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**Abstract:** In this paper,  $-10 \mu m$  rutile and  $-30 \mu m$  garnet particles were selected as samples. The effects of different reagents on the flotation of rutile and garnet single minerals were studied, and the mechanism was analyzed by the contact angle, zeta potential, and Fourier transform infrared (FTIR) measurements. The flotation results show that an optimal recovery is obtained with benzohydroxamic acid (BHA) as the collector for rutile and sodium silicofluoride (SSF) as the inhibitor for garnet. Even with BHA having a good collecting performance for both rutile and garnet, there are still some differences. BHA greatly improves the hydrophobicity of rutile and garnet, and changes the chemical environment of rutile but not garnet. SSF significantly reduces the hydrophobicity of rutile and garnet, and slightly affects the environment in which BHA interacts with rutile. However, the above reagents and combinations have little effect on the surface chemical environment of garnet.

Keywords: flotation; rutile; fine particle; separation; collector selectivity



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# 1. Introduction

Garnet is the main associated gangue mineral of rutile, affecting its efficient recovery. The specific gravity of the two minerals is similar [1]. The iron isomorphism in the rutile lattice makes the surface of rutile easily contaminated with iron, and reduces the magnetic difference between rutile and garnet [2]. Therefore, flotation has become the main research direction for rutile and garnet separation.

Recently, there was renewed interest in the research on flotation separation of rutile and garnet, especially with respect to flotation reagents. Huang et al. [3] studied the flotation separation of rutile and garnet using the cationic surfactant octadecylamine polyoxyethylene ether as a collector, proving that the adsorption of AC1815 on rutile surface is mainly due to the electrostatic interaction and the hydrogen bonding; Richard et al. [2,4] studied the flotation separation of rutile and garnet using the cationic surfactant octadecylamine polyoxyethylene ether as the collector, Na-CMC as the inhibitor, sodium sulfite as a regulator, and octadecylamine polyoxyethylene ether-styrene phosphonic acid mixed as a composite collector, discovering that sodium sulfite acting in the form of  $SO_3^{2-}$  is more selectively adsorbed on garnet surface compared to that of rutile, leading to a high selectivity for the flotation of rutile; Chen et al. [1] investigated the flotation of rutile from garnet using sodium fluorosilicate as an inhibitor and styrylphosphonic acid as a collector, finding that there is a strong interaction between sodium fluorosilicate and active Fe sites on garnet surface, reducing adsorption sites for the collector, thereby strongly depressing the flotation of garnet. The above studies are mainly aimed at the mechanism of conventional particle size rutile and garnet flotation reagents, but the studies on the reagents for the flotation separation of fine particles of the two minerals still needs to improve.

According to all of the above researches, rutile and garnet can be effectively separated using phosphate, oleate, hydroxamic acid, and benzylarsinic acid as collectors, and sodium fluorosilicate, sodium hexametaphosphate, and Pb<sup>2+</sup> as regulators. While carboxylic acid



collectors have a strong collection performance, but poor selectivity, phosphonic acid collectors have a better flotation effect but a high cost; arsonic acid collectors have good collection performance and selectivity, but are highly toxic [5–8]. It was indicated that the selection of proper reagent is very important for separation [9,10]. The current research on flotation separation experiments pays more attention to hydroxamic acid collectors [11] because of their better selectivity, and lesser toxicity, while due to its low cost, styrene phosphoric acid is a common collector in industrial applications.

At present, the research on the flotation separation of rutile and garnet mainly focuses on the reagents [12,13], while there are fewer studies on fine particles and various reagent combinations. In addition, in actual flotation, due to factors such as disseminated mineral particle size and hardness, the particle size of target and gangue minerals may be different, while the research on the flotation separation of two minerals with different particle sizes is rare. Therefore, it is essential to further research the relation between inhibitor, activator, and collector, as well as their effects on the separation of rutile and garnet with different particle sizes.

This paper focuses on the effects of styrene phosphoric acid and hydroxamic acid collectors, sodium fluorosilicate inhibitor, and activator lead ions on the flotation of rutile and garnet. Referring to the properties of the Zaoyang rutile deposit in Hubei, China,  $-10 \mu m$  rutile and  $-30 \mu m$  garnet were selected as the research objects, which provided a certain basis for the flotation separation of rutile and garnet of different particle sizes in actual minerals.

