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BENEFICIAL EFFECTS AND MECHANISM OF LEAD ION ON WOLFRAMITE FLOTATION

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Abstract: In this study the effects and mechanism of lead ions influence on wolframite flotation with benzohydroxamic acid (BHA) were studied through micro-flotation, adsorption experiments, zeta potential measurements, logarithmic concentration diagram, and X-ray photoelectron spectroscopy. It was observed that lead ions could significantly enhance the recovery of wolframite in flotation and adsorption density of collector BHA onto the wolframite surface. The results showed that Pb existed in the forms of lead ion, monohydric lead, and lead hydroxide at the water-wolframite interface respectively, at three pH ranges. They increased the zeta potential of wolframite. However, the zeta potential of wolframite was still negative, resulting in repulsive electrostatic force to anionic collector BHA. Combining with XPS spectra, it revealed the chemisorption of BHA onto the wolframite surface. In addition, PbO or $Pb(OH)_2$ was observed on the wolframite surface due to the reaction between lead ions and wolframite. These reaction products increased the adsorption site of BHA on the wolframite surface because Pb-hydroxamate was found on the wolframite surface.

Keywords: *activator, wolframite, lead ion, benzohydroxamic acid, flotation*

Introduction

Wolframite, as a high density mineral, can be concentrated by gravity separation. However, wolframite is prone to over-grinding. Therefore, the generation of fine wolframite cannot be avoided in production, let alone naturally fine-grained wolframite (Pascoe et al., 2007, Kazmi et al., 2011). Dealing with fine to ultrafine wolframite is a worldwide problem. For this reason, froth flotation would be more promising compared with fine gravity concentrators and high gradient magnetic separation devices (Pradip, 1996). Previously, octylhydroxamate and methylene

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phosphonate were applied as flotation reagents to obtain favorable outcomes (Hu and Wang, 1987; Clemente et al., 1993). However, no satisfactory and consistent flotation results were achieved in industrial production until benzohydroxamic acid (BHA) was found as a high-efficiency collector in wolframite flotation (Yang et al., 2014; Zhao et al., 2015; Deng et al., 2015). Considering the long term exploitation of wolframite and the fact that most of the wolframite ores contain less than 1% WO_3 (Luo et al., 2003), the wolframite flotation becomes crucially important both for theoretical and practical aspects.

On the other hand, the use of certain metal ions can largely improve the recovery of some minerals in froth flotation (Wills, 2011). For wolframite, lead ions as an activator can substantially improve its flotation recovery in industrial production (Chen and Ye, 1999). In fact, lead ions have been widely used as an activator in the flotation of many minerals such as ilmenite and sphalerite (Houot and Raveneau, 1992;, Fan and Rowson, 2000). Thus, it is beneficial to examine the effects and mechanism of lead ions on wolframite flotation in order to improve the recovery of wolframite.

The research in this area is becoming important due to the successful application of lead ions in fine wolframite flotation with chelating reagent in Shizhuyuan, China (Sheng, 2002; Luo et al., 2013). However, a clear mechanism has not given by the related literatures. Detection techniques such as ultraviolet spectroscopy and X-ray photoelectron spectroscopy (XPS), have not used as well. These techniques can provide direct information about the adsorption density of collectors and surface composition of minerals (Armagan et al., 2003; Bremmell et al., 2005; Yang et al., 2015). One latest paper published by Zhao et al. (2015) reported on density functional theory (DFT) simulations of BHA and metal ions, which clearly showed binding of $PbOH^+$ with BHA to form benzoyl hydroxamate thereby leading to activation. However, there are several limitations. Firstly, the lead ions can improve the wolframite flotation in a wide range of pH. However, the majority of lead ions existed on the wolframite-water interface in forms of Pb^{2+}, $PbOH^+$, and $Pb(OH)_2$, respectively, at different pH ranges. Secondly, elements at the wolframite surface were not mentioned in their hypothesis while the activation mechanism is a three-components interaction, including wolframite, lead ions, and collector BHA.

From a broader perspective, the chelating agents have become a main research area for new flotation collectors of oxide mineral such as scheelite and cassiterite (Wu and Zhu, 2006; Urbina, 2003). The collecting efficiency of chelating agents in flotation can be significantly improved by metal ions. It is necessary to figure out the activation mechanism.

In the present work, the effects of lead ions on wolframite flotation were investigated by using microflotation. The mechanism was studied by using the zeta potential measurements, the adsorption experiments, the logarithmic concentration diagram, and XPS tests.

Experimental

Materials

Samples and reagents

Wolframite sample used in this study was obtained from the Hukeng mine in Jiangxi Province, China. Large particles of gangue were picked out from the original wolframite ore. Then, pure wolframite was obtained after repeated elutriation and dry magnetic separation. After that, it was dry-ground using a porcelain mill and screened to 38-74 μm by size fraction. The chemical assay of the sample revealed that its composition was 74.30% WO_3, 12.59% Mn, 4.83% Fe, and 2.12% SiO_2. The X-ray diffractometers (XRD) analysis of the sample (Fig. 1) indicated that in addition to wolframite, quartz, faujasite, and muscovite impurities were also present. A Shimadzu powder diffractometer in the reflection mode was employed in XRD with graphite-filtered Cu*Kα* as a radiation source (50 mV, 100 mA). The JADE 6.0 was used for the XRD analysis.

