Utilization of Sodium Hexametaphosphate for Separating Scheelite from Calcite and Fluorite Using an Anionic–Nonionic Collector

Jianhua Kang [1,2]**, Yuehua Hu** [1,2,*]**, Wei Sun** [1,2,*]**, Zhiyong Gao** [1,2] and **Runqing Liu** [1,2]

[1] School of Minerals Processing and Bioengineering, Central South University, Changsha 410083, China; kangjianhua@csu.edu.cn (J.K.); zhiyong.gao@csu.edu.cn (Z.G.); liurunqing@126.com (R.L.)

[2] Key Laboratory of Hunan Province for Clean and Efficient Utilisation of Strategic Calcium-containing Mineral Resources, Central South University, Changsha 410083, China

* Correspondence: hyh@csu.edu.cn (Y.H.); sunmenghu@csu.edu.cn (W.S.);
  Tel.: +86-0731-88830482 (W.S. & Y.H.)

Abstract: This study presents a highly selective reagent system that utilizes sodium hexametaphosphate (SHMP) to improve the separation of scheelite from calcite and fluorite using an anionic–nonionic collector. The recoveries of calcite and fluorite decreased to 20% as the SHMP dose exceeded 6×10^{-6} mol/L, whereas that of scheelite remained at 85%. The interaction mechanisms of minerals with SHMP were investigated through equilibrium speciation, Zeta potential, Fourier transform infrared spectrometry, and X-ray photoelectron spectroscopy analyses. SHMP exists as hydrogen phosphate anion in the aqueous solution with a pH of 7–12. Moreover, it may be adsorbed intensively on the positively charged surfaces of calcite and fluorite via electrostatic force or chelation with calcium ion to impede further adsorption of the assembled collector. By comparison, the adsorption of SHMP is feeble on the scheelite surface because of its negative charge. The roughing grade of low-grade scheelite ore is substantially improved from 0.74% to 1.65% compared with that in the contrast test in the absence of SHMP.

Keywords: scheelite; flotation; sodium hexametaphosphate; selective depressant

1. Introduction

Tungsten is widely used in the industrial production of high-performance alloys and electro-optical materials because of its excellent properties [1,2]. According to the 2016 report in the United States Geological Survey [3], the mine production of tungsten worldwide was 87,000 tons in 2015, of which 71,000 tons were supplied by China. Moreover, the demand for tungsten is predicted to steadily grow in the future. Therefore, promoting the efficient utilization of tungsten, a nonrenewable resource, is an important pathway to satisfy the ever-increasing demand for tungsten. The natural sources of tungsten mainly include scheelite ($CaWO_4$) and wolframite ($(Fe, Mn)WO_4$). Wolframite was overexploited in the last century and gradually exhausted. Highly efficient mining and processing of scheelite have been the focus of research over the last decades [4,5]. Scheelite is a calcium-bearing mineral and is generally associated with calcite, wollastonite, and fluorite. Their uniform active site of calcium results in the analogical reaction model with anionic collectors, which exerts a major effect on the separation of scheelite from these gangue minerals [6]. Therefore, the development and utilization of highly selective collectors and depressants are effective approaches to amplify the floatability difference of scheelite with gangue minerals.

Sodium oleate (NaOL) is an emblematic anionic collector and exhibits excellent collecting performance for scheelite flotation by linking carboxyl groups with calcium ions through oxygen atoms

to generate calcium oleate [7]. However, NaOL has poor selectivity and adaptability for complex ores associated with calcium-bearing gangue minerals. Consequently, research on mixed collectors has been conducted to improve the selectivity of fatty acids. Dodecylamine (DDA) is a classical cationic collector that adsorbs on scheelite surface through the electrostatic force attributed to the cationic species of RNH_3^+ [8].The anionic–cationic mixed collector composed of sodium oleate and DDA exerts greater collecting ability and higher selectivity than a single collector for scheelite flotation [9,10]. The anionic–nonionic mixed collector composed of sodium oleate and polyoxyethylene ether exhibits better adaptability at low temperatures than a single sodium oleate [11,12]. Nonionic surfactants, such as polyoxyethylene ether and fatty acid amide, have excellent synergistic effect with other surfactants, owing to their outstanding abilities of emulsification, solubilization, and dispersion [13,14]. Oleamide is a typical nonionic surfactant and a potential reagent to improve the collective performance of sodium oleate as a synergistic agent.

Organic depressants, such as etidronic acid [15], citric acid [16], tannic acid [17], and carboxymethyl cellulose [18], exhibit excellent performance in depressing calcite-bearing gangue minerals. Acidified sodium silicate composed of sulfuric acid and sodium silicate is used to depress calcite in scheelite flotation [10,19]. Al–Na_2SiO_3 polymer, which is a mixture of aluminum sulphate and sodium silicate, exerts better selectivity than a single sodium silicate for the scheelite flotation from calcite [20]. Phosphate is an inorganic depressant which is diffusely used for scheelite flotation in laboratory research and industrial applications [21,22]. Sodium hexametaphosphate (SHMP) is a typical phosphate polymer with excellent chelating and dispersing abilities and can thus be applied to depress gangue minerals.

This study presents a novel anionic–nonionic assembled collector to improve the selectivity of the collector. SHMP was applied to facilitate the depression of calcite and fluorite, thereby establishing a highly selective reagent system for scheelite flotation. The flotation performance of scheelite, calcite, and fluorite and their interaction mechanism with SHMP were investigated by equilibrium speciation, Zeta potential, Fourier transform infrared (FTIR) spectrometry, and X-ray photoelectron spectroscopy (XPS) analyses. The performances of the assembled collector and SHMP on scheelite ore flotation were demonstrated through roughing experiments.

