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The hydrophobic mechanism of di(2-ethylhexyl) phosphoric acid to hemimorphite flotation

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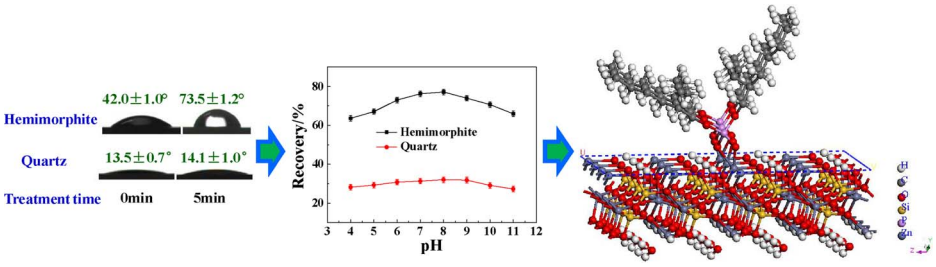
GRAPHICAL ABSTRACT

The selective flotation separation of hemimorphite from quartz under 1.0×10^{-4} mol L^{-1} DEHPA and its hydrophobic mechanism on hemimorphite {1 1 0} surface.



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ABSTRACT

In this paper, the flotation separation of hemimorphite from quartz was investigated by using di(2-ethylhexyl) phosphoric acid (DEHPA) as a collector. The results elucidated that DEHPA exhibited better flotation performances to hemimorphite than dibutyl phosphoric acid (DBP), tributyl phosphate (TBP), octanoic acid (OA) and palmitic acid (PA). And DEHPA also possessed good selectivity against quartz flotation and could realize the effective flotation separation of hemimorphite from quartz under pH 6.0–10.0. The adsorption and contact angle findings clearly indicated that DEHPA selectively adsorbed on hemimorphite, hardly on quartz. After DEHPA treatment, the hydrophobicity of hemimorphite was dramatically improved. Zeta potential suggested that DEHPA anion anchored on hemimorphite surfaces mainly through chemical bonds. FTIR inferred that DEHPA chemisorbed on to hemimorphite surfaces by formation of the Zn—O bonds between the O atoms of the P(=O)(OH) group and the surface zinc atoms, simultaneously with splitting the O—H bonds of the P—O—H group. XPS gave clear evidences that the adsorbed DEHPA combined with Zn(II) species on hemimorphite surfaces to generate the Zn(II)-DEHPA surface complexes.

1. Introduction

Zinc is the fourth most used metal, next only to aluminum, iron and copper, which is commonly applied in batteries and alloys [1–3]. Zinc sulfide minerals, as the primary sources for production of zinc, are commonly concentrated and recovered by froth flotation. In recent years, zinc sulfide minerals have become depleted due to the continuous exploitation [4,5]. So, zinc oxide minerals are attracting more and more attention.

Zinc oxide minerals such as hemimorphite, smithsonite and hydrozincite often exist with gangue minerals such as quartz and clay minerals [6,7]. The traditional technique for treatment of low-grade zinc oxide ores is hydrometallurgy. However, this technology needs a large consumption of acid and is environment-unfriendly [8]. Froth flotation,

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as an economic and environment-friendly technology, is bound to become the indispensable approach for beneficiation and recovery of zinc oxide minerals [9].

For being easy to be hydrated, the flotation recovery of zinc oxide minerals is more difficult than that of its sulfide minerals. Generally, there are three primary approaches for flotation recovery of zinc oxide minerals [10–14]:

(i) Presulfurization with sulfurizing agents, followed by flotation with traditional collectors such as amines or xanthates.
(ii) Direct flotation by fatty acids.
(iii) Direct flotation by chelating agents.

The unavoidable disadvantage of the first method is that the dose of sulfurizing agents including Na_2S, NaHS or NH_4HS is hard to be precisely controlled [15]. Excessive dose would depress the flotation of zinc oxide minerals, and less dose would result in an insufficient presulfurization with a low flotation efficiency. Furthermore, sulfurizing agents impact pulp pH values which have a significant effect on flotation recovery of zinc oxide minerals [6]. The direct flotation doesn't need presulfidization, which uses fatty acids, 8-hydroxyquinoline, salicylaldoxime or aminothiophenol (ATP) as zinc minerals collectors [13,14,16]. For fatty acids collectors, they display low selectivity against gangue minerals and high consumption [17]. While chelating agents such as 8-hydroxyquinoline and salicylaldoxime possess good affinity and selectivity to zinc oxide minerals [16], it is interesting and significant to explore novel chelating agents for further improving the flotation enrichment of zinc oxide minerals.

The phosphorous surfactants such as phosphinic, phosphonic and phosphoric acids own chelating characteristics and have been used as extractants for extraction recovery of metal ions such as zinc, copper, cadmium, nickel or cobalt [18–21]. Among those phosphorous surfactants, di(2-ethylhexyl) phosphoric acid (DEHPA) has been proved to be a selective extractant for zinc [18,19].

