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Influence of Ag, Sb, Bi and Zn impurities on electrochemical and flotation behaviour of galena

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ABSTRACT

The influences of Ag, Bi, Sb and Zn impurities on the electrochemical adsorption of butyl xanthate on a galena surface were investigated. The impurity-doped and pure galena samples were synthesised by chemical precipitation and tested by X-ray diffraction (XRD) analyses. The flotation results suggest that the Ag and Bi impurities can promote the flotation of galena, while the Zn and Sb inhibit it. Both the lead- and impurity-xanthate are observed on the galena surface by infrared spectra, which suggests that the impurities on galena surface also interact with xanthate. However, Ag-xanthate and Bi-xanthate at the galena surface doped Ag or Bi may need to be further verified. The cyclic voltammetric measurements on galena microelectrodes reveal two oxidation peaks for both the pure and impurity-doped PbS, while no obvious reduction peaks are observed. It is found that the presence of Ag and Bi enhances the oxidation of xanthate on the galena surface, while the Zn and Sb impurities inhibit the oxidation of xanthate on the galena surface. The amount of electrochemically adsorbed xanthate on the galena surface varies based on the type of impurity and has a positive correlation with the flotation recovery of galena.

1. Introduction

Galena is the primary source of lead, which has good floatability and floats easily with xanthate. Natural galena usually contains impurities, such as silver, copper, zinc, arsenic, stibium, bismuth, cadmium, thallium, indium and other elements. Among these impurities, the Ag impurities associated with galena are the major source for silver output. The lattice impurities have a great influence on the flotation behaviour of galena (Popov et al., 1998). For example, the Ag, Bi and Cu impurities enhance the floatability of galena, while the Zn, Mn and Sb impurities hinder it (Hu, 1987; Laajalehto et al., 1991). Chen et al. (2011) reported the electronic structures, which were calculated using density functional theory, of galena containing 10 typical types of impurities, and they suggested that the impurities might change the semiconducting properties of the galena, such as the semiconductor type, Fermi level and band gap; these impurities might also affect the oxidation behaviour of the galena.

Electrochemical studies have demonstrated that xanthate could produce lead salts after oxidation on a galena surface with a concomitant reduction of oxygen (Feng and Chen, 2014). Natural galena obtained from different deposits usually exhibits different levels of floatability, which might be due to the presence of impurities in the galena lattice. Lattice impurities in galena cell can strongly influence the semiconducting properties of galena, which playing an important role in the process of xanthate interacting with galena. For example, xanthate can spontaneously adsorb on fresh galena with strongly p-type properties, but the surface of freshly fractured galena that is strongly n-type must be oxidised to increase the free hole concentration enough for the xanthate to chemisorb (Plaksin and Shafeev, 1963; Eadington and Prosser, 1969; Richardson and O'Dell, 1985). In addition, the impurities on the galena surface may also be active sites for oxygen adsorption, favouring xanthate adsorption. Therefore, the role of the impurities on the galena surface during xanthate adsorption must be investigated.

The electrochemical behaviour and reactions occurring on the mineral electrode surface might be measured through cyclic voltammetry (Huerta-Cerdán et al., 2003; Pecina et al., 2006; Irma Cisneros-González et al., 1999). Previous studies (Zoski, 2002; Bond, 1994) have revealed that many of the limitations associated with conventional voltammetric electrodes (e.g., 1–5 mm radius

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disc) have either been removed or greatly minimised when using microelectrodes. One major feature of microelectrode voltammetry is its ready access to near-steady-state conditions (radial diffusion) where the influence of the ohmic (IR) drop is considerably reduced relative to that associated with the transient response (linear diffusion). Moreover, the minerals floated by butyl xanthate in industry are usually near 0.074 mm in size, which is closer to our prepared microelectrodes (smaller than 0.045 mm) than conventional voltammetric electrodes (e.g., 1–5 mm radius disc). Hence, the results measured with microelectrodes would be more accurate for the flotation process.

In this paper, galena microelectrodes bearing Ag, Bi, Sb and Zn impurities are prepared, and the electrochemical behaviours of the galena microelectrodes bearing impurities in the presence of butyl xanthate were investigated through cyclic voltammetry. In addition, the surface products of the interactions between the butyl xanthate and the galena with impurities were detected using infrared spectrometry.

2. Materials and methods

2.1. Chemicals and minerals

Lead acetate trihydrate ($Pb(CH_3COO)_2{\cdot}3H_2O$), sodium sulphide nonahydrate ($Na_2S{\cdot}9H_2O$), silver nitrate ($AgNO_3$), zinc chloride ($ZnCl_2$), antimony trichloride ($SbCl_3$) and bismuth nitrate pentahydrate ($BiCl_3{\cdot}5H_2O$) were purchased from Sinopharm Chemical Reagent Company in Shanghai, China, and all of the reagents is analytically pure. The redistilled water is also used. A natural galena sample, which was used for conducting XRD measurement, was obtained from the Fankou Mine in Guangdong province, China. Multi-elemental analysis indicated the galena sample was highly pure (86.47% Pb), containing only traces of Sb and Co (0.06% Sb, 0.08% Co); the sodium butyl xanthate (SBX) was synthesised by combining butyl alcohol with sodium hydroxide and carbon disulphide. The alumina powder was analytically pure and purchased from CH Instruments, Inc. The type of X-ray analytical instrumentation used in this text is D/MAX 2500V purchased from Rigaku.