2. Materials and Methods

2.1. Materials and Reagents

Pure scheelite, calcite, and fluorite were obtained from the Shizhuyuan mine in Chenzhou, China. They are natural mineral crystals collected by picking by hand, ball milling with a ceramic pot, and screening via standard sieves of 200 mesh and 400 mesh. The particle sizes of the pure minerals ranged from 0.037–0.074 mm. The purities of scheelite, calcite, and fluorite reached 96.08%, 98.36%, and 99.31%, respectively, based on chemical analysis. The smooth curves of X-ray diffraction (XRD) with regular peaks presented in Figure 1 indicate that the minerals had good crystallization. In addition, the absence of impurity peaks on the curves confirmed their high purities. The raw ore used for scheelite roughing was collected from a plant in Luanchuan, China. The results of X-ray fluorescence (XRF) analysis, listed in Table 1, indicate that the main valuable element was W. The impurity elements contained Ca, Si, and Fe. Figure 2 illustrates the XRD pattern of the scheelite raw ore. The characteristic peaks of scheelite did not obviously appear on the curve because of its low grade. The main gangue minerals included garnet, quartz, amphibole, feldspar, calcite, and fluorite. The grades of scheelite (WO_3), calcite, and fluorite were 0.11%, 9.68%, and 8.56%, respectively, in raw ore. The raw ore was screened with a standard sieve of 200 mesh, and the particle size distribution in −0.074 mm was 78.69%. The distribution rate of scheelite in this size fraction was 92.46%. The main reagents contained sodium oleate, oleamide, SHMP, and sodium carbonate, which were analytically pure. They were purchased from Tianjin Kemiou Chemical Reagent Co., Ltd., Tianjin, China.
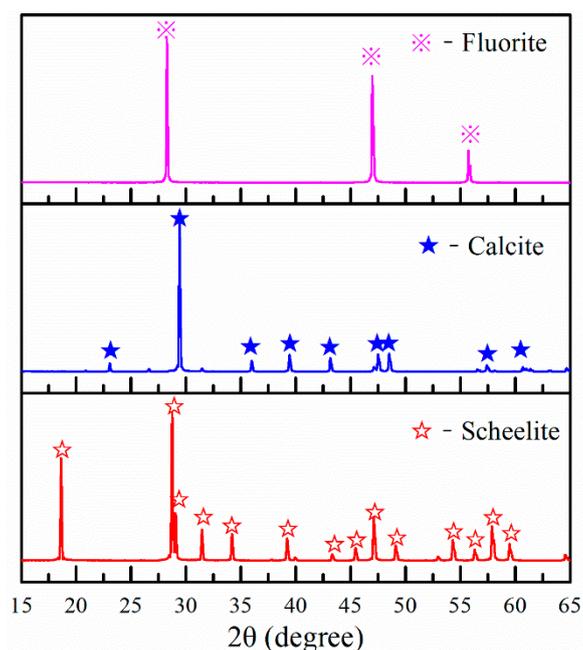
Figure 1. X-ray diffcration (XRD) patterns of scheelite, calcite, and fluorite pure minerals.

Table 1. X-ray fluorescence (XRF) analysis results of the scheelite raw ore.

Elements	O	F	Na	Mg	Al	Si	P	S	K	Ca	Mn	Fe	Mo	W
Contents (%)	35.25	4.46	0.51	1.81	2.45	18.34	0.69	0.81	1.64	21.91	1.08	10.94	0.02	0.09
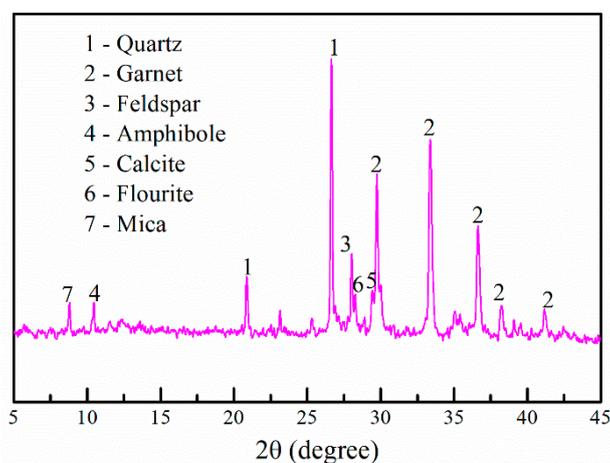
Figure 2. XRD pattern of the scheelite raw ore.

2.2. Experimental Procedures

A flotation machine (XFG$_{II}$, Jilin Prospecting Machinery Plant, Changchun, China) was used to conduct the flotation tests of a single mineral. The volume of the flotation cell was 40 mL, and the speed of impeller was 1650 rpm. The mineral suspension consisted of minerals (2 g) and deionized water. The pH was adjusted by adding sodium carbonate or hydrochloric acid solutions to the requested values. The anionic–nonionic assembled collector was composed of sodium oleate and oleamide with a mole ratio of 2:1. The froth and tailing were filtrated, dried, and weighed to obtain a recovery according to Equation (1). The flotation procedure of mixed minerals was similar to that of the single mineral flotation experiments. The mass ratio of scheelite, calcite, and fluorite in mixed minerals was 1:1:1. The grades of scheelite (WO$_3$), calcite, and fluorite were 26.85%, 33.33%, and 33.33%, respectively.

Figure 3 describes the reagent system and the process of scheelite roughing. The WO_3 grades of froth and tailing in the mixed mineral (1:1:1) flotation and scheelite roughing were measured by XRF. The scheelite recovery was quantified based on Equation (2).

$$R = \frac{M_1}{M_1 + M_2} \times 100 \tag{1}$$

$$R = \frac{M_1 \cdot \beta}{M_1 \cdot \beta + M_2 \cdot \theta} \times 100 \tag{2}$$

where R is the recovery (%), M_1 (g) and M_2 (g), denote the weights of froth and tailing, and β (%) and θ (%) refer to their grades, respectively.

Raw ore

3 min — Sodium carbonate
3 min — SHMP
3 min — Assembled collector

3 min

Concentrate   Tailing
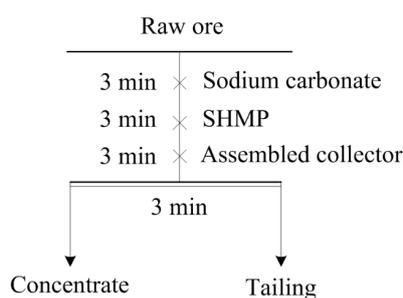
Figure 3. The reagent system and process of scheelite roughing.