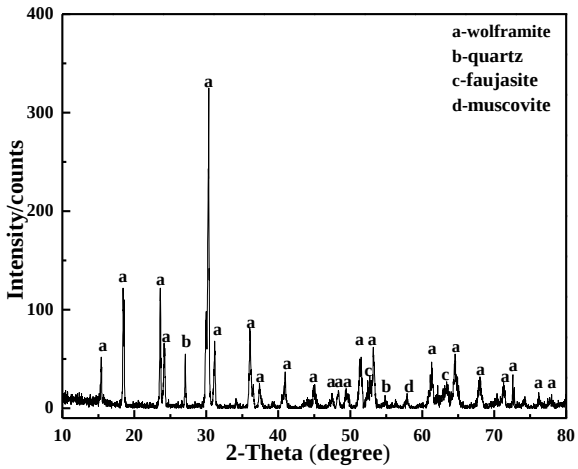


Fig. 1. XRD result of wolframite sample

BHA was synthesized in the laboratory according to the method by Dutta (1967), and then purified to 95%. The other reagents, comprised of lead nitrate as an activator, hydrochloric acid (HCl) and sodium hydroxide (NaOH) as pH regulators, methyl isobutyl carbinol (MIBC) as a frother were analytically pure, and purchased from Sinopharm Chemical Reagent Co., Ltd. Deionized double distilled water was used for all tests.

The reaction sediment between BHA and lead nitrate was generated by magnetic stirring at 60 °C and pH ~7. The infrared spectra of BHA and Pb-BHA compound was detected (Fig. 2).

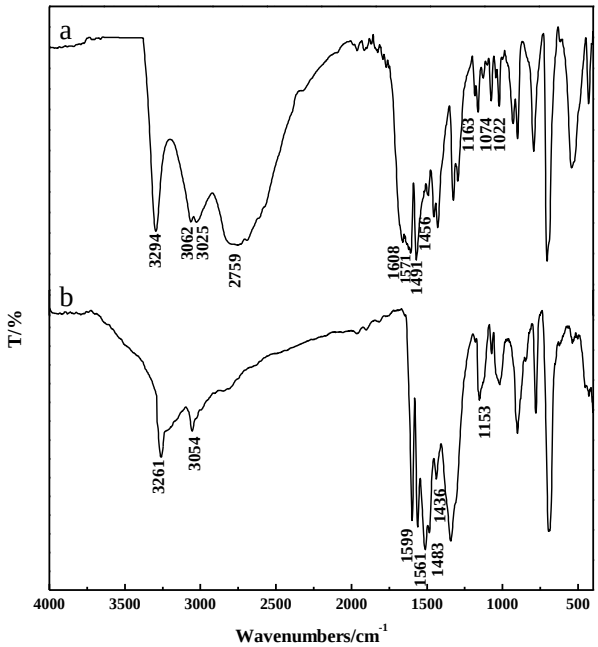


Fig. 2. Infrared spectra of (a) BHA, (b) Pb-BHA compound

The infrared spectrum of BHA is shown in Fig. 2(a) where the peak at 3294 cm^{-1} corresponds to the overlapped peaks of N-H and O-H stretching. The W-shaped broad adsorption band at 3025 to 3062 cm^{-1} is attributed to the peak of N-H stretching vibration. The broad peak at 2759 cm^{-1} stands for peak of O-H stretching vibration. The other adsorption band at 1608 cm^{-1} belongs to C=O or C=N vibration. The peaks at 3294 and 1608 cm^{-1} constitute the characteristics of hydroxamic acid (-CONHOH) (Wu and Zhu, 2006). In addition, the peaks at around 1500 and 1000 cm^{-1} are related to the vibration of the benzene ring and the splitting of N-O, respectively. Compared with the infrared spectrum of the BHA, the Pb-BHA compound exhibited the following remarkable changes: the O-H stretching adsorption band disappeared due to the formation of O-Metal bond, and the most characteristic peaks shifted to a lower wave number. All of these suggested the formation of Pb-hydroxamate (Wu and Zhu, 2006).

Methods

Micro-flotation

Microflotation experiments were carried out in a XFG-type laboratory flotation machine at 1800 rpm of impeller. The mineral suspension was prepared by adding 2.0 g wolframite to 40 cm^3 distilled water and agitated for 1 min. The pH of the mineral suspension was adjusted to the desired value by adding HCl or NaOH stock solution. After that, the activator (lead nitrate), collector (BHA), and frother (MIBC) were

added to the slurry in order. The conditioning periods were 3 min, 5 min, and 1 min, respectively. The concentrate and the tailings were filtered, dried, and weighed to calculate the flotation recovery of wolframite.

Zeta potential measurements

Zeta potential measurements were performed using a Coulter Delsa440SX zeta potential meter. Small amounts of wolframite were added to the desired amounts of solution and ultrasonicated for 3 min, magnetically stirred for 10 min, and the pH was then adjusted using the HCl or NaOH stock solution. The procedure and conditioning time of the reagents was the same as in the micro-flotation tests except that no frother was used for the zeta potential measurements. Pulp pH was recorded using a LeiCiPHS-3 pH meter. The zeta potential of each sample was then measured at the desired pH. This flow path was repeated 3 times for each sample, and the average value was used as the final result.

