

CARRIER FLOTATION OF ULTRAFINE

PARTICLE WOLFRAMITE^①

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ABSTRACT

Carrier flotation behaviour and mechanism of ultrafine particle wolframite using chelate reagent as collector have been studied. The recovery of $-5\mu\text{m}$ wolframite can be enhanced significantly through carrier flotation using chelating agent as collector. The adsorption mechanism of chelating agent on the surface of wolframite is that insoluble chelate settlement is produced due to chemical reaction between chelating agent and metallic ions on the surface of wolframite. The $-5\mu\text{m}$ wolframite particles are attached to coarse particles due to hydrophobic forces between hydrophobic wolframite particles resulting from collectors.

Key words: wolframite carrier flotation mechanism

1 INTRODUCTION

Carrier flotation is an effective method recovering fine mineral particles. Many researches have been reported in removing impurity from kaolin and recovering slime of manganese, iron and lead-zinc ores^[1-2]. Some mechanisms responsible for carrier flotation have been presented, such as "coating by ultrafine particles", "collision between fine and coarse particles" and "coarse particle effect—carrier, middle medium and promoting aggregation"^[3-4]. The mechanism of wolframite chelating agent flotation and that of fine particles attaching to the surface of coarse substrates have been investigated through flotation tests, measurement of adsorption amount and scanning electron micrograph based on surface and colloid chemistry in this paper.

2 EXPERIMENTAL METHOD

The wolframite samples from Yiao Gangxian were prepared through hand-sorting, crushing,

grinding, screening and hydraulizing into different size fractions. Purity of the samples is all above 95%.

Conventional flotation tests were conducted in a 100mL baffled cell. In carrier flotation tests, the $-5\mu\text{m}$ samples were put into beaker, immersed in distilled water, stirred at the speed of 2150 r/min for 30 min, transferred into another cell after dispersed completely, and then carrier particles and reagents were added to adjust suspension. Flotation tests were carried out in the similar baffled cell.

Adsorption amount of collector was measured with a 751-G ultraviolet spectrophotometer. Attachment of fine particles to the coarse ones was examined with a JCSA-733 scanning electron microscope.

3 RESULTS AND DISCUSSION

3.1 Flotation of Fine Particle Wolframite

Flotation recovery of $-19\mu\text{m}$ and $-5\mu\text{m}$ wolframite as function of pH are shown in Fig. 1

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and Fig. 2. It is obvious that the optimum range of pH of wolframite flotation is 6 to 9 with sodium hydroxamate, α -nitroso- β -naphthol, styryl phosphonic acid, sodium oleate as collectors. Flotability and recovery of fine particle wolframite were low using conventional collectors such as styryl phosphonic acid and sodium oleate, but improved using chelating agents as collectors.

Fig. 3 and Fig. 4 show the results of the $-5\ \mu\text{m}$ wolframite carrier flotation. Compared with Fig. 2, flotability is greatly improved through carrier flotation and recovery is increased by 10% ~ 30%. In the meantime, the recovery of carrier particles is also improved. In carrier flotation,

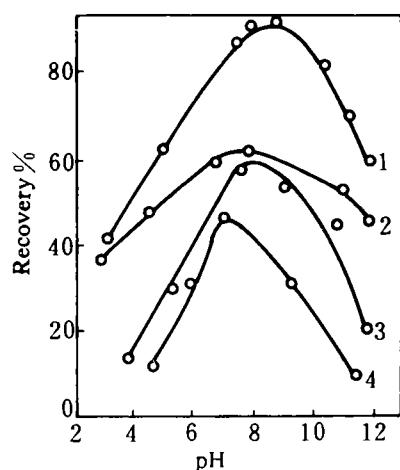


Fig. 1 Relation between the recovery of $-19\ \mu\text{m}$ wolframite and pH

1—sodium hydroxamate;
2— α -nitroso- β -naphthol; 3—sodium oleate;
4—styryl phosphonic acid (2.6×10^{-4} mol/L)