2.3. Equilibrium Speciation Modelling

The pC–pH diagram, namely the negative logarithm of ion concentrations with varying pH, was built based on the protonation reactions. The pH solution is a key factor that notably influences the hydrolytic equilibrium of SHMP, which was simplified and established by employing sodium phosphate (Na_3PO_4) as an example. The calculation of hydrolytic equilibrium at diverse pH values was conducted with Visual MINTEQ 3.1 (Version 3.1, Environmental Protection Agency, Washington, WA, USA).

2.4. Zeta Potential Tests

The Zeta potentials of scheelite, calcite, and fluorite before and after reacting with SHMP and the assembled collector were measured using a Nano-Z Zeta potential analyzer (Malvern Instruments, Malvern, UK). The mineral slurry was composed of minerals (0.04 g) and 40 mL of KNO_3 (0.01 mol/L) solution as an electrolyte. SHMP and the assembled collector were added to the suspension in order and the pH was adjusted to the desired value using sodium carbonate or hydrochloric acid solutions. The mixture was stirred for 10 min for sufficient reaction. After free settling for 5 min, the supernatant was taken for Zeta potential tests.

2.5. FTIR Tests

The mineral pulp consisted of minerals (0.5 g) and deionized water. SHMP and the assembled collector were added in order and the mixture was stirred for adequate reaction for 30 min. The reacted minerals were filtered with microporous membrane, washed, and air dried at room temperature for FTIR analysis (Nicolet iS50, Thermo, Waltham, MA, USA).

2.6. XPS Tests

XPS tests were conducted using an ESCALAB 250Xi spectrometer (Thermo Fisher Scientific, Waltham, MA, USA) with Al Kα as the sputtering source at 12 kV and 6 mA. The mineral samples were prepared by mixing minerals with SHMP in deionized water. The mixture was stirred for 30 min and filtrated through a microfiltration membrane. The filtration residue was washed and dried in natural

wind for XPS tests. The test results were fitted using Thermo Avantage 5.96 (Version 5.96, Thermo Fisher Scientific, Waltham, MA, USA).

3. Results and Discussions

3.1. Flotation Experiments of Pure Mineral

Sodium oleate possesses an excellent ability to collect scheelite but poor selectivity to float calcite and fluorite because of their same calcium action sites. The anionic–nonionic assembled collector, namely, sodium oleate mixed with oleamide at a mole ratio of 2:1, was created to improve the selectivity of the collector. SHMP was used to further enhance the floatability difference of scheelite with calcite and fluorite. The flotation performances of a single mineral at diverse pH levels are described in Figure 4. The scheelite recovery increased with the rise of pH and reached its maximum (about 85%) at a pH of 10. The calcite recovery maintained at 70–75% at the pH range of 7–10 and increased to 95% at the pH of 12. Whereas, the fluorite recovery decreased from 87% to 65% with the increase of pH from 7 to 12. Compared with the recovery variations of scheelite, calcite, and fluorite, the floatability difference of scheelite with calcite and fluorite reached the maximum at a pH of 10. The recovery of scheelite reached 86.6%, while those of calcite and fluorite were 74.4% and 69.8%, respectively. Figure 5 reveals the flotation behaviors of scheelite, calcite, and fluorite at different SHMP doses. Unlike the results of previous studies that used a single sodium oleate as the collector [2,23], the floatability of calcite and fluorite was significantly reduced, but that of scheelite remained the same. The recovery of scheelite reached 85.68% without using SHMP, whereas those of calcite and fluorite were only 73.26% and 71.58%, respectively. As the SHMP dose increased to 10×10^{-6} mol/L, the recoveries of calcite and fluorite were gradually reduced to 20%, whereas that of scheelite remained above 85%. These results indicate that SHMP exerted a preeminent ability to depress calcite and fluorite, but it had no effect on scheelite.
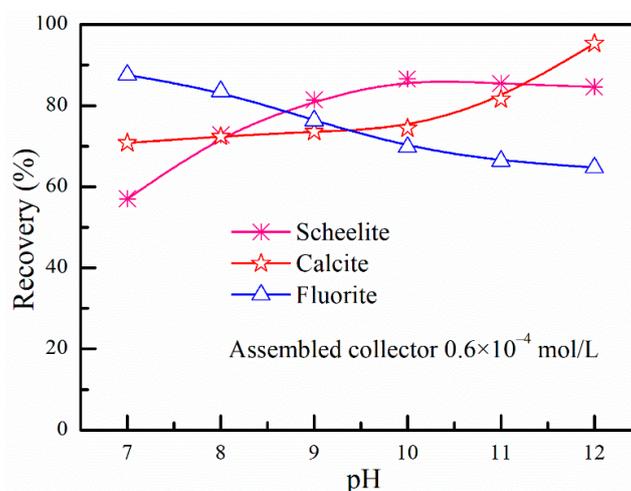
Figure 4. Flotation performances of single mineral at diverse pH levels when applying the assembled collector.

Considering the excellent performance of SHMP on single mineral flotation, it was utilized in the mixed mineral flotation to verify its ability to enhance the enrichment of scheelite. Figure 6 presents the flotation performance of scheelite in mixed minerals with diverse SHMP doses. With the absence of SHMP, the WO_3 grade of concentrate was 28.16% with a recovery of 79.86%. With increasing SHMP doses, the WO_3 grades gradually increased to the peak and then rapidly decreased. When the SHMP dose was 3×10^{-6} mol/L, the WO_3 grade was improved from 28.16% to 32.11% with an acceptable recovery of 69.18%. The results demonstrate that SHMP can effectively enhance the enrichment of scheelite in the flotation of mixed minerals with an appropriate dose. However, calcite

