Electrokinetic properties of smithsonite and its floatability with anionic collector

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HIGHLIGHTS

► Proposed mechanisms for interaction mechanisms between sodium oleate and smithsonite surface, at different pH ranges.
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► Smithsonite interface are determined by Zn, carbonate, and the hydrolysis species.
► The hydrolysis species depress the floatability of smithsonite.
► The isoelectric point was achieved at the pH 8.2 with sodium carbonate.
► Smithsonite's floatability was improved with sodium carbonate.

GRAPHICAL ABSTRACT

Proposed mechanisms for interaction mechanisms between sodium oleate and smithsonite surface, at different pH ranges.
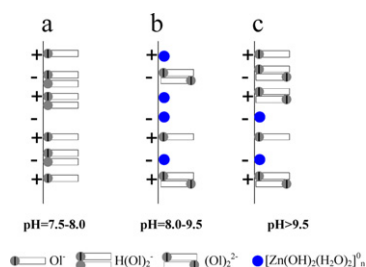
ABSTRACT

The effect of the smithsonite/water interface properties on the floatability of the mineral without and in the presence of sodium carbonate was examined through zeta potential measurements, microflotation tests, and the concentration of Zn^{2+} ions measurement, in the pH range from 7 to 11. The isoelectric point value of the mineral was achieved at pH 8.0, and the species Zn^{2+}, OH^-, HCO_3^-, CO_3^{2-}, and H^+, as well as the reabsorption of hydrolysis products would determine the smithsonite–solution interface properties. Smithsonite presents high floatability with sodium oleate (1.5×10^{-4} mol/L) between pH 7.0 and 8.0. Above pH 8.0, the smithsonite floatability decreases abruptly, and the polymeric zero-charged Zn(II) hydrolyzed species $[Zn(OH)_2(H_2O)_2]_n^0$ is proposed for depressing the floatability of smithsonite. With the sodium carbonate added into the solution, the isoelectric point value of the mineral was achieved at pH 8.2. The smithsonite interface, having more surface cation sites and zinc species in the Stern layer, gives rise to the floatability in the pH range from 7.0 to 8.7. Due to the formation of $Zn(CO_3)_2^{2-}$, the decrease of the concentration of the hydrolyzed species $[Zn(OH)_2(H_2O)_2]_n^0$ makes smithsonite more floatable than that without the Na_2CO_3 at 8.7 < pH < 10 (flotation recovery from 30% to 75% at pH 9.5). The results show that the anionic flotation of smithsonite is a promising route to recover Zn with the sodium carbonate.

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1. Introduction

Smithsonite is a native zinc carbonate, $ZnCO_3$. It is hexagonal with point group 3 bar 2/m. Carbonates with intermediate sized divalent cations normally crystallize in the calcite structure [1]. As the primary source of zinc, natural sulfide ores are steadily becoming depleted, therefore, there is an obvious recognition that the

recovery of low grade oxidized zinc ores has become more important for future demand. This situation increases the need to process these ores for a marketable product [2,3].

In practice, the commonly used method for recovering oxidized lead and zinc minerals from ores is flotation [3–7]. The flotation of oxidized zinc ore is more difficult than that of corresponding sulfide mineral [8]. The mineral surface activity of the mineral increases in water, and the adsorption of water molecules are by chemisorptions, which make smithsonite lack of natural floatability [9]. Sulfidization–flotation using sodium sulfide as the sulfidizing agent has been widely used in most flotation systems with cationic

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Table 1
The chemical analyses of pure smithsonite.

Component	ZnO	Fe	SiO$_2$	Al$_2$O$_3$	CaO	L.O.I
Amount in pure smithsonite (%)	64.1	0.10	0.75	0.015	0.05	34.98

collectors such as amines. The major problem in processing smithsonite is the large amount of fines and slimes inhibiting a selective flotation, so de-sliming is usually commended, which causes a low efficiency of these processes for the recovery of zinc [5,10,11].

Flotation by using carboxylic acid is applicable when the gangue is silica or clay minerals [12–14], and it is very difficult to separate smithsonite from carbonate gauge by flotation, due to the dissolution characteristics of smithsonite and those carbonate gauge. There are large amount of dissolved metal ions due to the dissolution of the semi-soluble minerals (such as smithsonite, calcite and dolomite) and soluble minerals (such as lead sulfate and gypsum), which can play a major role in determining the nature of the interactions taking place in the bulk solution or on the mineral surfaces. In salt-type mineral systems, the solubility is markedly higher than that in most other systems such as oxides and silicates. The interaction of minerals with several dissolved metals can lead to sorption processes such as precipitation/coprecipitation, adsorption, and ionic substitution. Therefore, how to recover smithsonite efficiently and effectively is still a challenge.