Adsorption tests

In the adsorption tests, 1.0 g wolframite was added to 20 cm^3 100 mg/dm^3 BHA solution, and then $1 \cdot 10^{-4}$ mol/dm^3 lead ions were added when necessary. The pH was adjusted using HCl or NaOH stock solution. The sample was placed in the vibrator and shaken for 4 h at constant pH and temperature (298 K). After the adsorption process was completed, the suspension was centrifuged at 9000 rpm for 10 min, and the supernatant was extracted for further analysis. According Chen et al. (2008), the absorbance of each sample was measured in 0.1 mol/dm^3 HCl solution at the wavelength from 185 to 400 nm using a TU1810 ultraviolet-visible spectrophotometer. An absorption peak of 228.4 nm was found as a suitable wavelength for quantitative measurement. The concentration of BHA can be calculated by Lambert-Beer law at the range from 1 to 32 mg/dm^3. The equation of linear regression is:

$$\mathrm{A} = 0.05683C + 0.11835 \quad R^2 = 0.99947$$

where A and C stand for the absorbance and the concentration of BHA, respectively. The coefficient of determination R^2 is high enough to meet the requirement of quantitative analysis. Based on the residual concentration of BHA in the supernatant, the adsorption density (Γ) of BHA onto the wolframite surface can be calculated as:

$$\Gamma = \frac{(C_i - C_r)V}{S\,m} \tag{1}$$

Γ – adsorption density in mg/m^2
C_i – initial concentration of the BHA solution in mg/dm^3
C_r – residual concentration of BHA in the supernatant in mg/dm^3
V – volume of BHA solution in dm^3

S – specific surface area of the wolframite in m^2/g
m – mass of the wolframite sample in g.

The inputs for the equation parameters in the present experiments were as follows: C_i = 100 mg/dm^3, V = 0.02 dm^3, m = 2 g, S = 0.1221 m^2/g for Hukeng wolframite (38-74 μm) as determined by BET method.

Infrared spectroscopy

An infrared spectrum of BHA and Pb-BHA compounds was recorded with an infrared spectrometer (IRAffinity-1). The infrared spectroscopy was performed out using a KBr disk that contained 0.5 wt.% of the required sample to scan the infrared spectra in the wave number range of 400-4000 cm^{-1}. A pure KBr disk was used as a blank. The Shimadzu IR Solution FTIR software was used to analyze the data with atmosphere correction mode, which can automatically eliminated the effects of moisture and carbon dioxide in the atmosphere. All the samples were measured applying 40 scans and 4 cm^{-1} resolution. The Pb-BHA compound was prepared by the reaction between BHA and lead nitrate solution under the condition of 5 min magnetic stirring, 60 °C, and pH ~7, then filtered and dried in a vacuum drying oven.

XPS tests

Corresponding reagents and 2.0 g wolframite (-2 μm) were added into 40 cm^3 distilled water as required, and magnetically stirred for 30 min. The ultrafine wolframite samples were acquired by grinding using TENCAN JM-1L lab stirred ball mill. Then the mixture was centrifuged at 3500 rpm for 10 min followed by rinsing twice using distilled water. Finally, the sample was put into a vacuum drying oven whose temperature was controlled below 60 °C. All these samples were measured under air pressure of 10^{-9} bar using a K-Alpha 1063 XPS instrument.

Results and discussion

Effects of lead ions on wolframite flotation with BHA as the collector

Figure 3 shows the effects of lead ions on wolframite flotation as a function of pH. Evidently, the flotation recovery of wolframite in the absence of lead ions was low with respect to pH, and the maximum recovery was obtained 48.5% at pH 8. However, the recovery of wolframite was improved in the presence of $1\cdot10^{-4}$ mol/dm^3 lead ions, and increased from 48.5% to 91.7% at pH 8. The results also indicated that the lead ions broaden the pH range suitable for flotation from pH 7-10 to pH 4-10.5.

Figure 4 shows the relationship between BHA concentration and flotation recovery of wolframite in the presence or absence of lead ions. It was found that lead ions can largely improve the wolframite recovery with less usage of collector. The flotation recovery held to be at a stable level of 51.15% with 60 mg/dm^3 BHA in the absence of lead ions. However, after the addition of lead ions, wolframite recovery remarkably

increased to 85.3% with only 40 mg/dm^3 BHA, but little improvement in recovery was observed with further BHA addition.

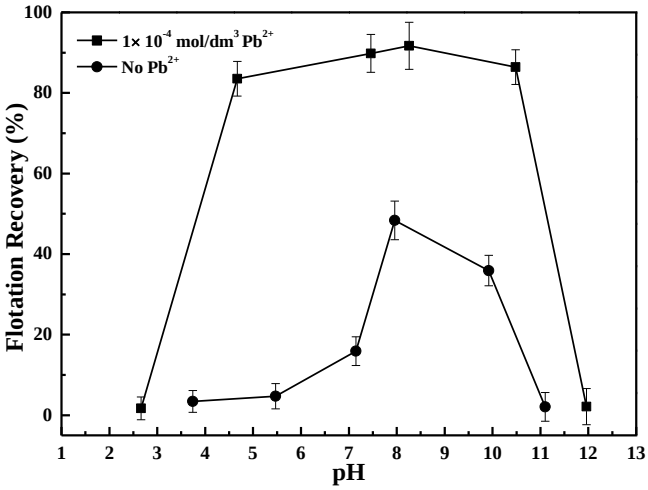


Fig. 3. Recovery of wolframite as a function of pH in the presence or absence of lead ions [BHA] = 100 mg/dm^3

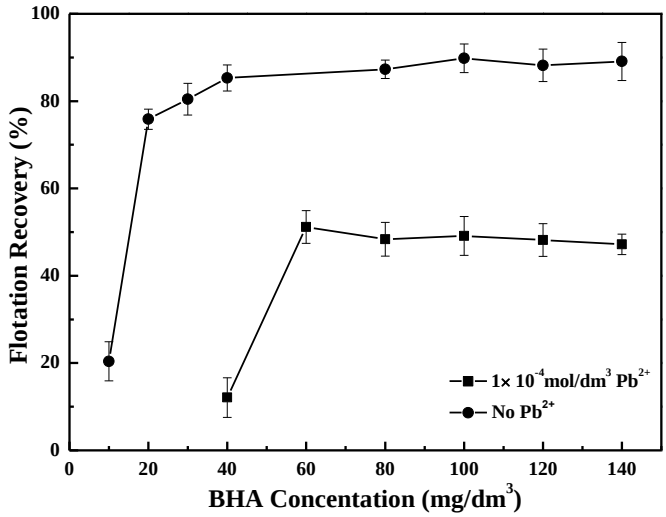


Fig. 4. Recovery of wolframite as a function of BHA concentration in the presence or absence of lead ions (pH = 8)

The effects of lead ions on adsorption density of BHA on the wolframite surface were studied and shown in Fig. 5. The results in Fig. 5 showed that the adsorption of BHA on wolframite increased in the studied pH range with the addition of lead ions, especially for the slightly acid solution. The results are in agreement with the findings of the microflotation.