and fluorite cannot be completely depressed in the mixed mineral flotation, which results in a lower grade of concentrate than pure scheelite (WO_3 80.56%). When the SHMP dose exceeded 4×10^{-6} mol/L, the scheelite flotation deteriorated, and consequently, the grade and recovery sharply decreased. Compared to the results in single mineral flotation, scheelite was also depressed to a certain extent in the mixed mineral flotation. The possible reasons that result in the different behaviors of scheelite flotation may be attributed to the influence of dissolved ions. In the single mineral flotation, scheelite was not affected by the presence of impurity ions because the ions in the solution were dissolved from itself. However, in the mixed mineral flotation, scheelite, calcite, and fluorite dissolved and released calcium ions, tungstate ions, carbonate ions, and fluorine ions in the aqueous solution. These ions dissolved and deposited continually on the three minerals surfaces until reaching an equilibrium of dissolution and precipitation. During this process, the precipitations were transformed into each other on the surfaces of three minerals. The precipitations of scheelite, calcite, and fluorite may exist on each mineral surface at the same time, which causes the surface properties of scheelite to vary, thus resulting in the different flotation behavior from that of the single mineral flotation.
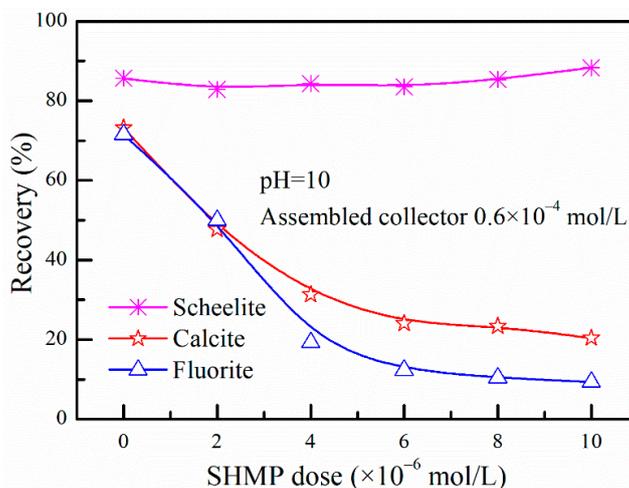
Figure 5. Flotation performances of a single mineral with diverse SHMP doses when applying the assembled collector at a pH of 10.
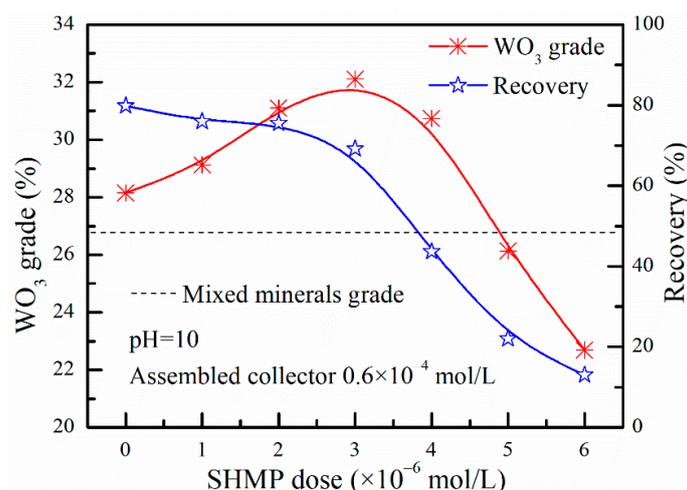
Figure 6. Flotation performance of scheelite in artificial mixed minerals with diverse sodium hexametaphosphate (SHMP) doses when applying the assembled collector at a pH of 10.

3.2. Equilibrium Speciation Analysis

SHMP is a hexamer of sodium metaphosphate and will degrade into lower phosphates [24], such as Na_3PO_4, Na_2HPO_4 and NaH_2PO_4, in the aqueous solution [25,26]. In the mineral flotation, the active ingredients of SHMP were hydrogen phosphates, namely $H_2PO_4^-$ and HPO_4^{2-}, which adsorb on the minerals surfaces via electrostatic force or chelation with metal ions [27]. The equilibrium speciation analysis of SHMP was simplified and established with sodium phosphate (Na_3PO_4) by protonation reactions and material balance. Figure 7 illustrates the pC–pH diagram of trisodium phosphate (3×10^{-6} mol/L) solution. H_3PO_4 is the dominant species when pH is below 2, whereas the dominant components turn into $H_2PO_4^-$ and HPO_4^{2-} at pH ranges of 2–7 and 7–12, respectively. When pH exceeds 12, PO_4^{3-} becomes the predominant species. The appropriate pH range for the flotation of scheelite is 10. Thus, the active species to depress calcite and fluorite is HPO_4^{2-}, which is a negatively charged hydrogen phosphate anion.
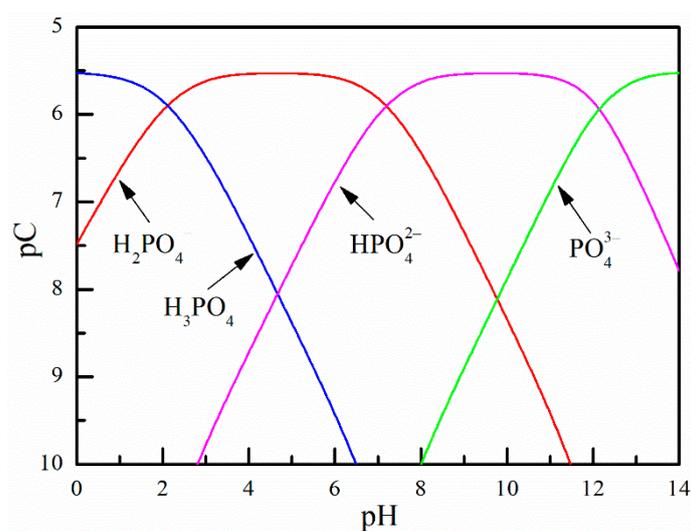
Figure 7. pC–pH diagram of 3×10^{-6} mol/L Na_3PO_4 solution.