The shortage of fundamental studies addressing the physicochemical surface properties of smithsonite is one of the factors that hindered the development of selective flotation processes in the system under investigation. With the objective, we try to evaluate the physicochemical surface properties of smithsonite (on the electrokinetic behavior of smithsonite) and the effect on its floatability with the use of anionic collectors.

2. Materials and methods

2.1. Materials and reagents

The pure smithsonite samples were taken from the Yunnan province, China. The sample was comminuted in a porcelain mortar and the coarse fraction (−100 μm +19 μm) was used in the microflotation tests. The finer (−19 μm) was ground in an agate mortar and then separated on a dry classifier. The fine product from the classifier (size −5 μm) was used for electrophoretic measurements. The chemical analyses of smithsonite were shown in Table 1. Sodium oleate of analytical grade was used as a collector. Sodium carbonate, sodium hydroxide, zinc sulfate and potassium chloride were also of analytical grade. The deionized water was employed for all experimental work.

2.2. Methods and procedures

Zeta potential measurements on smithsonite were carried out using a plus zeta potential meter (Brookhaven, Zetaplus, USA). Potassium chloride was used to maintain the ionic strength at 10^{-3} mol/L. Samples of 0.030 g in the size −5 μm were added into 50 ml of the electrolyte solution or reagent solution with desired pH using hydrochloric acid (HCl) and sodium hydroxide (NaOH). The suspensions were then magnetically stirred for 10 min, and the final pH was measured and recorded. The zeta potential of samples was then measured alone or in the presence of sodium oleate. With the objective to evaluate the effect of carbonate ions on the smithsonite surface characteristics, the zeta potential of samples was also measured with the pH regulated by sodium carbonate alone or in the presence of sodium oleate.

The mineral-solution would be pre-conditioned for 10 min in order to obtain the dissolution equilibrium of minerals in open system. The sodium hydroxide or sodium carbonate was added to get a desired pH value. After that, the solution was agitated for 10 min at 800 rpm and the pH was kept constant. The suspensions were centrifugally separated at 9000 rpm for 10 min by means of a centrifuge. The concentration of Zn^{2+} ions in the supernatant liquid was measured by ICP optical emission spectrometry.

The microflotation tests were carried out in a mechanical agitation flotation machine at a constant rate. The mineral suspension was prepared by adding 2.0 g of minerals to 40 ml of solutions. Smithsonite was added at the beginning of the conditioning period. The pH of the mineral suspension was adjusted to a desired value by adding NaOH or HCl stock solutions. The collector was added to the slurry and the slurry was conditioned during 3 min before flotation. The flotation time was 5 min. Both floated and unfloated particles were collected, filtered and dried. The flotation recovery was calculated based on solid weight distributions between the two products.

3. Results and discussion

Zeta potential and flotation recovery of the natural smithsonite as a function of pH in the absence/presence of sodium oleate as a surfactant (collector) are shown in Fig. 1. The isoelectric point (IEP) value of the mineral without sodium oleate was achieved at pH 8.0, showing that above this pH value the negative surface sites in the Stern layer predominate.

Smithsonite is a semi-soluble solid [15]:

$$ZnCO_3 = Zn^{2+} + CO_3^{2-}, \log k = -10.00 \tag{1}$$
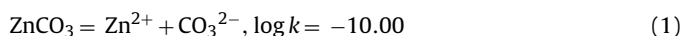
Semi-soluble minerals may have its surface charge developed by non-stoichiometric dissolution that results in the hydrolysis of the ions released to solution. The hydrolysis products of the ions are capable of readsorption onto the minerals surface. The interactions between the ions of the crystal structure and the hydrolysis products also can determine the mineral surface charge. However,
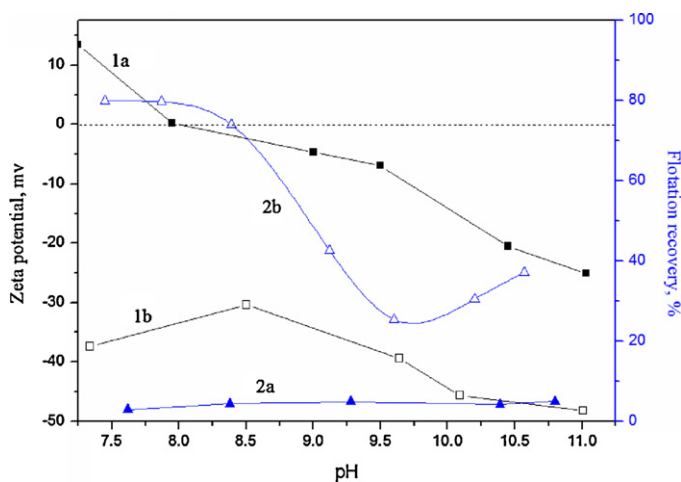

Fig. 1. Zeta potential (1) and flotation recovery (2) of smithsonite as function of pH: (a) smithsonite without sodium oleate; (b) smithsonite with 1.5×10^{-4} mol/L sodium oleate.