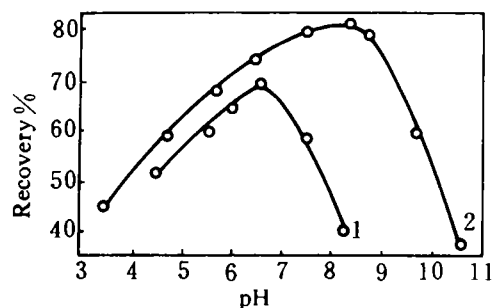


Fig. 2 Recovery of $-5\ \mu\text{m}$ wolframite as a function of pH

1—sodium hydroxamate (2.6×10^{-4} mol/L);
2—styryl phosphonic acid (2.6×10^{-4} mol/L)

collecting ability of chelating collectors is also better than that of conventional collectors.

Fig. 5 presents the effect of different size of carrier particles on the recovery of $-5\ \mu\text{m}$ wolframite. As can be seen, there is an optimum carrier size range to make the recovery of $-5\ \mu\text{m}$ wolframite the biggest.

3.2 Mechanism for the action of Chelating Collector on the Surface of Wolframite

Chemical reaction between chelating collector and metallic ions on the surface of wolframite can produce insoluble chelate. According to the knowledge of solution chemistry, the smaller the conditional solubility product of the reaction product, the easier the reaction to take place. Chemical reaction between octyl hydroxamic acid (OHA) and manganese ions on the surface of wolframite may be expressed as:



The conditional solubility of the manganese octyl hydroxamate may be expressed as:

$$K'_{sp} = K_{sp} \alpha_{\text{Mn}} \alpha_{\text{OHA}}^2 \quad (2)$$

where $\text{p}K_{sp} = 14.09$, K_{sp} is the solubility product of $\text{Mn}(\text{OHA})_2$; α_{Mn} can be determined by:

$$\alpha_{\text{Mn}} = 1 + K_1[\text{OH}^-] + K_2[\text{OH}^-]^2 + K_3[\text{OH}^-]^3 + K_4[\text{OH}^-]^4 \quad (3)$$

where K_1, K_2, K_3, K_4 are equilibrium constants of the following equations:

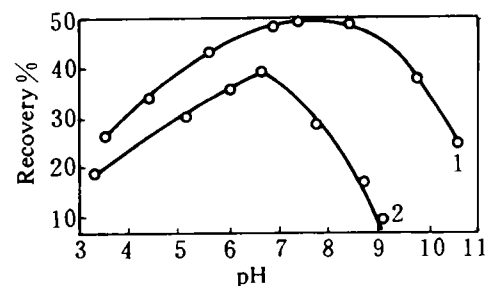
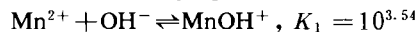
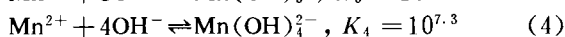
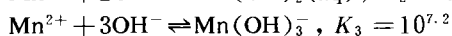
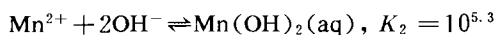


Fig. 3 Flotation recovery of $-5\ \mu\text{m}$ wolframite as a function of pH

(size of carrier particles is about $25 \sim 38\ \mu\text{m}$, the ratio of coarse to fine particles is 3:2)

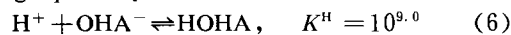
1—sodium hydroxamate (2.6×10^{-4} mol/L);
2—styryl phosphonic acid (2.6×10^{-4} mol/L)



The α_{OHA} can be determined by:

$$\alpha_{\text{OHA}} = 1 + K^{\text{H}}[\text{H}^+] \quad (5)$$

where K^{H} is the equilibrium constant of the following equation:



According to the above equations, the negative logarithmic value of conditional solubility product of manganese octyl hydroxamate as a function