3.3. Zeta Potential Analysis

Zeta potential is an important factor to characterize the surface electrokinetic properties of minerals. Figure 8 presents the Zeta potentials of scheelite, calcite, and fluorite with the absence and presence of SHMP and the assembled collector. The Zeta potentials of raw scheelite were negative at a pH range of 7–11 because the localized ions on scheelite surface were WO_4^{2-} [18]. With the presence of SHMP, the Zeta potentials of scheelite negatively shifted to some extent. With the presence of SHMP and the assembled collector, the Zeta potentials of scheelite had a significant further negative shift. The Zeta potentials of calcite and fluorite were positive at a pH range of 7–10 due to their localized ions of Ca^{2+} [2] and gradually decreased to negatives when the pH exceeded 10, which indicates that the isoelectric point (IEP) of calcite and fluorite was 10–11 [8,28]. With the presence of SHMP, the Zeta potentials of calcite and fluorite had significant negative shifts that were greater than that of scheelite. With the presence of SHMP and the assembled collector, the Zeta potentials of calcite and fluorite had no obvious further negative shift. These results indicate that the adsorption of SHMP on calcite and fluorite surfaces was stronger than that on scheelite surface. The negatively charged SHMP may be adsorbed on the positively charged surfaces of calcite and fluorite by electrostatic force and hinder the further adsorption of the assembled collector. Whereas, the adsorption of SHMP on the negatively charged surface of scheelite was weak, thus having less effect on the adsorption of assembled collector.
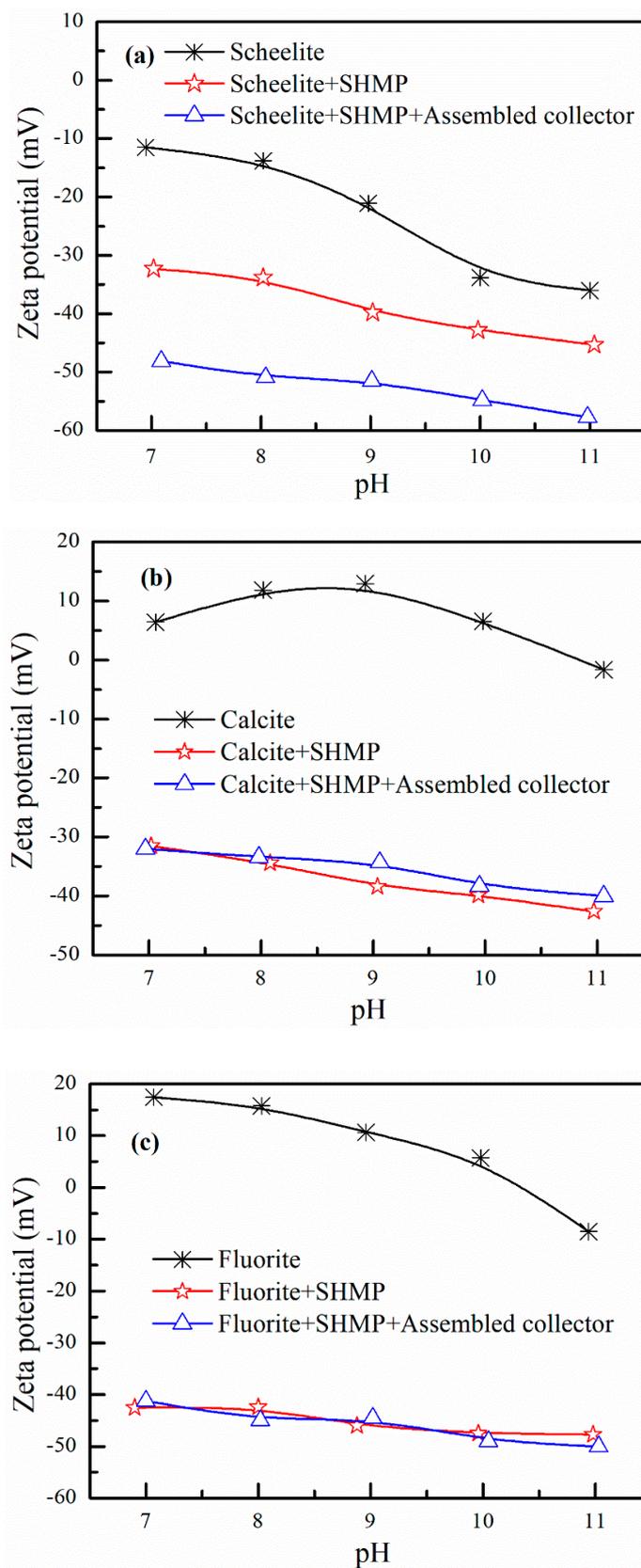
Figure 8. Zeta potentials of scheelite (**a**), calcite (**b**), and fluorite (**c**) at the different pH with the absence and presence of SHMP and the assembled collector.

3.4. FTIR Analysis

The adsorption mechanism of SHMP on the mineral surfaces was demonstrated by comparing the changes in the FTIR spectra curves, which are presented in Figure 9 before and after the reaction with SHMP and the assembled collector. The FTIR spectra of SHMP are consistent with those reported by previous studies [27,29]. The main characteristic peaks were located at 3444 cm^{-1}, 1646 cm^{-1}, 1283 cm^{-1}, 1097 cm^{-1}, 879 cm^{-1}, 519 cm^{-1}, and 472 cm^{-1}. The peak at 1283 cm^{-1} refers to the asymmetric stretching vibration of the P–O group [24]. The peaks at 1097 cm^{-1} and 472 cm^{-1} were due to the antisymmetric stretching vibration and symmetric variable angular vibration of the P–O groups, respectively. The peak at 879 cm^{-1} represents the symmetrical stretching vibration of the P–O–P group [30,31]. As shown in Figure 9b, the main characteristic peaks of scheelite at 809 cm^{-1} and 441 cm^{-1} represent the stretching and bending vibration of the W–O bonds, respectively [6]. After reacting with SHMP, no obvious new peak was observed on the scheelite spectrum. After reacting with the assembled collector, new peaks emerged at 2920 cm^{-1}, 2850 cm^{-1}, 1646 cm^{-1}, 1542 cm^{-1}, and 1458 cm^{-1}. The peaks at 2920 cm^{-1} and 2850 cm^{-1} represent the stretching vibration of methylene and methyl groups [32] in the sodium oleate or oleamide. The peaks at 1542 cm^{-1} and 1458 cm^{-1} refer to the asymmetric stretching and symmetrical vibration of the carboxyl [33] in the sodium oleate. The peak at 1646 cm^{-1} represents the characteristic peak of acylamino. After reacting with SHMP and the assembled collector, the location and strength of the characteristic peaks of sodium oleate and oleamide exhibited no obvious change. The changes in FTIR spectra demonstrate that SHMP was hardly adsorbed on scheelite surface, which had less influence on the further adsorption of the assembled collector.

