



## Novel catalysis mechanisms of benzohydroxamic acid adsorption by lead ions and changes in the surface of scheelite particles

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### ABSTRACT

To improve the floatability of tungsten minerals, lead ions (lead nitrate) were used to modify the surface properties of the minerals and benzohydroxamic acid (BHA) was used as a collector in the flotation system.  $Pb^{2+}$ -BHA complexes are inevitably present in this process and the role of it is unclear. This investigation is going to describe a new approach and the mechanism of catalyzing BHA adsorption onto scheelite by lead ions. Chemical speciation, zeta potential, FTIR, and XPS studies were conducted to establish the important role of lead ions. Indeed,  $Pb^{2+}$ -BHA complexes were shown to be the active species responsible for flotation. The speciation and zeta potential results showed the presence of the adsorbed  $Pb^{2+}$ -BHA complexes on the scheelite. The XPS results for atomic composition and binding energies confirmed  $Pb^{2+}$ -BHA species adsorbed on the scheelite surface, which contributed to more adsorption of BHA. The new method would increase the recovery of scheelite, simplify the flowsheet and reduce the processing cost.

### 1. Introduction

Tungsten as a hard, refractory and rare metal is important for many applications (Misono, 1987; Dermatas et al., 2004; Granqvist, 2000; Habazaki et al., 1991). Examples include many key alloys of tungsten in the productions of incandescent light bulb filaments, X-ray tubes, electrodes in welding, radiation shielding and superalloys. Wolframite  $[(Fe, Mn)WO_4]$  and scheelite  $[CaWO_4]$  are the two main tungsten minerals with sufficient abundance of economic significance. These two tungsten minerals are heavy in specific gravity and have an increased magnetic susceptibility; therefore, can be extracted by gravity and magnetic separation methods (Plimer, 1987). For fine particles of these minerals, surface properties such as hydrophobicity are often applied to extract tungsten by flotation using air fine bubbles (Warren, 1975; Gao et al., 2015a, 2015b; Sun et al., 2011; Yin and Wang, 2014).

Since the tungsten minerals are often associated with many other carbonate minerals such as calcite  $[CaCO_3]$  and dolomite  $[CaMg(CO_3)_2]$ , flotation separation of these minerals, especially scheelite, is difficult because of the similar surface properties (Arnold and Warren,

1974; Deng et al., 2016, 2015; Ozcan and Bulutcu, 1993; Yongxin and Changgen, 1983). The conventionally used surfactants (collectors) to hydrophobize scheelite particles are fatty acids or fatty acid derivatives (Bo et al., 2015; Oliveira and Sampaio, 1988; Shi et al., 2014; Sivamohan, 1988; Yongxin and Changgen, 1983). It is difficult to separate scheelite, especially from calcite, with these typical reagents because the adsorption mechanism of these collectors occurs through chemisorption of the oleate ion onto the mineral surface, showing a poor selectivity (Atademir et al., 1979; Changgen and Yongxin, 1983; Hıçyılmaz et al., 1993; Hu et al., 2011). Cationic collectors, such as amine and quaternary ammonium (Yang et al., 2015) have been developed to improve the selectivity of scheelite flotation from calcite. However, they have not been applied in the industry due to the poor selectivity for silicate minerals, such as quartz, muscovite, and garnet.

Hydroxamate collectors, such as benzohydroxamic acid (BHA) (Yin and Wang, 2014; Zhong et al., 2013), naphthenic hydroxamates (Zhao et al., 2013) and amide hydroxamate (Deng et al., 2015) were also used for scheelite flotation in recent years. Their ability to function as collectors in mineral flotation has been documented by Fuerstenau (2001).

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The formation of stable aqueous complexes between the cationic species constituting the mineral lattice and the BHA ligand appears to be a necessary condition for the BHA flotation of minerals (Xu et al., 2017; Ohji et al., 2016; Wu and Zhu, 2006). Lead ions (lead nitrate) were introduced to modify the surface properties of tungsten minerals, efficiently and selectively improving their floatability. It has been applied in Shizhuyuan Polymetallic Mine (Han et al., 2017a, 2017b; Tang et al., 2002) which is one of the biggest tungsten deposits and a typical representative of processing plants for tungsten minerals in China. However, the active species responsible for the flotation of tungsten minerals and the mechanism of adsorption were unconfirmed. Fuerstenau et al. (Fuerstenau and Cummins, 1967; Fuerstenau et al., 1966) postulated that the active species responsible for quartz flotation may be a basic aqueous complex, such as  $\text{Ca}(\text{OH})(\text{RCOO})_{(\text{aq})}$  and  $\text{Pb}(\text{OH})(\text{RSO}_3)_{(\text{aq})}$ , indicating an important role of these complexes in flotation.

In this work, the focus is on gaining a better understanding of the catalysis of BHA adsorption onto the scheelite surface by lead ions and changes in the surface properties of scheelite particles. A series of experimental studies were conducted to demonstrate the active species responsible for the flotation of scheelite. The mechanism of the adsorption of  $\text{Pb}^{2+}$ -BHA was studied by chemical speciation, FTIR, surface charging experiments, and XPS measurements. All of these modeling and experimental results have allowed us to determine the difference in the affinity (hydrophobicity) of modified scheelite to air bubbles.

## 2. Materials and methods

### 2.1. Materials

High-purity scheelite samples were obtained from Shizhuyuan Mine, Hunan, China. X-ray diffraction (XRD, D/max 2500 Model, Rigaku, Japan) and X-ray fluorescence (XRF, Zetium, PANalytical, Netherlands) data confirmed that the purity of scheelite samples had more than 97% purity. The fine fraction ( $-74\ \mu\text{m}$ ) was used for the experiments. Analytical grade BHA and lead nitrate were purchased from Tianjin Guangfu Fine Chemical Co. Ltd. (Tianjin, China). pH was adjusted with NaOH or HCl. Deionized water produced using Ultrapure Water Polishing System VE-DS (Hongsen Environmental Protection Technology Co. Ltd. (Shenzhen, China) was used in all the experiments.