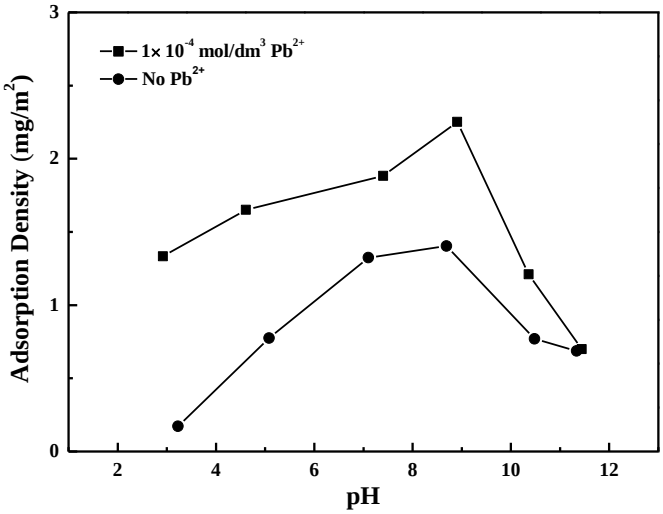


Fig. 5. Adsorption density of BHA on the wolframite surface as a function of pH in the presence or absence of lead ions [BHA] =100 mg/dm^3

Effects of lead ions on electrical properties of wolframite

The zeta potential-pH profile of wolframite with different reagent conditions as a function of pH is shown in Fig. 6. Line 1 shows that the isoelectric point (IEP) of Hukeng wolframite is 2.5, which is between the theoretical IEP of ferberite (2.0) and huebernite (2.8) (Xu et al., 1998). The zeta potential of wolframite was negative within the pH region from 2.5 to 12. Comparing lines 1 and 2, a slight increase in negative charge was observed in the presence of BHA indicating a small amount of BHA was adsorbed on the wolframite surface. As can be seen from lines 1 and 3, the zeta potential of wolframite increased in the presence of lead ions but remained negative within the pH region from 3.2 to 12 suggesting the adsorption of lead ions. Comparing with lines 3 and 4, an obvious increase in negative charge was observed in the presence of BHA and lead ions, which might be due to the adsorption of BHA. This change suggests that lead ions increased the adsorption density of BHA. In addition, the presence of lead ions improved the zeta potential of wolframite while it remained negative, which resulted in repulsive electrostatic force to BHA. Thus, the adsorption of BHA on the wolframite surface cannot attribute to the electrostatic adsorption.

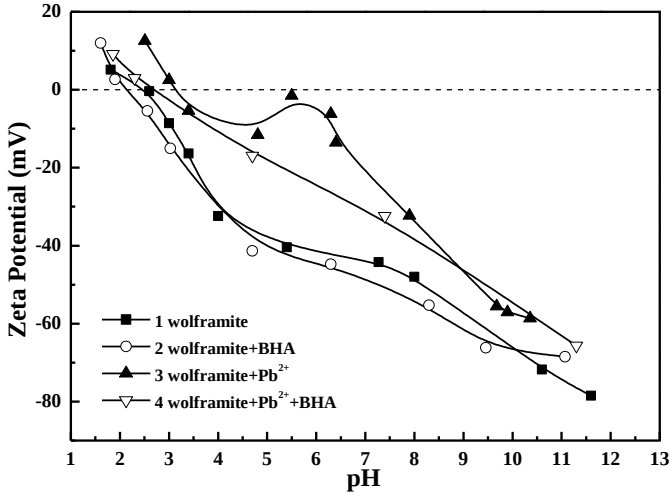


Fig. 6. Effect of lead ions on the zeta potential of wolframite as a function of pH $[Pb^{2+}] = 1 \cdot 10^{-4}$ mol/dm^3 and [BHA] = 100 mg/dm^3

Calculation and analysis of logarithmic concentration of lead ions

To examine which form of lead in the solution enhanced the adsorption of BHA onto the wolframite surface, the logarithmic concentrations diagram of lead ions in the interface between mineral and solution was made, and the results are shown in Fig. 7. All the constant values are selected from references (Wang and Hu, 1988; Somasundaran and Wang, 2006). The process is shown below.