As presented in Figure 9c, the primary characteristic peaks of calcite at 1429 cm^{-1}, 876 cm^{-1}, and 712 cm^{-1} refer to the asymmetric stretching vibration and deformation vibration of carbonate (CO_3^{2-}) groups [19,34]. After reacting with SHMP, no obvious new peak appeared on the spectrum curve of calcite. After reacting with the assembled collector, the characteristic peaks of methylene and methyl groups at 2923 cm^{-1} and 2854 cm^{-1}, respectively, emerged on the calcite spectrum curve. After reacting with SHMP and the assembled collector, the intensities of methyl and methylene absorption peaks considerably weakened. This behavior demonstrates that SHMP impeded the further adsorption of the assembled collector on the calcite surface and reduced its adsorption amount. As exhibited in Figure 9d, the variations in fluorite spectra were similar to those of calcite after reacting with SHMP and the assembled collector. The characteristic peaks of SHMP did not emerge on the fluorite spectra, whereas the characteristic peaks of the assembled collector at 2924 cm^{-1}, 2853 cm^{-1}, 1646 cm^{-1}, 1541 cm^{-1}, and 1461 cm^{-1} were present. The characteristic peak intensities of the assembled collector weakened after the sequential reaction with SHMP and assembled collector.

Combined with the results of Zeta potential and FTIR analyses, the absence of SHMP characteristic peaks and the presence of assembled collector characteristic peaks on the minerals surfaces indicates that SHMP was likely to be adsorbed on the surfaces of scheelite, calcite, and fluorite via electrostatic force, whereas the assembled collector was adsorbed on these minerals surfaces by chemical adsorption. When the solution pH was 10, the dominant component on scheelite surface was the negatively charged tungstate species, whereas the localized ions on the surfaces of calcite and fluorite were the positively charged calcium species [18]. By contrast, SHMP was more likely to be adsorbed on the surfaces of calcite and fluorite through electrostatic force, thereby occupying the active sites and impeding the further adsorption of the assembled collector. Nevertheless, SHMP was feebly adsorbed on the scheelite surface because of its negative charge, thus exhibiting less effect on scheelite flotation.
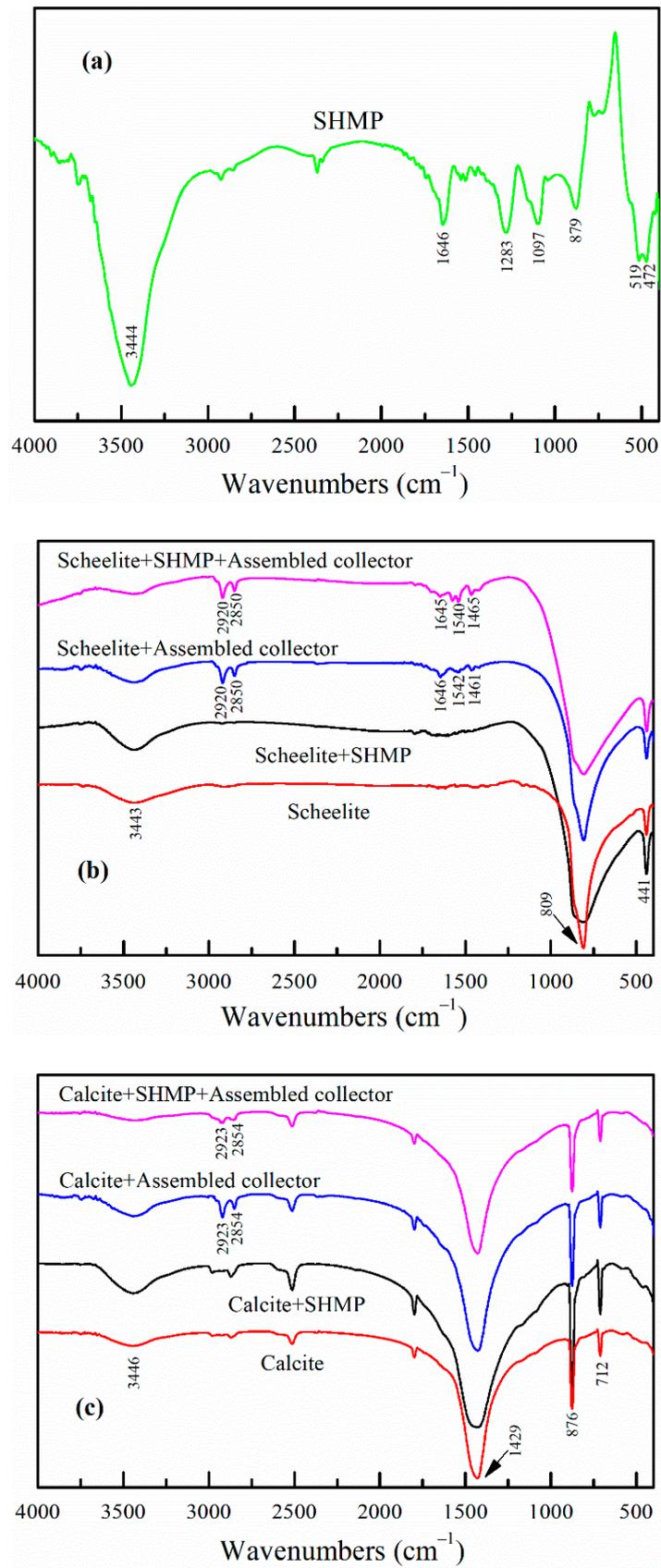
Figure 9. *Cont.*
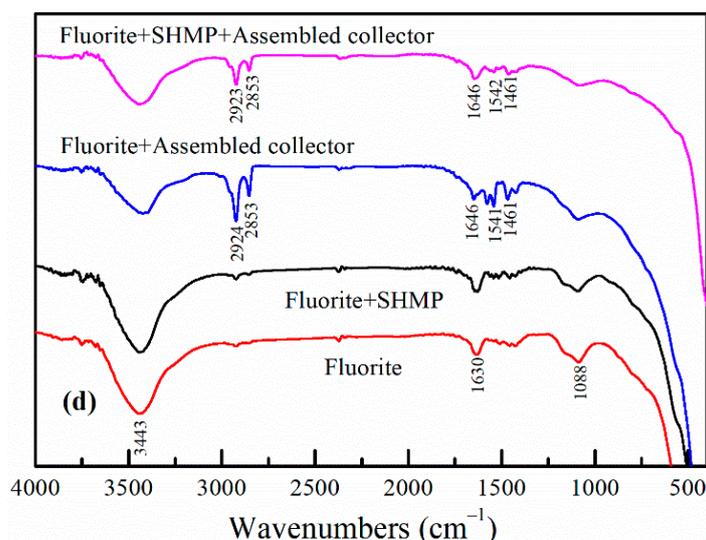
Figure 9. Fourier-transform infrared (FTIR) spectra of SHMP (**a**) and scheelite (**b**), calcite (**c**), and fluorite (**d**) before and after reacting with different reagents.