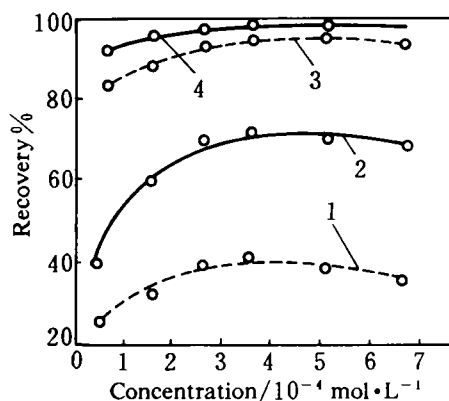


Fig. 4 Carrier flotation recovery of $-5 \mu\text{m}$ wolframite as a function of concentration of styryl phosphonic acid

1—conventional flotation, $-5 \mu\text{m}$;

2—carrier flotation, $-5 \mu\text{m}$;

3—conventional flotation, $25 \sim 38 \mu\text{m}$;

4—carrier flotation, $25 \sim 38 \mu\text{m}$

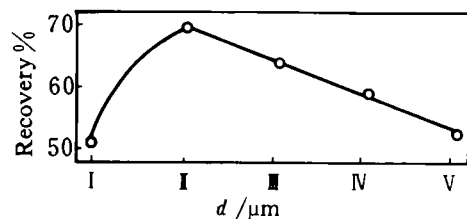


Fig. 5 Carrier flotation recovery of $-5 \mu\text{m}$ wolframite versus carrier size

(styryl phosphonic acid $2.6 \times 10^{-4} \text{ mol/L}$;

pH 6.9; ratio of coarse to fine particles 3:2;

stirring speed 2900 r/min)

I— $10 \sim 25 \mu\text{m}$; II— $25 \sim 38 \mu\text{m}$;

III— $38 \sim 53 \mu\text{m}$; IV— $53 \sim 74 \mu\text{m}$;

V— $74 \sim 150 \mu\text{m}$

of pH can be determined, which is shown as curve 1 in Fig. 6. The adsorption amount on the surface of wolframite was tested and given as curve 2 in Fig. 6. Curve 3 in Fig. 6 shows flotation recovery of $-19 \mu\text{m}$ wolframite as a function of pH with hydroxamic acid as collector. It is obvious that there is correlation between them. When pH is in the range of 6~9, the $\text{p}K'_{\text{sp}}$ is bigger, i. e. the conditional solubility product is less, the manganese hydroxamate is easier to be produced, the adsorption amount on the surface of wolframite is bigger, the collecting ability of OHA for wolframite is stronger and the flotation recovery of wolframite is higher.

3.3 Attaching Mechanism of Fine Particles to Surface of Coarse Wolframite Particles

3.3.1 Explanation Depending on Classical DLVO Theory

The aim examining attachment of fine particles on coarse particles is to investigate interfacial interactions between particles. According to the classical DLVO theory, there exist electrostatic forces and van der Waals forces. The interfacial interactions can be determined by attractive van der Waals forces and repulsive electrostatic forces. The interactions between fine and coarse particles can be calculated according to the ball-plate equation.

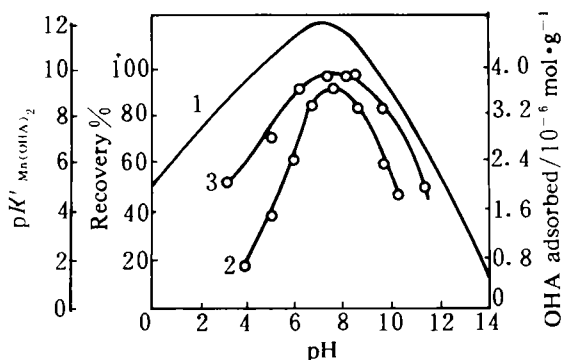


Fig. 6 $\text{p}K'_{\text{Mn}(\text{OHA})_2}$, adsorption amount and recovery versus pH

(the initial concentration of OHA is 50 mg/L)