## 2. Experimental Section

# 2.1. Sample and Reagents

The rutile and garnet samples used in this paper were from Hubei Province, China. According to the chemical analysis results of rutile in Table 1, the grade of rutile is 96%. The sample is of high purity from the X-ray diffraction analysis of the garnet sample in Figure 1. Both rutile and garnet samples meet the pure mineral flotation standard. According to the dissemination size of the two minerals in the rutile deposit in Zaoyang City, Hubei Province, the particle size fraction of rutile was selected to be  $-10 \mu$ m, and for garnet was  $-30 \mu$ m. After crushing with XPC-60 × 100 jaw crusher (Produced by China Henan Jiufu Machinery Equipment Co., Ltd., Zhengzhou, China), wet screening, and grinding with MJ-2A stirring mill at 500 rpm for 40 min, the D90 of the final rutile sample is 7  $\mu$ m ( $-10 \mu$ m), and the D90 of the garnet sample is 25.38  $\mu$ m ( $-30 \mu$ m).



Figure 1. XRD pattern of garnet.

TiO <sub>2</sub>	ZrO <sub>2</sub>	$Nb_2O_5$	SiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	Cr <sub>2</sub> O <sub>3</sub>	CaO	ThO <sub>2</sub>
96.21	0.73	0.61	0.51	0.44	0.31	0.22	0.19	0.19

**Table 1.** Analysis results for the chemical composition of rutile/%.

The reagents used in this paper included benzohydroxamic acid (BHA), salicylic hydroxamic acid (SHA), styrene phosphoric acid (SPA), sodium fluorosilicate (SSF), (NaPO<sub>3</sub>)<sub>6</sub>, Pb(NO<sub>3</sub>)<sub>2</sub>, NaOH, H<sub>2</sub>SO<sub>4</sub>, and terpineol oil. All reagents except SPA were purchased from Shanghai Aladdin Reagent and all of analytical grade, while SPA was purchased from an industrial production site, and was technical grade pure. The test water was ultrapure, with a conductivity of 18.25 MΩ.cm.

#### 2.2. Microflotation Tests

For microflotation tests, a XFGII flotation machine with a 50 mL cell was used at 1902 rpm. BHA, SHA, and SPA were used as collectors, SSF and  $(NaPO_3)_6$  as inhibitors,  $Pb^{2+}$  as activator, and terpineol oil as frother. Except for terpineol oil, the reagents used at a concentration of 1 mg/mL 3 g of sample were examined in each experiment. Following pH adjustment (pH = 5~9), after each reagent addition (regulator, inhibitor, activator, collector), the mixture was stirred for three minutes. Afterwards, terpenic oil was added and the pulp was conditioned for 2 min, followed by 2 min flotation with the air flow rate of 0.1 m<sup>3</sup>/h. The detailed flow of the flotation experiment is shown in Figure 2. The effects of collectors on rutile and garnet flotation were studied, then the effects of inhibitors under different collector conditions were explored, and finally, the effect of activators was determined.



Figure 2. Flowsheet of flotation.

# 2.3. Zeta Potential Measurement

A nano-ZS90 zeta potentiometer was used to measure the electrophoretic mobility of rutile and garnet to examine the effect of different reagents on the electric surface potential of the two minerals. The test temperature was kept at 25 °C, the sample particle size was  $-5 \mu m$ , and the reagent concentration was 50 mg/L. After the reagent was added, the slurry was stirred for 15 min and then allowed to settle for 5 min, before the supernatant was taken for measurement. Each group of tests was performed in triplicate, and the average results were used for analysis.

## 2.4. FTIR Tests

A Nicolet 6700 Fourier transform infrared spectrometer was used to study the adsorption of the reagents on the surface of the two minerals, and the rutile and garnet samples before and after the conditioning with collectors, inhibitors, activators, and their combinations. A total of 1 g of the sample was used to prepare the slurry with the same concentration as the flotation concentration. After adding the reagent, it was stirred for 15 min, and then filtered and dried for testing. The adsorption performance of each reagent on the sample surface was compared and analyzed by the test results.

### 2.5. Contact Angle Measurements

To study the effect of the reagents on the contact angle of the two minerals, the rutile and garnet samples were conditioned with each reagent and then dried at low temperature, and each group of samples was pressed into a tablet shape by a tablet machine for testing. The contact angles of the rutile and garnet before and after each reagent's action were measured by a JC2000D. A droplet of  $0.3 \,\mu$ L volume was produced and the stage carrying the tablet-pressed sample was raised to contact the droplet, and then lowered, and the contact angle of the droplet on the surface of the sample was measured. Each surface with or without reagent was tested 3 times.