3.5. XPS Analysis

XPS analysis is an efficient approach to examine the adsorption mode and model of minerals with reagents. Table 2 presents the changes in atomic contents of various elements on the surfaces of scheelite, calcite, and fluorite after the reaction with SHMP. The carbon on the surfaces of raw fluorite and scheelite may result in the pollution of CO_2 in the air due to sample preparation in the wild. The contents of calcium, tungsten, and oxygen on scheelite surface were reduced by −0.37%, −0.83%, and −1.47%, respectively, whereas that of phosphorus was augmented by 0.51%. The calcium and carbon contents on calcite surface were reduced by −3.13% and −2.23%, respectively, whereas those of oxygen and phosphorus increased by 3.45% and 1.91%, respectively. The calcium and fluorine contents on fluorite surface were reduced by −4.78% and −8.41%, respectively, but those of oxygen and phosphorus increased by 6.72% and 2.13%, respectively. The variations in the atomic content variation of each element indicate that the adsorption strength of SHMP on these mineral surfaces was diverse. In contrast with the variations in calcium and phosphorus contents, the decrease in calcium and the increase in phosphorus on the surfaces of calcite and fluorite were larger than that in scheelite. These results indicate that the adsorption amounts of SHMP on the surfaces of calcite and fluorite were greater, thereby covering their original surfaces and reducing the relative content of elements. SHMP was weakly adsorbed on scheelite surface and it had minimal impact on the atomic content of each element.

Table 2. Variations in atomic contents of the elements on mineral surfaces after the reaction with SHMP.

Elements	Atomic Contents Changes (%)		
	Scheelite	Calcite	Fluorite
C	2.16	−2.23	4.34
O	−1.47	3.45	6.72
W	−0.83	-	-
F	-	-	−8.41
Ca	−0.37	−3.13	−4.78
P	0.51	1.91	2.13

The Ca2p XPS spectra of scheelite, calcite, and fluorite before and after the reaction with SHMP are shown in Figure 10. The peaks of Ca2p1 and Ca2p3 on raw scheelite surface, located at 350.51 eV and 346.94 eV, respectively, are consistent with those reported in the literature [27,35], and they have a

slight shift after the interaction with SHMP. The peaks of Ca2p1 and Ca2p3 of calcite were located at 350.56 eV and 346.99 eV and distinctly moved to 350.69 eV and 347.13 eV, respectively. The Ca2p spectrum of raw fluorite presented two characteristic peaks located at 351.37 eV and 347.79 eV, which are similar to those reported in the literature [36,37]. After the reaction with SHMP, the peaks of Ca2p1 and Ca2p3 remarkably shifted to 351.82 eV and 348.25 eV, respectively. Compared with the binding energy shifts of Ca2p after reaction with SHMP enumerated in Table 3, the shifts of Ca2p1 and Ca2p3 peaks on scheelite surface were only 0.03 eV and 0 eV, respectively, whereas those on calcite surface reached 0.13 eV and 0.14 eV, respectively. The shifts of Ca2p1 and Ca2p3 peaks on fluorite surface reached 0.45 eV and 0.46 eV, respectively. The binding energy shifts of Ca2p prove that SHMP was likely to be adsorbed on the surfaces of calcite and fluorite via chelation with calcium species, whereas the adsorption of SHMP was feeble because the localized ion on scheelite surface is a tungstate species.
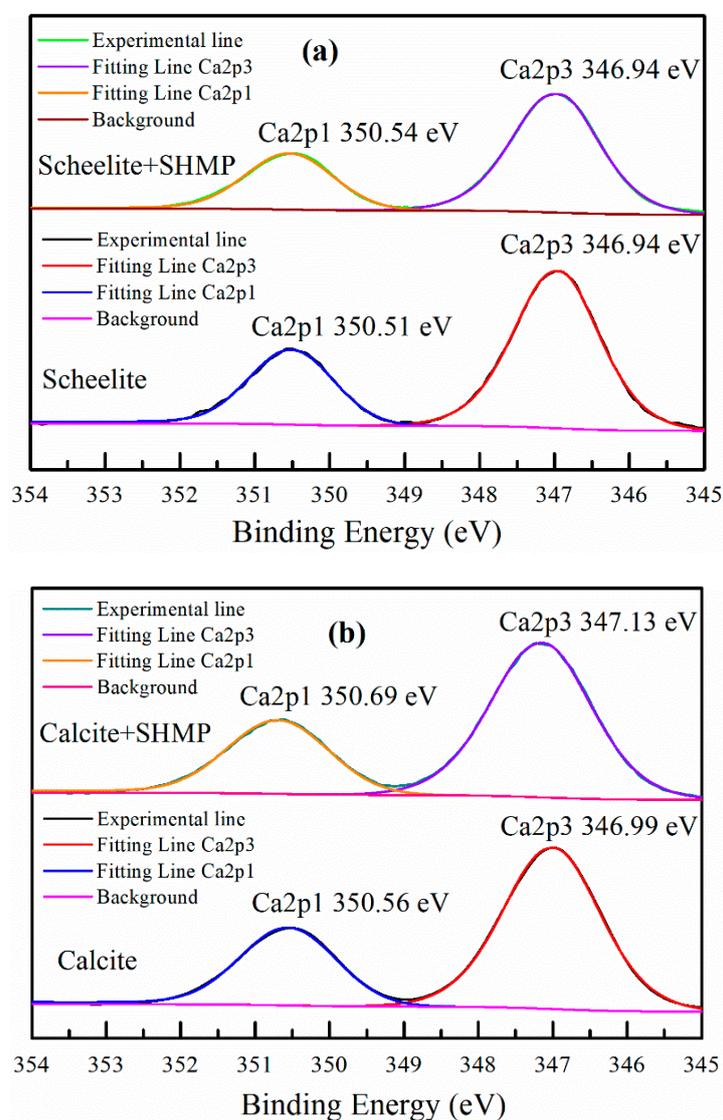
Figure 10. *Cont.*
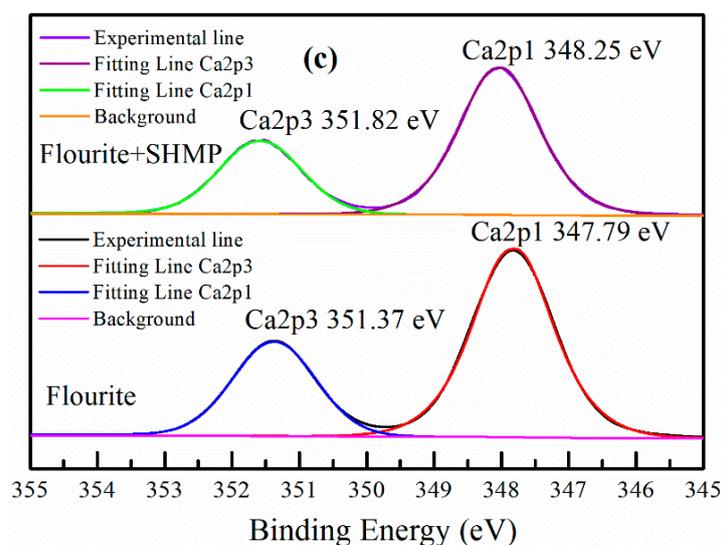
Figure 10. Ca2p X-ray photoelectron spectroscopy (XPS) of scheelite (**a**), calcite (**b**), and fluorite (**c**) before and after the reaction with SHMP.