1—negative logarithm of conditional solubility product of manganese octyl hydroxamate; 2—adsorption amount of OHA on the surface of wolframite; 3—flotation recovery of $-19 \mu\text{m}$ wolframite

Repulsive electrostatic energy can be expressed:

$$\Gamma_{ER} = 4\pi\epsilon_a R\psi_0^2 \ln[1 + \exp(\kappa H)] \quad (7)$$

where R is the radius of the interacting particles; ψ_0 is the surfacial potential; H is the interacting distance; ϵ_a is the absolute dielectric constant of the dispersed medium; and

$$\epsilon_a = \epsilon_0 \epsilon_r \quad (8)$$

where ϵ_0 is the absolute dielectric constant in vacuum ($8.854 \times 10^{-12} \text{ C}^{-1} \text{ J}^{-1} \text{ m}^{-1}$); ϵ_r is the relative constant of dispersed medium, for water medium, $\epsilon_r = 78.5$; κ^{-1} is the Debye length, which can be given by:

$$\kappa = \left(\frac{2e^2 N_A C Z^2}{\epsilon_r k T} \right)^{1/2} \quad (9)$$

where e is the electron charge ($1.602 \times 10^{-19} \text{ C}$); N_A is the Avogadro constant ($6.022 \times 10^{23} \text{ mol}^{-1}$); Z is the valence charge of ions; C is the molar concentration per unit volume (mol/L); k is the Boltzmann constant ($1.38 \times 10^{-23} \text{ J/K}$); T is the absolute temperature (K). For 1:1 type electrolyte, $T = 298 \text{ K}$, $\kappa^{-1} = 0.304 / \sqrt{C} \text{ (nm)}$. The Zeta potential of wolframite in the solution added with $10^{-3} \text{ mol/L KNO}_3$, $2.6 \times 10^{-4} \text{ mol/L}$ styryl phosphonic acid was measured ($\zeta = -55 \text{ mV}$) for substituting surfacial potential ψ_0 .

Electrostatic energy between fine particle ($R = 5 \mu\text{m}$) and coarse particle wolframite can be calculated by:

$$\begin{aligned} \Gamma_{ER} &= 4\pi \times 8.854 \times 10^{-12} \times 78.5 \times 5 \\ &\times 10^{-6} \times (0.055)^2 \ln[1 + \exp(-\kappa H)] \\ &= 1.32 \times 10^{-16} \ln[1 + \exp(-\kappa H)] \end{aligned} \quad (10)$$

when $\kappa = 0.104 \text{ nm}^{-1}$, then equation (10) is changed into the following form:

$$\Gamma_{ER} = 1.3 \times 10^{-16} \ln[1 + \exp(-0.104H)] \quad (11)$$

Fig. 7 shows Γ_{ER} as a function of interfacial distance. It is obvious that the smaller the H , the bigger the Γ_{ER} .

Attractive van der Waals interactions between fine and coarse particles can be expressed as:

$$\Gamma_w = \frac{A_{131}R}{6H} \quad (12)$$

where A_{131} is the effective Harmaker constant.

$$A_{131} = (\sqrt{A_{11}} - \sqrt{A_{33}})^2 \quad (13)$$

where A_{11} and A_{33} respectively are interfacial interaction Harmaker constants of substance 1 and medium 3 in vacuum. For wolframite, $A_{11} = 20 \times 10^{-20} \text{ J}$; for water, $A_{33} = 4 \times 10^{-20} \text{ J}$ ^[5]. Then:

$$\begin{aligned} A_{131} &= (\sqrt{20} - \sqrt{4}) \times 10^{-20} \\ &= 6.11 \times 10^{-20} \text{ (J)} \end{aligned}$$

Interfacial van der Waals interaction between fine ($R = 5 \mu\text{m}$) and coarse particles can be calculated by:

$$\begin{aligned} \Gamma_w &= \frac{6.11 \times 10^{-20} \times 5 \times 10^{-6}}{6 \times H} \\ &= -5.09 \times 10^{-26} \left(\frac{1}{H} \right) \text{ (J)} \end{aligned} \quad (14)$$

