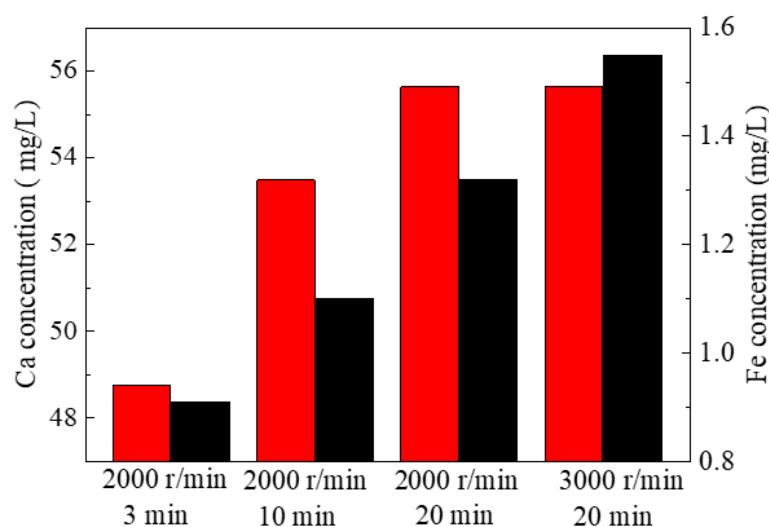


Figure 13. Ca and Fe concentrations of the pulp water under different stirring conditions.

5. Conclusions

In this study, the hydrophobic flocculation flotation of fine scheelite ($-10\ \mu\text{m}$) and cassiterite ($-37 + 10$ and $-23\ \mu\text{m}$) were studied in the presence of NaOL, BHA, and $\text{Pb}^{2+} + \text{BHA}$, and the following conclusions were drawn.

In the presence of NaOL, the fine mineral particles could aggregate, and the aggregate size increased with increasing stirring time and speed, while the aggregate rate of scheelite was higher than that of cassiterite. In comparison to $-37 + 10\ \mu\text{m}$ cassiterite, $-23\ \mu\text{m}$ cassiterite required a higher concentration of NaOL to form aggregates than conventional flotation. BHA did not induce hydrophobic flocculation of scheelite or cassiterite. When $\text{Pb}^{2+} + \text{BHA}$ was added, the minerals could form small, low-strength, and easily broken aggregates at a low stirrer speed. The flotation rate and recovery of the minerals with added NaOL and BHA increased with increasing stirring time and speed; however, when $\text{Pb}^{2+} + \text{BHA}$ was added, the changes in the flotation rate and recovery were not obvious with the changes in stirring conditions. The yield and recovery of the concentrate decreased as the stirring time of the actual ore suspensions increased, while the Sn grade increased, which contradicts the single mineral experiment results. To produce larger, stronger aggregates, hydroxamic acids with longer carbon chains should be introduced.

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