Table 3. Binding energies and their shifts of Ca2p1 and Ca2p3 of minerals before and after the interaction with SHMP.

Minerals	Scheelite		Calcite		Fluorite	
Elements	Ca2p1	Ca2p3	Ca2p1	Ca2p3	Ca2p1	Ca2p3
Before (eV)	350.51	346.94	350.56	346.99	351.37	347.79
After (eV)	350.54	346.94	350.69	347.13	351.82	348.25
Shifts (eV)	0.03	0	0.13	0.14	0.45	0.46

3.6. Low-Grade Scheelite Ore Flotation Tests

The tungsten ore, obtained from Luanchuan, was a representative skarn scheelite. The WO_3 grade was only 0.1%. The raw ore underwent roughing with a fatty acid collector and then underwent heating cleaning by applying the Petrov method. However, the associated calcite and fluorite were also enriched during the roughing stage due to the poor selectivity of the collector. Owing to the outstanding ability of SHMP to depress calcite and fluorite, it was applied to promote the scheelite roughing efficiency. Figure 11 presents the roughing performance of scheelite with varying SHMP doses applied to the assembled collector. In the blank test, namely, in the absence of SHMP, the roughing WO_3 grade of scheelite was only 0.74% with a considerable recovery of 84.66%. When the SHMP dose was increased to 15 g/t, the roughing grade increased to 1.65%, while the recovery decreased to 72.83%. The roughing grade was increased by two-fold compared with that in the blank test. The results prove that SHMP is an effective depressant to depress the gangue minerals at a low dose, thereby improving the scheelite roughing efficiency.
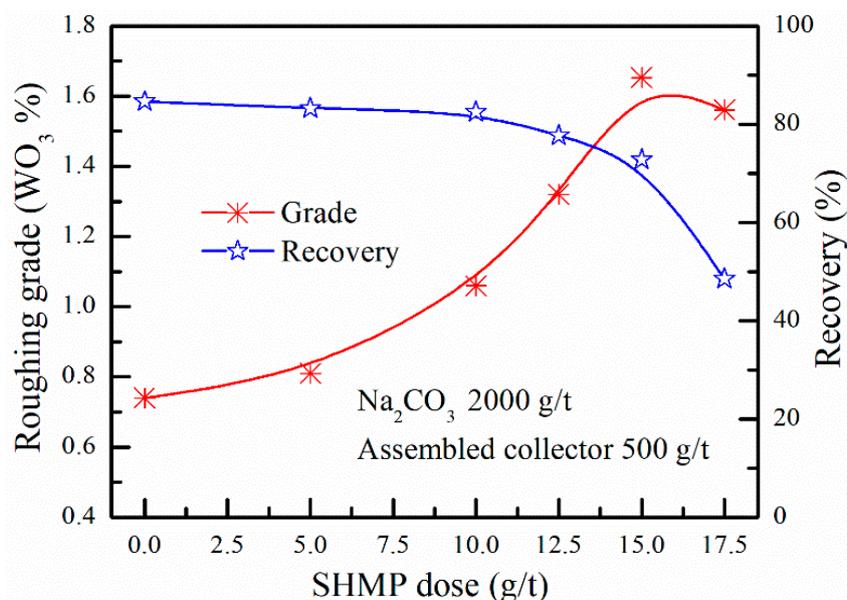
Figure 11. Scheelite roughing performance with diverse SHMP doses when applying the assembled collector.

4. Conclusions

A highly selective reagent system that utilizes SHMP as depressant and sodium oleate mixed with oleamide as the collector to enhance the enrichment of scheelite was presented. The flotation behaviors of scheelite, calcite, and fluorite were examined through flotation tests. The reaction mechanism of minerals with SHMP was performed by equilibrium speciation, Zeta potential, FTIR, and XPS analyses. Finally, the highly selective reagent system was applied to improve the roughing performance of low-grade scheelite ore. The following conclusions were drawn.

(1) SHMP exhibited outstanding performance to depress calcite and fluorite, thus facilitating the flotation enrichment of scheelite.

(2) SHMP degraded into lower phosphates and hydrolyses into HPO_4^{2-} at a pH of 10. HPO_4^{2-} may be adsorbed on the positively charged surfaces of calcite and fluorite via electrostatic force or chelation with calcium species, whereas it was hardly adsorbed on scheelite surface because of its negative charge.

(3) The scheelite roughing grade was considerably improved from 0.74% to 1.65% in the presence of SHMP. The application of SHMP presented a practical case to depress gangue minerals, thereby promoting the roughing efficiency of scheelite.

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