Homogeneous system

There is no $Pb(OH)_2$ sediment in this system and every hydrolysis product is balanced with Pb^{2+}.

$$Pb^{2+} + OH^- \Leftrightarrow Pb(OH)^+ ; \beta_1 = \frac{[Pb(OH)^+]}{[Pb^{2+}][OH^-]} = 10^{6.3} \tag{2}$$

$$Pb^{2+} + 2OH^- \Leftrightarrow Pb(OH)_{2(aq)} ; \beta_2 = \frac{[Pb(OH)_{2(aq)}]}{[Pb^{2+}][OH^-]^2} = 10^{10.9} \tag{3}$$

$$Pb^{2+} + 3OH^- \Leftrightarrow [Pb(OH)_3^-] ; \beta_3 = \frac{[Pb(OH)_3^-]}{[Pb^{2+}][OH^-]^3} = 10^{13.9} \tag{4}$$

where β_1, β_2, β_3 stand for stability constants and [] represents the concentration of component. The total amount of Pb in the solution is:

$$C_{Pb} = [Pb^{2+}] + [Pb(OH)^+] + [Pb(OH)_{2(aq)}] + [Pb(OH)_3^-] \tag{5}$$

and

$$[Pb^{2+}] = C_{Pb}(1 + \beta_1[OH^-] + \beta_2[OH^-]^2 + \beta_3[OH^-]^3)^{-1} \quad (6)$$

$$\alpha_{Pb} = \frac{C_{Pb}}{[Pb^{2+}]} = 1 + \beta_1[OH^-] + \beta_2[OH^-]^2 + \beta_3[OH^-]^3 \ . \quad (7)$$

Then, according to Eqs. 2–7

$$[Pb^{2+}] = \frac{C_{Pb}}{\alpha_{Pb}} \quad (8)$$

$$[Pb(OH)^+] = \beta_1[Pb^{2+}][OH^-] \quad (9)$$

$$[Pb(OH)_{2(aq)}] = \beta_2[Pb^{2+}][OH^-]^2 \quad (10)$$

$$[Pb(OH)_3^-] = \beta_3[Pb^{2+}][OH^-]^3 \ . \quad (11)$$

Heterogeneous system

According to Eq. 10, Pb^{2+} decreases with the increase of pH. Therefore, when $[Pb^{2+}] = \frac{K_{sp}}{[OH^-]^2}$, the $Pb(OH)_{2(s)}$ begin to emerge in the solution, and this pH is defined as pH_c. When pH > pH_c, every hydrolysis product is balanced with $Pb(OH)_{2(s)}$. The reactions are:

$$Pb(OH)_{2(s)} \Leftrightarrow Pb^{2+} + 2OH^-; K_{sp} = [Pb^{2+}][OH^-]^2 = 10^{-15.2} \quad (12)$$

$$Pb(OH)_{2(s)} \Leftrightarrow Pb(OH)^+ + OH^-; K_{s1} = [Pb(OH)^+][OH^-] = 10^{-8.9} \quad (13)$$

$$Pb(OH)_{2(s)} \Leftrightarrow Pb(OH)_{2(aq)}; K_{s2} = [Pb(OH)_{2(aq)}] = 10^{-4.31} \quad (14)$$

$$Pb(OH)_{2(s)} + OH^- \Leftrightarrow [Pb(OH)_3^-]; K_{s3} = \frac{[Pb(OH)_3^-]}{[OH^-]} = 10^{-29.1} \quad (15)$$

where K_{sp}, K_1, K_2, K_3 are hydrolysis constants.

Then, according to Eqs. 12–15

$$[Pb^{2+}] = \frac{K_{sp}}{[OH^-]^2} \quad (16)$$

$$[\mathrm{Pb(OH)}^{+}] = \frac{K_{s1}}{[\mathrm{OH}^{-}]} \tag{17}$$

$$[\mathrm{Pb(OH)}_{2(\mathrm{aq})}] = K_{s2} \tag{18}$$

$$[\mathrm{Pb(OH)}_{3}^{-}] = K_{s3}[\mathrm{OH}^{-}] \tag{19}$$

However, because of the existence of an electric field, the dielectric constant of the surface of wolframite is much lower than that of the solution, which will change their chemical environments as well as the corresponding solubility product constant. The change is shown as follows (Hu et al., 1997):

$$\log \frac{K_{\mathrm{sPb(OH)}_{2(\mathrm{S})}}}{K'_{\mathrm{sPb(OH)}_{2(\mathrm{S})}}} = 1.42 \tag{20}$$

where K_{sp} is hydrolysis constant in the solution, K'_{sp} is hydrolysis constant at the interface between minerals and the solution.

Based on Eq. (20), where $K'_{\mathrm{sp}} = 10^{-16.62}$, because $K_{\mathrm{sp}} = 10^{-15.2}$, then K_{sp} can be replaced by K'_{sp} in Eq. 12. According to Eqs. 8–11 and 16–20, the logarithmic concentration diagram of lead ions in the interface between the mineral and the solution was plotted.

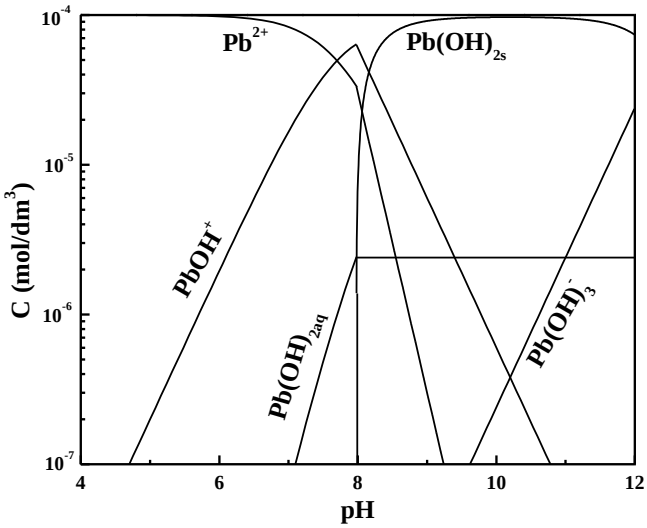


Fig. 7. Logarithmic concentration diagram of Pb^{2+} as a function of pH at the interface between minerals and solution $[Pb^{2+}] = 1 \cdot 10^{-4}$ mol/dm^3

Figure 7 shows that the main forms of lead ions in the interface between the wolframite and the solution ($1 \cdot 10^{-4}$ mol/dm^3) are Pb^{2+}, $Pb(OH)^+$, and $Pb(OH)_2$, respectively, at three different pH ranges. Specifically, lead ions exist mainly as Pb^{2+} at less than pH 7.68 as $Pb(OH)^+$ from pH 7.68 to 8.16, and as $Pb(OH)_2$ at above pH 8.16. According to Fig. 3, the appropriate pH range for lead ions to increase the wolframite flotation recovery is 4.5 to 10.5, in which the lead ions can improve the floatability of wolframite in three forms of the Pb^{2+}, $Pb(OH)^+$, and $Pb(OH)_2$.