#### 3. Results and Discussion

#### 3.1. Flotation Results of Different Types of Collectors

The effect of pH on flotation is shown in Figure 3. With BHA as the collector, the recoveries of rutile and garnet both reach their maximum at pH = 7, and simultaneously the largest difference (34.67%) between the recoveries of the two minerals is obtained. When using SHA as the collector, the recovery of garnet reaches its maximum at pH = 6, while that of rutile reaches its maximum at pH = 7. The difference between the recoveries of the two minerals at pH = 9 is larger, namely, 20.80%. With SPA as the collector, the recoveries of the two minerals reach their maximum values at pH = 8, and the difference of this is also the largest (21.95%). It is demonstrated that BHA probably works best for flotation separation of rutile and garnet in the above collectors.



**Figure 3.** Effect of pH on the flotation of rutile and garnet with different types of collectors. (Concentration of collectors = 40 mg/L).

The effect of collector concentration on the flotation recovery is shown in Figure 4. With BHA as the collector, the increasing trend of the recoveries of rutile and garnet is linear with a low inclination when the concentration is 50 mg/L and 30 mg/L, and the recoveries are constant at 89.92% and 59.27%, respectively. When using SHA as the collector, the recoveries of rutile and garnet tend to be stable when the collector concentration is 40 mg/L, and are constant at 67.14% and 63.1%, respectively. With SPA as the collector, the recoveries of rutile and garnet also tend to be constant when the collector concentration is 40 mg/L, and are constant at 45.37% and 31.44%, respectively. In the BHA flotation system, the flotation recovery of the two minerals are maximum at different concentrations, which may be due to their selectivity to the two minerals resulting in more interaction sites with rutile [11].



**Figure 4.** Effect of concentration on the flotation of rutile and garnet. (pH = 7 with BHA, pH = 9 with SHA, pH = 8 with SPA).

The selectivity and hydrophobization of BHA are better, while the hydrophobization and selectivity of SHA for fine particles are both poor, and the collecting ability of SPA was the worst, and the selectivity better than SHA, lower than BHA. With BHA as collector, the recovery difference between the two minerals is the largest when the concentration is 20 at pH = 7. However, it is difficult to achieve a great separation effect by using only a collector. Therefore, the effect of inhibitors on the flotation of two minerals was further studied.

#### 3.2. Flotation Results of Inhibitors

Flotation results of inhibitors are as follows. Figure 5 shows the effect of pH on flotation under different inhibitor conditions. When SSF and BHA are used as reagents, the recoveries of rutile and garnet reach their maximum at pH = 7, and the difference between the recoveries of the two minerals is the largest at pH = 7, namely, 38.9%. The recovery of rutile in (NaPO<sub>3</sub>)<sub>6</sub> and BHA flotation systems reaches the maximum at pH = 7, while the recovery of garnet reaches the maximum at pH = 8. The difference is the largest at pH = 7, but only 7.35%. (NaPO<sub>3</sub>)<sub>6</sub> has a great inhibitory effect on the flotation of rutile, and has no obvious selectivity. This may be because (NaPO<sub>3</sub>)<sub>6</sub> acts as a dispersant to disperse the fine rutile particles in the pulp, and it is difficult to achieve hydrophobic flocculation even under the action of the collector, which reduces the collision probability between the mineral particles and the bubbles, thus, affecting the floating effect.



**Figure 5.** Effect of pH on the flotation of rutile and garnet by SSF and  $(NaPO_3)_6$  (concentration of BHA = 20 mg/L, concentration of SSF = 10 mg/L, concentration of  $(NaPO_3)_6 = 10 \text{ mg/L}$ ).

Figure 6 shows the effect of inhibitor concentration on flotation. The recovery of the two minerals decreases with the increase in inhibitor concentration. In the SSF and BHA flotation systems, the recoveries of rutile and garnet are constant at 63.11% and 30.47% when the SSF concentration is 50 mg/L and 30 mg/L, respectively. In the (NaPO<sub>3</sub>)<sub>6</sub> and BHA flotation systems, when the (NaPO<sub>3</sub>)<sub>6</sub> concentration is increased to 30 mg/L and 50 mg/L, the recoveries of rutile and garnet are stable at 17.85% and 35.76%, respectively. The difference in inhibitor concentration for the two groups of minerals to achieve constant recovery may be due to the finer particle size of the rutile, the high specific surface area, and more action sites of the reagent. The inhibitory effect of (NaPO<sub>3</sub>)<sub>6</sub> on rutile even exceeds that of garnet, proving that (NaPO<sub>3</sub>)<sub>6</sub> is not available as an inhibitor for the flotation separation of rutile and garnet.



**Figure 6.** Effect of concentration on the flotation of rutile and garnet by SSF and  $(NaPO_3)_6$  (pH = 7, concentration of BHA = 20 mg/L).