In mineral processing, phosphorous surfactants have been adopted as collectors for flotation recovery of metal oxide minerals [22–32]. For examples, styryl phosphonic acid (SPA) exhibited good flotation response to finely disseminated rutile [23] and cassiterite [24]. Diphosphonic acid surfactants possessed good collecting ability towards niobium oxide minerals [25–27]. α-Hydroxyl octyl phosphinic acid (HPA) was recommended as a collector for ilmenite, cassiterite and malachite [28–31]. Nevertheless, phosphorous surfactants as collectors for flotation separation of zinc oxide minerals have not been frequently reported in the previous literatures.

For the selective affinity to zinc ions [18,19], DEHPA was selected as a collector for beneficiation of zinc oxide minerals in this paper. And its flotation performances to hemimorphite and quartz were evaluated and compared with those of dibutyl phosphoric acid (DBP), tributyl phosphate (TBP), octanoic acid (OA) and palmitic acid (PA). The flotation separation of hemimorphite from quartz by using DEHPA collector was also performed. After that, DEHPA' adsorption mechanism to hemimorphite was further explored by the experiments and analyses of adsorption, contact angle, zeta potential, FTIR and XPS.

2. Materials and methods

2.1. Materials

The hand-picked hemimorphite and quartz samples purchased from Guilin, Guangxi province of China, were crushed, comminuted in an agate mortar, and screened to get the desired fine particles. The size fraction ranging from +37 to −74 μm was employed for micro-flotation and adsorption experiments. The portion with a diameter below 5 μm was employed for zeta potential, FTIR and XPS measurements. The XRD (X-ray diffraction) of hemimorphite and quartz samples were presented in Fig. 1, which was measured on Rigaku D/max 2550 (Rigaku Co., Tokyo, Japan). The mineral compositions were assigned by comparing the experimental XRD peaks with the PDF2-2004 database. The XRF (X-ray fluorescence) of the two mineral samples were listed in Table 1. The detection results illuminated that hemimorphite or quartz was dominated in their individual samples. The specific surface area (SSA) for the +37 to −74 μm portion was determined as 0.76 $m^2 g^{-1}$ for hemimorphite and 0.12 $m^2 g^{-1}$ for quartz via BET (Brunauer-Emmett-Teller) method (Nova1000 surface area analyzer, Quantachrome Instru., USA).

Collectors adopted here were shown in Table 2 and their purities were greater than analytical grade (AR). Other chemicals used in the studies were AR. Distilled water was used during the whole experiments.

2.2. Flotation tests

Flotation experiments were conducted in a modified Hallimond tube. For each experiment, 2.0 g mineral samples were placed into a beaker with 50 mL distilled water and stirred for 1 min at 298 K. After that, the pulp pH was controlled by dilute HCl or NaOH solutions and stirred for another 3 min. And then, collector, methyl isobutyl carbinol (MIBC) and extra distilled water were introduced into the suspension to reach 220 mL with 1×10^{-4} mol L^{-1} MIBC. After agitating of 3 min, the pulp pH was recorded and the micro-flotation test was performed for 3 min with a 0.2 L min^{-1} nitrogen flow rate. The froth products and tailings were filtered, desiccated and weighted and the flotation recovery was computed according to Eq. (1) for single mineral, Eq. (2) for hemimorphite and Eq. (3) for quartz in the artificially mixed minerals, respectively.

$$\varepsilon = \frac{m_1}{m_1+m_2} \times 100\% \quad (1)$$

$$\varepsilon_{\text{Hemimorphite}} = \frac{m_1 \times \beta_1}{m_1 \times \beta_1 + m_2 \times \beta_2} \times 100\% \quad (2)$$

$$\varepsilon_{\text{Quartz}} = \frac{m_1(1-\beta_1)}{m_1(1-\beta_1) + m_2(1-\beta_2)} \times 100\% \quad (3)$$

Where ε is the recovery of hemimorphite or quartz, m_1 and m_2 are the weight of froth products and tailings (g), β_1 and β_2 are the zinc grade of the froth products and tailings (%, w/w), respectively. The presented recovery was the average value of two independent flotation tests.

2.3. Adsorption experiments

0.5 hemimorphite or quartz samples and 50 mL distilled water were put into a 150-mL conical flask. After conditioning the suspension pH with dilute HCl or NaOH solutions to a given value, DEHPA solutions with a certain concentration were fetched in to reach a total volume of 100 mL. The pulp was oscillated for 4 h at 298 K in the constant temperature shaker bath. After separation of mineral particles by filtration, the residual concentration of DEHPA in filtrate was measured by a TOC-VCPH analyzer (Shimadzu, Japan). The amount of TOC (total organic carbon) is the difference of total carbon minus inorganic carbon, and the adsorption amount of DEHPA on mineral surfaces was calculated by Eq. (4).

$$Q_e = \frac{V(C_o - C_e)}{WS} \quad (4)$$

Where Q_e (mol m^{-2}) is the amount of DEHPA adsorbed on hemimorphite or quartz, V (L) is the volume, C_o and C_e (mol L^{-1}) are the concentration of DEHPA before and after adsorption, S ($m^2 g^{-1}$) and W (g) are the SSA and mass of hemimorphite or quartz, respectively.