2.2. Synthesis of pure and impurity-doped galena

Natural samples will have mixtures of impurities or contain inclusions of different phases. The natural galena sample containing a single impurity is difficult to be collected. Therefore, chemical precipitation method was used to prepare the synthetic galena samples with different impurities.

The pure galena was synthesised using sodium sulphide as the sulphur source and lead acetate as the lead source. The theoretical molar ratio of these two compounds in a completed reaction is 1:1. To precipitate the Pb^{2+} completely, a slight overdose of sodium sulphide is often applied. The synthetic process used in this work was as follows: First, 74.8 g of $Pb(CH_3COO)_2{\cdot}3H_2O$ was added to a 5000-mL beaker, and the appropriate amount of water was added to the beaker to obtain solution A upon complete dissolution of the $Pb(CH_3COO)_2{\cdot}3H_2O$. Next, 52.8 g of $Na_2S{\cdot}9H_2O$ was added to a 2500-mL beaker, and the appropriate amount of water was to dissolve this salt completely, producing solution B. Afterwards, solution B was added to solution A to obtain black galena. Finally, this mixture was stirred evenly until the mixture was fully precipitated, producing pure galena.

The impure galena was prepared by reacting sodium sulphide with lead acetate and metal X salts, which act as impurities; X refers to Ag, Zn, Bi, or Sb. First, the lead acetate trihydrate and metal X salts were dissolved in deionised water, and, subsequently, a sodium sulphide solution was added. The resultant mixture was stirred for 12 h before being filtered; the black solid was washed with large amount of water. Finally, the solid product was dried in oven at 90 °C for 48 h. The impurity contents were determined through chemical analysis (Rock and mineral analysis group, 2011). The doped samples contained approximately 5% of an impurity by mass, or the molar ratio of the reactants would be adjusted. The mass percentages of the Ag, Zn, Sb and Bi impurities were 4.98%, 4.96%, 5.01% and 5.02%, respectively, which are within the scope of limited content. The acceptable samples were ground to 75–150 μm and used for the flotation experiments. The samples used for XRD characterisation were ground to smaller sizes below 45 μm.

2.3. Electrode preparation

During this test, saturated calomel, platinum and glassy carbon electrodes are used as the reference, counter and working electrodes, respectively. In this study, the PbS microelectrodes with particle sizes below 320 meshes and their preparation are key for the cyclic voltammetry tests. The process for preparing the working electrode is as follows: first, 0.5 g of chitosan and 100 mL of 0.05 mol/L acetic acid are added into a 250-mL conical flask, and the solution is ultrasonically vibrated for 1 h to obtain a chitosan suspension; after standing for 12 h, the supernatant of the chitosan solution is extracted and named the chitosan solution; 1 mg of synthesised pure or impurity-bearing PbS (<45 μm) and 4 mL of chitosan solution are added to a dry test tube with ultrasonic oscillation for 1 h to produce an even suspension; finally, the suspension is dropped onto the surface of a glassy carbon electrode using a 10 μL microsampler. Before dropping the PbS suspension onto the surface, the glassy carbon electrode surface is ground with 0.3-μm and 0.05-μm alumina powder for 5 min. The ground electrode is sequentially soaked in concentrated HNO_3 in a 1:1 ratio by volume, absolute ethyl alcohol and distilled water before being ultrasonically vibrated for 5 min. Next, the cleaned electrode is dried with filter paper and inversely inserted into a foam board with the round electrode surface facing upward. Finally, the wet glassy carbon electrode with the drop of suspended PbS is dried by placing it under an infrared lamp.

2.4. Flotation tests

An inflatable hanging slot flotation machine (XFGC-80) with a usable capacity of 40 mL is used as the main device during the flotation test. The flotation machine worked at 2502 r/min. Before the flotation test, a 2.2-g ore sample is put into a beaker with a weak acid solution (pH 5–6) for ultrasonic cleaning over approximately 10 min to remove the oxide layer from the ore surface. After standing for a certain time, the solution in the upper portion of the beaker is discarded, and the ore sample in the beaker is washed with distilled water several times. During flotation, the reagents were added in the following order: (a) distilled water and an appropriate amount of sodium hydroxide solution were added to the slot to produce 40 mL of a weakly alkaline solution pH = 8.5; (b) a butyl xanthate solution (synthesised by our laboratory) was added into the slot to maintain the concentration at the collector at $1 \times 10^{-3-}$ mol/L for conditioning over 5 min; (c) 5 g/t of a frothing agent (MIBC) was added to the pulp for conditioning over 2 min; (d) the concentrated product and the tailings were filtered, dried and weighed to obtain their masses.

2.5. Infrared spectrometry

All of the ore sample used in infrared spectrometry (IR) measurement is synthesised by chemical precipitation. One gram of pure or impurity-bearing PbS sample and 20 mL distilled water