The calculated result of Γ_w versus H can be seen from Fig. 7. Based on DLVO theory, interfacial interactions can be determined by the following two parts:

$$\Gamma_T^D = \Gamma_{ER} + \Gamma_w \quad (15)$$

The curve Γ_T^D of Fig. 7 demonstrated Γ_T^D as a function of H . Hence, on the above conditions, the total interfacial interaction Γ_T^D manifested repulsion due to strong repulsive electrostatic interactions between fine and coarse particles. The result based on DLVO theory is that fine particle wolframite can not attach to the surface of the coarse particles. Thus, DLVO theory can not be applied to explain carrier flotation behaviour of fine particle wolframite.

3.3.2 Explanation on the Basis of Extended DLVO Theory

Depending on extended DLVO theory, hydration and hydrophobic forces also exist between hydrophilic and hydrophobic particles in addition to

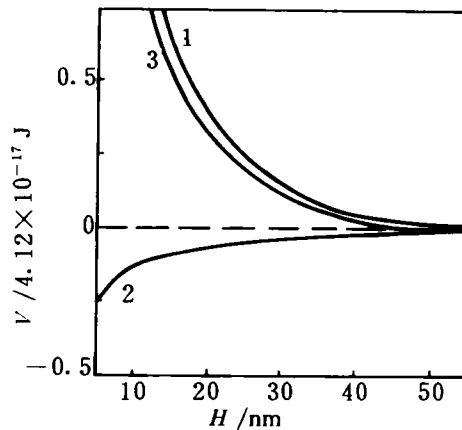


Fig. 7 Γ_T^D , Γ_{ER} and Γ_w versus H

1—electrostatic energy; 2—van der Waals energy between fine and coarse particle wolframite; 3—DLVO energy curves

electrostatic forces. In this disperse system, since styryl phosphonic acid was added to make the surface of wolframite hydrophobic, hydrophobic interactions must exist between hydrophobic wolframite particles. The relation between hydrophobic interactions and interfacial distance can be expressed as follows:

$$V_H = 2\pi R h_0 V_H^0 \exp\left(\frac{H_0 - H}{h_0}\right) \quad (16)$$

where h_0 is the decay length, $h_0 = 10 \text{ nm}$; H_0 is the interfacial distance between particles, $H_0 = 0.2 \text{ nm}$; V_H^0 is the hydrophobic interaction constant.

$$V_H^0 = -2\gamma_{SL}^{AB}$$

where γ_{SL}^{AB} is the polar component of surface and interfacial energy between solids and liquids, which can be given by the following equation^[7-8]:

$$\gamma_{SL}^{AB} = 2(\sqrt{\gamma_s^+ \gamma_s^-} + \sqrt{\gamma_L^+ \gamma_L^-} - \sqrt{\gamma_s^+ \gamma_L^-} - \sqrt{\gamma_s^- \gamma_L^+}) \quad (18)$$

where γ_s^+ , γ_s^- , γ_L^+ , γ_L^- respectively, are the electron acceptor and electron donor component of interfacial energy of solids and liquids. For monopolar surface of solids, $\gamma_s^+ \approx 0$ (or $\gamma_s^- \approx 0$), then:

$$\gamma_{SL}^{AB} = 2(\sqrt{\gamma_L^+ \gamma_L^-} - \sqrt{\gamma_s^- \gamma_L^+}) \quad (19)$$