### 2.2. FTIR experiments

For the FTIR (Fourier Transform Infrared) measurements, 0.5 g of pure scheelite ( $-38\ \mu\text{m}$ ) were individually suspended in 200 mL of the desired reagents solutions for 25 min at  $\text{pH } 8.8 \pm 0.2$  under ambient conditions. The pulps were then centrifuged and washed at least three times with deionized water and dried in a vacuum oven at  $40\ ^\circ\text{C}$ . The samples were subjected to FTIR measurements using a Bruker Alpha FTIR spectrometer (Model No. 740, Thermo Scientific, USA) at room temperature ( $20\ ^\circ\text{C}$ ) in the range from  $400\ \text{cm}^{-1}$  to  $4000\ \text{cm}^{-1}$ .

### 2.3. XPS experiments

X-ray photoelectron spectroscopy (XPS) analysis of the scheelite surface prepared following the experimental procedure described above for the FTIR measurements was carried out to identify the chemical species formed. The XPS data were acquired using an ESCA LAB 250Xi X-ray Photoelectron Spectrometer incorporating a hemispherical electron energy analyzer. Survey (wide) scans were taken with an analysis area of  $300\text{--}700\ \mu\text{m}$  at an analyzer pass energy of 100 eV. Multiplex (narrow) high-resolution scans were carried out with an analysis area of  $300\text{--}700\ \mu\text{m}$  and an analyzer pass energy of 30 eV. Survey scans were carried out over a  $1200\text{--}0\ \text{eV}$  binding energy range with 1.0 eV steps and a dwell time of 100 ms. Narrow high-resolution scans were run with 0.05 eV steps, and 200 ms dwell time. Spectra were charge-

corrected using the main line of the carbon 1 s spectrum photoelectron peak (adventitious carbon) as an internal reference to account for sample charging, with an assigned BE of 284.8 eV. The surface was first analyzed by a single survey scan to identify the elements present, and then multiplex high-resolution scans of each elemental region were carried out to identify the relative elemental concentrations as well as oxidation state and chemical bonding associations. Relative elemental atomic concentrations were determined by peak fitting using the CASA XPS software package and the Kratos library of relative sensitivity factors. The XPS data for all regions was fitted using Shirley background subtraction and Gaussian-Lorentzian peak profiles.

### 2.4. Zeta potential measurements

Zeta potential measurements were conducted at  $20\ ^\circ\text{C}$  using a zeta potential analyzer (ZetaPlus, Bruker, USA). Mineral suspensions containing 0.02 g of solids and 40 mL 0.01 M KCl background were prepared in a beaker at a given pH and a reagent concentration. After settling for 5 min, the supernatant liquor was collected and used for zeta potential measurement. The Smoluchowski equation was applied to calculate the zeta potential from the electrophoretic mobility of the particles measured by the instrument. The presented results were the average of three independent measurements.

### 2.5. Flotation experiments

Single scheelite mineral flotation tests were carried out in an XFG flotation machine with a 40 mL Plexiglas™ cell. The impeller speed was 1900 rpm. The mineral suspension was prepared by adding 2.0 g of minerals to 30 mL of deionized water, followed by the adjustment of the suspension pH. Once the desired reagent was added, the suspension was agitated for 3 min, and the pH was measured before introducing air bubble to the flotation cell. Hydrophobized scheelite particles by adsorption of BHA were collected by air bubbles which raised to the surface to overflow the cell. After 3 min of flotation, the products of the overflowing particles (the concentrate) and the remaining particles inside the cell (the tailings) were collected, dried and weighed for further analysis. Each flotation test was conducted three times, and the average mass recovery was calculated by dividing the concentrate mass by the initial mass of particles (the feed) and reported.

## 3. Results and discussions

### 3.1. Species of $\text{Pb}^{2+}$ solution versus pH

Fig. 1 shows the distribution diagram of  $\text{Pb}^{2+}$  species versus pH in aqueous solution at a  $\text{Pb}^{2+}$  concentration of  $1 \times 10^{-4}\ \text{mol/L}$ , which has been documented in many literatures (Li et al., 2016; Fuerstenau et al., 1985). There are two specific values of pH which should be paid attention: the first pH value presents the beginning of the solid lead hydroxide formation, which can be obtained by assigning the concentration to the critical value of saturation concentration ( $4.898 \times 10^{-5}\ \text{M}$ ) and solving the corresponding equation for pH. This specific value  $\text{pH} = 9.401$  is for  $C_t = 1 \times 10^{-4}\ \text{M}\ \text{Pb}^{2+}$  as shown in Fig. 1. The second specific value of pH presents the upper limit of the modeling beyond which the model gives a negative number for a species concentration. This second value  $\text{pH} = 10.997$  can be obtained for  $C_t = 1 \times 10^{-4}\ \text{M}\ \text{Pb}^{2+}$  as shown in Fig. 1. The solid lead hydroxide is formed between the two values of  $\text{pH} = 9.401$  and  $\text{pH} = 10.997$  as can be seen in Fig. 1. As we see later, the catalysis of BHA adsorption is not effective when solid lead hydroxide is formed, leading to depletion of the catalytically active species in solutions. Therefore, knowing the critical pH values is important. The typical results of speciation shown in Fig. 1 would be useful for investigating the changes in the surface properties of scheelite in the presence of BHA: some of the species can facilitate the adsorption of BHA. Several studies indicated that lead species adsorbed on mineral

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