Activation mechanisms of lean ions

The wolframite crystal structure is shown in Fig. 8. As known from the literature, wolframite structure can be described as a distorted hexagonal close packing of O atoms with A and W atoms each occupying one-fourth of the octahedral voids (Macavei and Schulz, 1993; Morell et al., 1980).

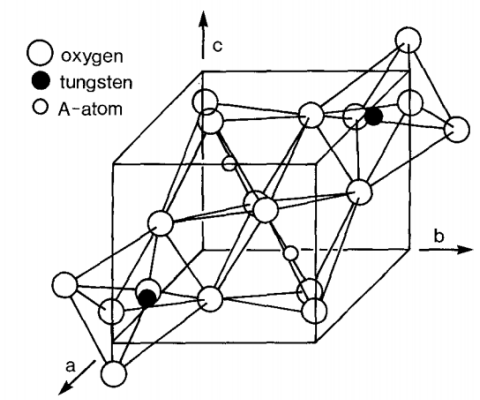
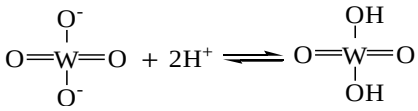


Fig. 8. Wolframite crystal structure (Morell et al., 1980)

The ionic bond energy between $Fe^{2+}(Mn^{2+})$ and O^{2-} is less than the covalent bond energy between W^{6+} and O^{2-} ions. In addition, the average bond length between $Fe^{2+}(Mn^{2+})$ and O^{2-} ion (0.21 nm) is longer than that between W^{6+} and O^{2-} ions (0.185 nm) (Dawei et al., 1987). Thus, the ionic bond of Fe(Mn)-O will break in the direction vertical to the b axis when wolframite is crushed. As a result, the $Fe^{2+}(Mn^{2+})$ and O^{2-} ions are easier exposed on the surface. However, the relative positions of those ions on the surface are different. Since the position of O^{2-} ions is higher than those of $Fe^{2+}(Mn^{2+})$ ions, the $Fe^{2+}(Mn^{2+})$ ions are easily shielded by O^{2-} ions so as to stop the adsorption of collectors, thereby the adsorption of collector by natural wolframite without activator is poor (Dawei et al., 1987). Thus, the $Fe^{2+}(Mn^{2+})$ ions are either sheltered by O^{2-} ions or dissolved in the solution, leaving the WO^{2-}_4 as the main chemical component on the wolframite surface. It is worth noticing that the WO^{2-}_4 is stable with two O^- ions, which shares one covalent bond respectively with W atom.

Wolframite is an electronegative mineral, and BHA is a weak electrolyte collector. Therefore, the following reactions occurred:

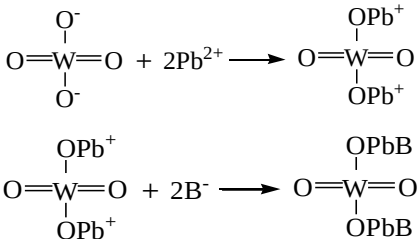


$$HB \rightleftharpoons H^+ + B^-.$$

The activation mechanisms of the three forms of lead ions are illustrated in the next sections.

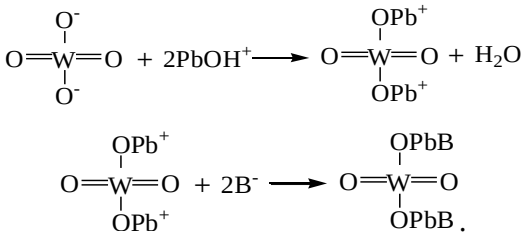
Activation mechanism of Pb^{2+}

At pH<7.68, Pb^{2+} may react directly with electronegative oxygen atom on the surface of wolframite, which enhances the activity of wolframite. The reactions are as follows:



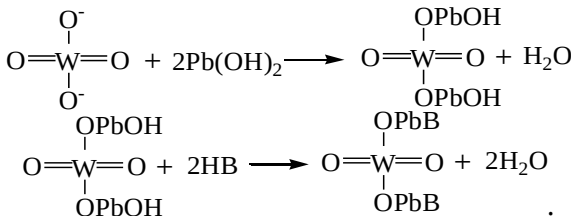
Activation mechanism of $Pb(OH)^+$

The metal hydroxyl complex is the main activated component. Thus, from pH 7.68 to 8.16 $PbOH^+$ may react with wolframite which has already adsorbed H^+ (Fuerstenau and Raghavan, 1976). The reactions are as follows:



Activation mechanism of $Pb(OH)_2$

According to the hypothesis, the effective component of metal ions cannot be simply attributed to metal hydroxyl complex. The metal hydroxide sediment on the mineral surface is the main activated component (James and Healy, 1972, Clark and Cooke, 1968), then from pH 8.16 to 10.5, $Pb(OH)_2$ may react with wolframite which has already adsorbed H^+ as follows:



The above proposed activation mechanisms suggest that the lead ions can interact with the oxygen atom on the surface of wolframite resulting in the change of surface composition. The surface composition of minerals can be investigated by XPS tests (Buckley et al., 1989, Boulton et al., 2003). In this research, the information was extracted from the XPS spectrum of each element on the wolframite surface, and peak-differentiation analysis was conducted using the software of Thermo Avantage.

