Journal of Industrial and Engineering Chemistry xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Journal of Industrial and Engineering Chemistry

journal homepage: www.elsevier.com/locate/jiec

Synthesis of acetic acid-[(hydrazinylthioxomethyl)thio]-sodium and its application on the flotation separation of molybdenite from galena

Zhigang Yin, Wei Sun*, Yuehua Hu, Runqing Liu, Wei Jiang, Chenhu Zhang, Qingjun Guan, Chenyang Zhang*

School of Minerals Processing and Bioengineering, Central South University, Changsha, Hunan 410083, China

ARTICLE INFO

Article history:
Received 12 December 2016
Received in revised form 13 March 2017
Accepted 19 March 2017
Available online xxx

Keywords:
Molybdenite
Galena
Depressant
Flotation separation

ABSTRACT

A novel organic compound acetic acid-[(hydrazinylthioxomethyl)thio]-sodium was synthesized and characterized. The flotation performance and adsorption mechanism of AHS to galena were investigated by micro, bench flotation tests, UV spectra, zeta potential, FTIR and XPS measurements. The results demonstrated that AHS exhibited superior depressing power to galena and could be used as selective depressant for flotation separation of molybdenite from galena. The results of UV spectra, FTIR, zeta potential and XPS measurements demonstrated that AHS chemisorb on galena surface by forming five-membered cheat ring with releasing of H ions. Therefore, the possible adsorption mode of AHS on galena surface was recommended.

Introduction

As a strategic metal, molybdenum has a wide applications in industry. It is reported that about 80% of the world's molybdenum is used for alloy steels, such as stainless steels and cast irons, and the rest is used in hydrogenation, chemical application and agricultural field, etc [1]. As known, lead ions or its oxide products may cause problems including deteriorate the quality of alloy product and environmental contamination due to the evaporation of lead oxide during the smelting process of producing molybdenum oxides [2]. Therefore, the strict market standards for molybdenum concentrates require that the impurity should be reduced to a specific level, for lead, usually less than 0.05% [3]. In order to meet the market requirement for a high purity product, the supplier always adopt either physical, chemical methods or biohydrometallurgy to remove the impurity from molybdenum concentrate [4].

For the adoption of chemical methods to remove galena from molybdenum concentrate (PbS), various hydrometallurgical or biohydrometallurgy methods have been adopted for purification of molybdenite. Over the past decades, several leach systems have been used to selectively remove impurities (such as lead and copper) from molybdenum concentrates, including alkaline leaching, cyanide leaching, nitrate leaching, ferric chloride leaching, dry chlorination followed by leaching, roasting followed by leaching, pressure leaching, aminopolycarboxylic acid leaching, sodium hypochlorite leaching and pyrometallurgical process with oxygen-free inert gas system [1,2,5–7]. Recently, the bioleaching methods have attracted the researchers' attention to purify the molybdenum concentrate by optimize the parameter of leaching system which including, pH, temperature, microorganism, etc [8–11]. Although these roasting or leaching processes are technically available, the disadvantages (such as the inevitable cost for discharge the leaching solution, the treatment of roasting tailing gases) of this methods hampered their commercial application [5]. For bioleaching, the serious drawback is the extended leaching time for the dissolution of certain amount of metal sulfides which presented as low efficiency.

On the other hand, physical method usually involves the selectively separating molybdenite from other sulphide ores by froth flotation. As well know, flotation is a physicochemical separation technique that take the advantages of separating the hydrophobic particles from the gangue minerals (hydrophilic particles) [12], which usually including direct/reverse flotation methods or the combinations. To take one example, molybdenite is first flotated with the addition of collector and frother followed by addition of various reagents to depress other sulphide ores [13]. In the application of commercial scale, the reported inorganic depressants usually including potassium dichromate, sulfur

* Corresponding authors.
E-mail addresses: sunmenghu@csu.edu.cn (W. Sun), zhangchenyang@csu.edu.cn (C. Zhang).

http://dx.doi.org/10.1016/j.jiec.2017.03.027
1226-086X/

dioxide, Nokes reagent, sodium hydrosulfide, sodium sulfide and the combination of Nokes and sodium sulfide, even sodium cyanide, etc [14]. However, potassium dichromate, sulfur dioxide and cyanide are toxic and their application may cause a significant environmental contamination. As for Nokes reagent, sodium hydrosulfide and sodium sulfide, the preparation and addition of these depressant solution at mining site is unavoidably associated with some unpredictable problems and difficulties, such as the seriously corrosion of pipeline and the unsafe working conditions because of the volatilization of toxic gases under acid condition [14], e.g. hydrogen sulfide and sulfur dioxide. With the increasingly stringent environmental protection and safety regulations all over the world, efforts have been done to develop alternative selective depressants to replace these environmental unfriendly chemicals [15].