#### 3.3. Flotation Results of Activator

According to the above experiments, BHA was selected as the collector and SSF as the inhibitor, and the effect of  $Pb^{2+}$  as the activator on the flotation behavior of rutile and garnet was studied. As shown in Figure 7, the flotation recovery for both minerals reaches maximum at pH = 7. The best recoveries of rutile and garnet are 72.51% and 49.44%, respectively, while without adding  $Pb^{2+}$ , the recoveries of the two minerals are 67.4% and 31.5%, respectively (Figure 6).  $Pb^{2+}$  can activate both rutile and garnet, but the difference between the two recoveries after activation is reduced to 23.07%, indicating that  $Pb^{2+}$  has a stronger activation effect on garnet and could not improve the separation effect of the two minerals.



**Figure 7.** Effect of pH on rutile and garnet activated by  $Pb^{2+}$  (concentration of BHA and SSF = 40 mg/L, concentration of  $Pb^{2+} = 10 \text{ mg/L}$ ).

The effect of the concentration of  $Pb^{2+}$  on the flotation of rutile and garnet is shown in Figure 8. The recovery of both minerals increases with the increase in  $Pb^{2+}$  concentration. When the  $Pb^{2+}$  concentration is 15 µg/mL, the recovery values tend to be stable. The recovery of rutile increases from 65.96% to 72.74%, and the recovery of garnet increases from 31.4% to 45.95%, showing that the activation effect of  $Pb^{2+}$  on garnet is greater than that on rutile.



**Figure 8.** Effect of concentration on  $Pb^{2+}$  activation of rutile and garnet (pH = 7, concentration of BHA and SSF = 40 mg/L).

The addition of Pb<sup>2+</sup> does not lead to better separation of garnet and rutile. Therefore, BHA was selected as the collector and SSF as the inhibitor, and the 1:1 artificial mixed ore of rutile and garnet was used for mixed flotation. The results of mixed flotation are shown in Figure 9. It can be seen that the index does not meet the separation standard, and the separation of the two is not achieved. This may be because the particle size of rutile and garnet is different, and the rutile particle size was too fine, meaning it was seriously entrained in the mixed flotation [14]. In addition, the use of terpineol oil, a foaming agent, may also increase the recovery of garnet in mixed flotation.



Figure 9. Mixed flotation results (concentration of BHA = 20 mg/L, SSF = 10 mg/L).

## 3.4. Contact Angle Measurements Results

Figure 10 shows the measurement results of the surface contact angle of rutile and garnet under the action of different reagents at pH = 7. The contact angles of pristine rutile and garnet samples are 32° and 24.5°, respectively. Compared to the contact angle of pristine mineral samples, the contact angle of rutile and garnet after the action of BHA is the largest, which is 50.5° and 38.5°, respectively, and the hydrophobicity is the maximum, followed by SHA, and SPA has the smallest change in the hydrophobicity of the two minerals. The contact angle difference between rutile and garnet after SHA is the largest, which is 12°, indicating that the selectivity of SHA is better. Among the two inhibitors, SSF has a greater effect on the contact angles of the two minerals, and significantly reduces their hydrophobicity, while the inhibitor (NaPO<sub>3</sub>)<sub>6</sub> and the activator Pb<sup>2+</sup> have few effects on the contact angles of the two minerals.



Figure 10. Effects of reagents on the hydrophobicity of rutile and garnet.

The effects of different chemical combinations on the surface hydrophobicity of rutile and garnet are shown in Figure 11. In the absence of the activator  $Pb^{2+}$ , the chemical combination of SSF and SPA has the greatest difference in the influence of the contact angle of rutile and garnet, which is more conducive to the separation of the two minerals. The contact angle of rutile and garnet after the action of BHA and SSF is the largest, and the hydrophobicity of minerals improves the most. With the addition of  $Pb^{2+}$ , the hydrophobicity of the two minerals does not change. This may be because  $Pb^{2+}$  affects the floatability of the minerals through other modes, which is also consistent with the results of the previous set of experiments and floation experiments [8]. In addition, the results of the contact angle measurements may be smaller than that of the flaky mineral samples. This may be because the samples for the contact angle test are pressed from mineral powders, which affects the wettability of the samples under the action of capillary force, but has few effects on the study of the overall trend of hydrophobicity.