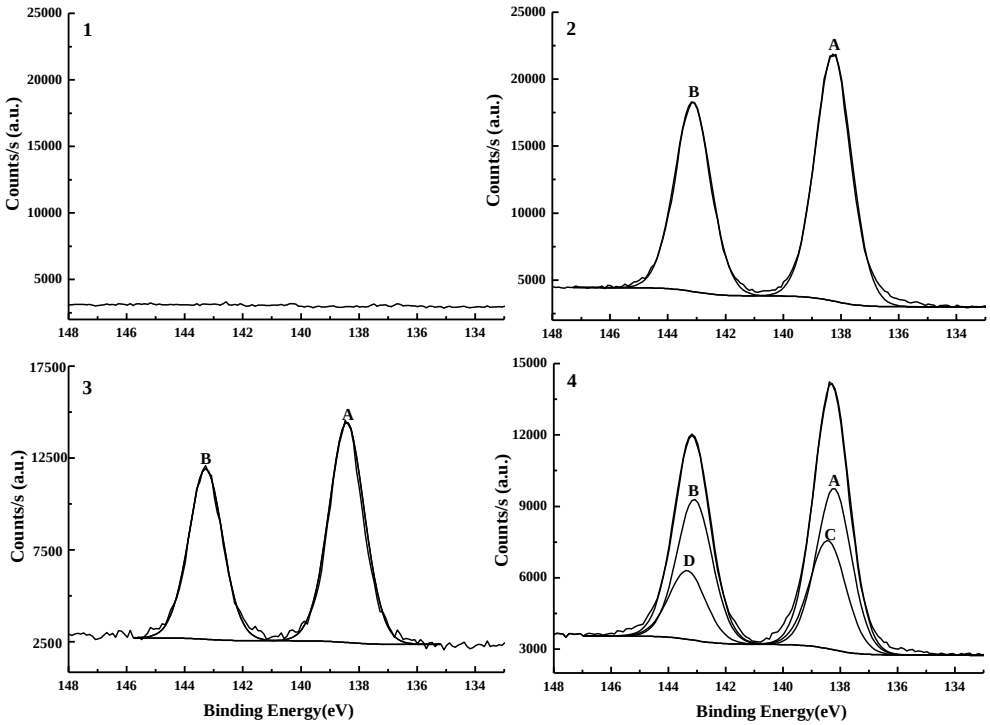


Fig. 9. Effects of lead ions on Pb4f spectra of wolframite surface at different pH:
1 – wolframite; 2 – wolframite, $5\cdot10^{-4}$ mol/dm^3 $Pb(NO_3)_2$, pH = 6.5;
3 – wolframite, $5\cdot10^{-4}$ mol/dm^3 $Pb(NO_3)_2$, pH = 8;
4 – wolframite, $5\cdot10^{-4}$ mol/dm^3 $Pb(NO_3)_2$, pH = 9

The effects of lead ions on Pb4f spectra of wolframite at different pH values were measured, and the results are shown in Fig. 9. The Pb4f spectra of a wolframite is

shown in Fig. 9-1. Clearly, wolframite had no obvious peak on the Pb4f spectra revealing the wolframite sample had no lead compounds on the surface. The Pb4f spectra of wolframite after the addition of lead ions at pH 6.5 and 8 is illustrated separately in Figs. 9-2 and 9-3. Both of them display two peaks where peak A at 138.26 eV and B at 143.13 eV, respectively. Pb4f region shows well separated spin-orbit components, so according to the reference (Rondon and Sherwood, 1998), peak A stands for $Pb4f_{7/2}$ of PbO, and peak B stands for $Pb4f_{5/2}$ of PbO, respectively. The distance between these two peaks is 4.87eV which is the same as the literature (Laajalehto et al., 1993). This indicates that lead oxide generated on the wolframite surface which came from the chemical reaction between lead ions and the oxygen atom on the wolframite surface. Figure 9-4 shows the Pb4f spectra of wolframite in the presence of lead ions at pH 9. Apart from two peaks of PbO, peaks C and D are emerged. Peak C at 138.43 eV corresponds to $Pb4f_{7/2}$ of $Pb(OH)_2$ and 143.34 eV corresponds to $Pb4f_{5/2}$ of $Pb(OH)_2$ (Nefedov et al., 1980). It suggests that both of lead oxide and lead hydroxide formed on the wolframite surface at pH 9. To sum up, Fig. 9 demonstrates that lead ions can chemically react with oxygen atom of wolframite surface at wide pH ranges, and the reaction product can be PbO or $Pb(OH)_2$.