For the reasons mentioned above, all over the world, much attention has been paid on the use of organic depressant reagents as an alternative depressant for conventional depressants due to their abundance, biodegradability and environmental friendly, etc [16]. The applications of starch, dextrin, guar gum, tannin, carboxymethyl cellulose (CMC), chitosan, lignosulfonate-based biopolymers, polyacrylamide polymers (PAM) and their derivatives in the separation of minerals have been reported [16,17–18]. The macromolecule contains large numbers of hydroxyl groups and hydrated polar groups, such as HO^-, SO_3^{2-} and $-COO^-$, which could act as active site and adsorbed on the surface of minerals via various interactions, such as through hydrogen bonding or electricity force, thus depress the mineral [16]. It is reported that dextrin and chitosan have been applied in the differential flotation of sulfide minerals [19], such as separation of galena from chalcopyrite, separation molydenite from chalcopyrite and the separation of chalcopyrite from galena [20]. Despite the widespread application of macromolecule organic compounds in the laboratory scale to separate an artificial mixtures, there are limited reports on the successful use of these compounds in the flotation separation of molybdenite from galena because of they not only depress galena but also adsorbed on molybdenite thus cause poor selectivity [21–23].

Although, much efforts have been focused on the research of macromolecule on the selective separation of molybdenite from other sulfide ores, it is still a change task to apply these compounds in a commercial scale. Compared with the non-selective (poor selective index of sulphide to sulphide) of macromolecule depressants, the small molecule organic compounds with the advantages of reasonable selectivity. According to the recent studies, the application of DPS [24], pseudo glycolythiourea acid [25], disodium carboxymethyltrithiocarbonate [26] and thioglycolic acid [27], sodium 2,3-dihydroxypropyl dithiocarbonate [28], 2,3-disulfanylbutanedioic acid [29] in the separation of sulfide minerals indicate that it is possible to adopt these reagents as selectively depressants for the differential separation of sulfide minerals by flotation. Although the reports indicated that they may be used as selective depressants in the field of differential flotation of sulfide minerals, due to their high price or poor performance in pilot scale test that restricts their widely application. Therefore, more efforts need to be focused on the research of novel, nontoxic and good selectivity organic compounds due to the rigid environmental pollution control regulations and capital cost.

The object of this research was to evaluate the possibility of using the synthesized novel organic compounds as a selectively depressant in the flotation separation of molybdenite from galena. The micro and batch flotation results suggest that the novel compound could be used as an alternative depressant, which with the advantages of excellent performance and environmental friendly. The interaction mechanism of AHS on galena has been studied through UV–vis spectra, zeta potential, FTIR spectroscopic and XPS measurements to elaborate the observed phenomenon in flotation tests.

Materials and methods

Materials

Molybdenite and galena obtained from Shanxi province in China, were crushed in a porcelain mortar and sieved. The fraction containing particles between 38–74 μm fraction was used for flotation. The chemicals used in experiments were analytical grade and purchased from the local supplier. The preparation and characterization of both the minerals and reagent could be available from supplementary information.

FTIR spectra measurement

The sample was prepared by adding 100 mg of minerals to 50 mL solution with the depressant concentration of 10^{-2} mol/L at pH 8. After stirring for half an hour, the mineral samples were filtered, dried and collected for measurement. The infrared spectra of samples were recorded by a IRAffinity-1 (Shimadzu, Japan) FT-IR spectrometer at room temperature (25 ± 1 °C) in the range from

Zeta potential measurement

Zeta potential experiments were conducted using the Malvern Zeta Sizer Nano Series (manufactured in England) with electrolyte solution of 0.01 M KNO_3. A suspension containing 0.01 wt% freshly-ground mineral particles (100% passing 5 μm) was prepared in the electrolyte solution. The pH of the mineral suspension was adjusted to the desired operating value by adding dilute either HCl or NaOH solutions. In each case, the average of three independent measurement with a typical variation of ±2 mV was reported.

Evaluation of reaction between AHS and Pb^{2+} ions

Pb^{2+} aqueous solutions (10^{-3} mol/L) was prepared from the dissolution of lead nitrate. The solution of depressant (10^{-3} mol/L) was prepared by dissolving 0.001 mol of AHS in one liter distilled water. After the preparation of solutions, 20 mL of each of the solution was separated and mixed together in a beaker, the absorbance of the supernatant against the blank (Millipore syringe filter with size of 13 mm × 0.45 μm was adopted for filtration) was measured after 20 min oscillation followed 24 h of standing.

XPS measurements

The preparation of samples for XPS measurements were conducted on by polishing a piece of galena which was pasted on a slide glass by Canada balsam. After that, the polished slide was cut to a piece with size of 4 mm × 4 mm × 2 mm and used for tests. The XPS spectra of mineral particles before and after depressant adsorption were recorded with a K-Alpha 1063 (Thermo Scientific Co., USA) spectrometer with Al Ka as sputtering source at 12 kV and 6 mA, with pressure in the analytical chamber at 1.0×10^{-12} Pa. All binding energies were referenced to the neutral C 1s peak at 285.0 eV to compensate for the surface-charging effects. XPS Peak 4.1 software was used to fit the XPS peaks.

Flotation tests

A flotation machine of XFG-1600 type (mechanical agitation) with the volume of 40 mL was used in micro-flotation tests, which was manufactured by Jilin prospecting machinery factory (China),