### 3.5. Reagent Adsorption Results

Figures 12 and 13 show the infrared test results of the interaction of reagents and minerals. After conditioning rutile with BHA, the adsorption bands appearing at 3434, 1714, and 1646 cm<sup>-1</sup> are related to the stretching vibration of –OH, C=O, and the benzene ring in BHA [15,16]. The chemical environment of rutile is altered by BHA. Compared with the absorption bands 3434, 1714, and 1646 cm<sup>-1</sup> under the action of BHA only, the absorption bands of each functional group under the action of BHA and SSF (3519, 1734, and 1643 cm<sup>-1</sup>) have a slight shift and are very weak. This indicates that SSF affects the adsorption of BHA on rutile. Compared with the infrared spectrum of rutile treated with BHA, the absorption peaks of each functional group in the infrared spectrum of rutile

under the action of  $Pb^{2+}$  and BHA show slight shifts. In addition, more complex absorption bands appear in the infrared spectrum, and the transmittance also changes, which indicates that  $Pb^{2+}$  has obvious changes on the chemical environment of rutile.



Figure 11. Effect of reagent combination on the hydrophobicity of rutile and garnet.



Figure 12. Infrared spectra of rutile before and after the interaction with reagents.



Figure 13. Infrared spectra of garnet before and after the interaction with reagents.

Figure 13 shows the adsorption results of reagent on the surface of the garnet. After conditioning with BHA, the absorption bands at 3444, 1700, and 1450 cm<sup>-1</sup> have only slight changes in transmittance, which are related to the stretching vibration of OH, C=O, and benzene rings, respectively [17]. It suggested that there is little change in its chemical environment. Compared with the garnet treated with BHA, the infrared spectrum of the garnet treated with SSF and Pb<sup>2+</sup> and then treated with collectors has only a difference in transmittance, and the change in transmittance is slight. It shows that both SSF and Pb<sup>2+</sup> cause slight changes in the chemical environment of BHA, but due to the little environment alteration of BHA on garnet, the influence of inhibitors and activators is small.

# 3.6. Zeta Potential Measurement Results

The zeta potential test results of rutile and garnet before and after the action of each reagent are shown in Figure 14. The zeta potential of rutile shifts negatively with the increase in pH, because with the increase in OH<sup>-</sup> concentration, the surface of rutile adsorbs OH<sup>-</sup> to form a TiOH interface, which hydroxylates the surface of rutile [18]. When pH > 9, the adsorption of  $H^+$  on the surface of garnet to the anionic active sites in the pulp exceeds the adsorption of the cationic active sites (Ti<sup>+</sup>) and OH<sup>-</sup>, causing the zeta potential to shift positively [19]. With the addition of BHA, the zeta potential of rutile shifts negatively, resulting in instability of the system, and the possibility of agglomeration of rutile particles. The garnet has a small negative shift, which may be because BHA does not change the chemical environment of garnet much and has little effect on zeta potential. With the addition of SSF, in comparison to the BHA action environment, the zeta potential of the rutile under the action of BHA shifts slightly positively, while that garnet shifts negatively. This indicates that either BHA and SSF compete for adsorption on the rutile surface, so the addition of SSF has little effect on the zeta potential of the rutile [20], or that SSF hinders the adsorption of BHA, leading to a lower negative shift in the zeta potential in the presence of both reagents. While SSF is adsorbed in garnet, the positively charged ions (the active site  $Fe^{2+}$ ,  $Fe^{3+}$ ,  $Al^{3+}$ ) on its surface are adsorbed with negative ions in the solution, so that the surface of the garnet is negatively charged. SSF competes with anionic collectors for adsorption, which reduces the adsorption of BHA on the surface of the garnet, so SSF has an inhibitory effect on the garnet [21].



Figure 14. Effects of different reagents on the zeta potential of rutile and garnet.

#### 4. Conclusions

(1) Among the collectors used in this paper, BHA has a better collection performance, and the difference in recovery between flotation rutile and garnet is the largest;

(2) SSF reduces the contact angles of rutile and garnet from 32° and 24.5° to 25° and 19°, respectively, significantly reducing their hydrophobicity. Among the collectors, BHA

increases the contact angles of the two minerals to 50.5° and 38.5°, which greatly improves their hydrophobicity;

(3) BHA has little effect on the surface potential of garnet, but negatively shifts the surface potential of rutile. The potential of rutile and garnet are adversely affected by the addition of SSF, and the effect on rutile is less;

(4) BHA and SPA change the chemical environment of rutile but not garnet. SSF slightly affects the environment in which BHA and SPA interact with rutile. However, various reagents and reagent combinations have little effect on the surface chemical environment of garnet. This provides a certain basis for the flotation separation of fine rutile and garnet, In the future, in addition to flotation reagents, the separation of the two can also be studied in terms of particle size.

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