The relation between these parameters and the contact angle can be expressed as:

$$(1 + \cos\theta)\gamma_L = 2(\sqrt{\gamma_s^+ \gamma_L^+} + \sqrt{\gamma_s^- \gamma_L^-}) \quad (20)$$

where γ_L is the surfacial tension of liquid; γ_s^+ , γ_s^- and γ_L^+ , γ_L^- are nonpolar and polar component of interfacial energy of solids and liquids. For water, $\gamma_L = 72.8 \text{ mJ/m}^2$, $\gamma_L^+ = 21.8 \text{ mJ/m}^2$, $\gamma_L^- = 25.5 \text{ mJ/m}^2$. For wolframite, $\gamma_s^+ = 84.89 \text{ mJ/m}^2$, contact angle between water and wolframite treated by styryl phosphonic acid is 60° . Thus, from equation (20), $\gamma_s^- = 11.04 \text{ mJ/m}^2$, from equation (19), $\gamma_{SL}^{AB} = 17.44 \text{ mJ/m}^2$, $V_H^0 = -34.89 \text{ mJ/m}^2$.

According to equation (16), V_H can be obtained by:

$$\begin{aligned} V_H &= 2\pi \times 5 \times 10^{-6} \times 10 \times 10^{-9} \\ &\times (-34.89) \times 10^{-3} \exp\left(\frac{0.2 - H}{10}\right) \\ &= -1.10 \times 10^{-14} \exp\left(\frac{0.2 - H}{10}\right) \quad (21) \end{aligned}$$

The curve (b) of Fig. 8 shows V_H as a function of interfacial distance. It is obvious that the smaller the H , the bigger the V_H . Depending on extended DLVO theory, the total interfacial interactions between hydrophobic wolframite particles can

be determined by the following two parts:

$$V_T^{ED} = V_T^D + V_H \quad (22)$$

The relation between V_T^{ED} and H is given as curve (b) in Fig. 8. Compared with DLVO potential energy curve (a), strong hydrophobic attractive forces between particles exist, which overcome repulsive electrostatic forces and make total interfacial interactions manifest attraction because the surface of wolframite attached by styryl phosphonic acid is hydrophobic. That is $-5 \mu\text{m}$ wolframite particles can attach to the surface of coarse particles. The attachment and aggregation of fine particle wolframite to the surface of coarse particles through scanning electron micrograph can be seen in Fig. 9. Hence, fine particle wolframite can be carried by the coarse particles due to interfacial hydrophobic interactions between fine and coarse particles.

4 CONCLUSION

The investigation of this paper states that the flotation recovery of fine particle wolframite can be significantly improved through chelating agent flotation and carrier flotation. The mechanism for

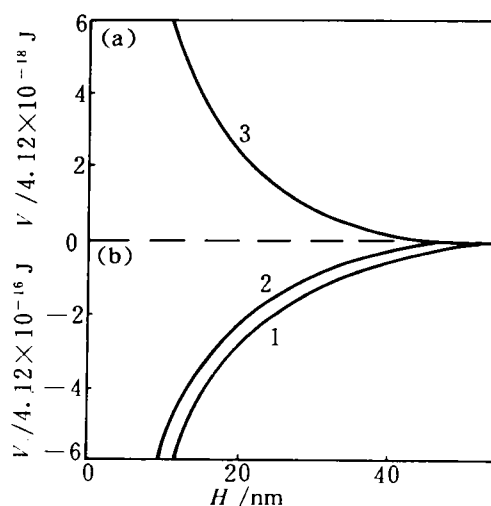


Fig. 8 Potential energy curves of DLVO and EDLVO interfacial interactions between fine ($R = 5 \mu\text{m}$) and coarse particle wolframite (styryl phosphonic acid $C = 2.6 \times 10^{-4} \text{ mol/L}$)
1—hydrophobic interaction energy V_H ;
2—total interfacial interaction energy V_T^{ED} ;
3—DLVO energy V_T^D

chelating agent attaching to the surface of wolframite is that insoluble collector metallic salt can be produced due to chemical reaction between chelating agents and the metallic ions on the surface of the wolframite. Classical DLVO theory can not explain the behaviour for fine particle

wolframite attaching to the surface of the coarse particles. Based on extended DLVO theory, strong hydrophobic attractive forces between particles make fine particles attach to the surface of the coarse particles.

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Fig. 9 SEM micrograph of adhesion of 5 μm wolframite to coarse wolframite