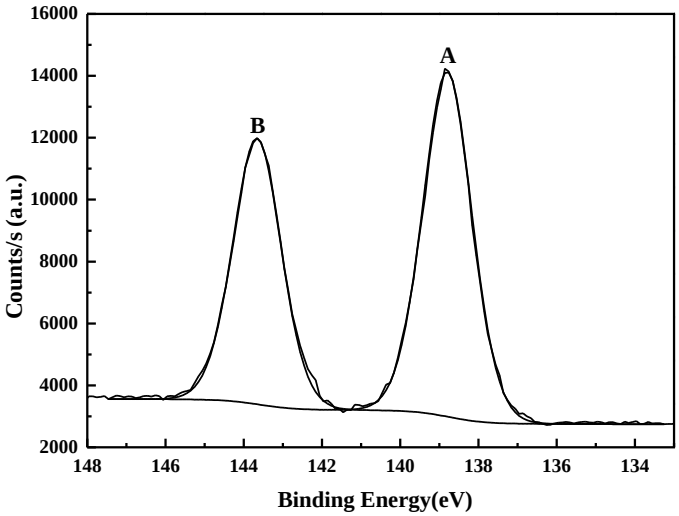


Fig. 10. Pb4f spectra of Pb-hydroxamate

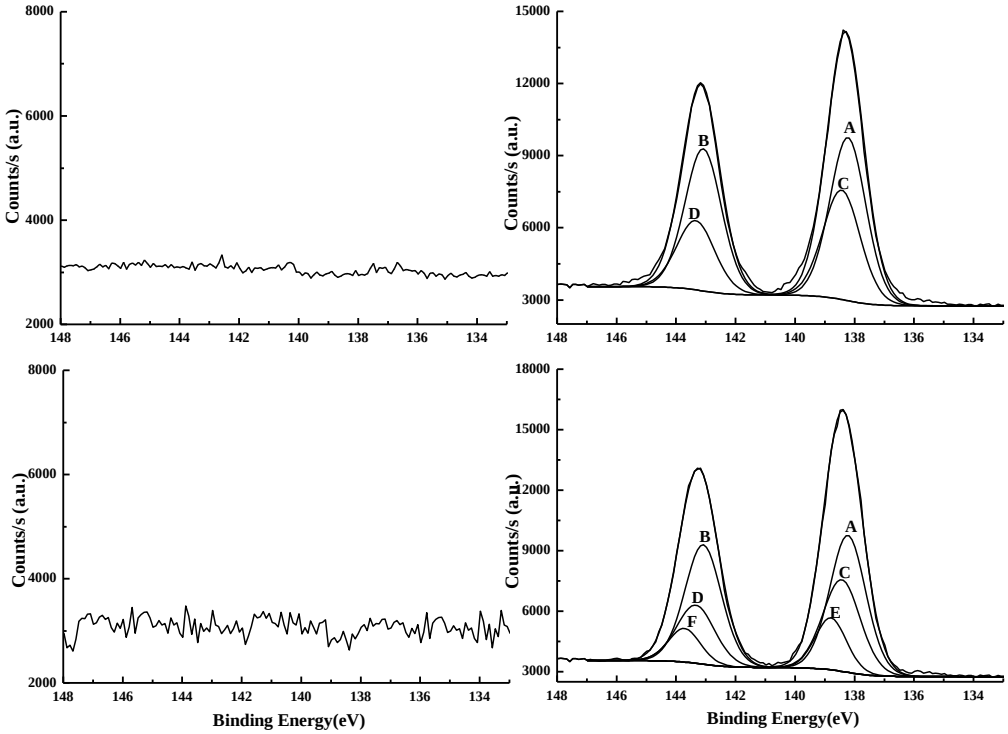


Fig. 11. Pb4f spectra of wolframite surface at different conditions (pH = 9):
1 – wolframite; 2 – wolframite, $5\cdot10^{-4}$ mol/dm^3 $Pb(NO_3)_2$; 3 – wolframite, 500 mg/dm^3 BHA;
4 – wolframite, $5\cdot10^{-4}$ mol/dm^3 $Pb(NO_3)_2$, 200 mg/dm^3 BHA)

According to the proposed hypothesis, the adsorption product of lead ions on the wolframite surface can generate Pb-hydroxamate by reacting with BHA. Thus, Pb4f spectrum of Pb-hydroxamate was measured, and shown in Fig. 10. Obviously, there are two characteristic peaks in Pb4f spectra of Pb-hydroxamate where peak E at 138.79 eV stands for $Pb4f_{7/2}$ of Pb-hydroxamate, peak F at 143.72 eV stands for $Pb4f_{5/2}$ of Pb-hydroxamate. On the other hand, the Pb4f spectra of wolframite at pH 9 in the presence or absence of the reagents (BHA/$Pb(NO_3)_2$) is shown in Fig. 11. It can be seen from Figs. 11-1 and 11-3 that there are no obvious peaks on Pb4f spectra of wolframite after the addition of BHA. Nevertheless, the peaks can be observed on Pb4f spectra of wolframite in the presence of lead ions. Specifically, Fig. 11-2 is similar to Fig. 9-4, revealing Pb4f spectra of PbO and $Pb(OH)_2$. On the other hand, two new peaks at 138.85 eV and 143.79 eV are shown in Fig. 11-4, which are related to the characteristic peaks of Pb-hydroxamate. Overall, Pb-hydroxamate is observed by the reaction between BHA and lead compounds as proposed hypothesis.

Conclusions

This study clearly reveals the positive role of lead ions in wolframite flotation with BHA as collector, and explains the mechanism. The following observations are drawn.

Lead ions can largely improve the recovery of wolframite in flotation, and the adsorption density of BHA onto the wolframite surface at the same pH range from 4 to 10.5.

The majority of lead ions exist at the wolframite-water interface in forms of Pb^{2+}, $PbOH^{+}$, and $Pb(OH)_2$ respectively in three pH ranges. Therefore, the addition of lead ions improves the zeta potential of wolframite. However, the zeta potential of wolframite is still negative in the presence of lead ions causing repulsive electrostatic force to anionic collector BHA. Combining with the XPS measurement, it reveals the chemisorption of BHA at the wolframite surface.

After the addition of lead ions, the adsorption product PbO or $Pb(OH)_2$ generated on the wolframite surface at different pH indicating lead ions react with oxygen atom of wolframite surface. It increases the number of active sites to adsorb BHA at the wolframite surface since Pb-hydroxamate is found on the wolframite surface after the addition of BHA and lead ions.

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