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A review of zinc oxide mineral beneficiation using flotation method

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ABSTRACT

In recent years, extraction of zinc from low-grade mining tailings of oxidized zinc has been a matter of discussion. This is a material which can be processed by flotation and acid-leaching methods. Owing to the similarities in the physicochemical and surface chemistry of the constituent minerals, separation of zinc oxide minerals from their gangues by flotation is an extremely complex process. It appears that selective leaching is a promising method for the beneficiation of this type of ore. However, with the high consumption of leaching acid, the treatment of low-grade oxidized zinc ores by hydrometallurgical methods is expensive and complex. Hence, it is best to pre-concentrate low-grade oxidized zinc by flotation and then to employ hydrometallurgical methods. This paper presents a critical review on the zinc oxide mineral flotation technique. In this paper, the various flotation methods of zinc oxide minerals which have been proposed in the literature have been detailed with the aim of identifying the important factors involved in the flotation process. The various aspects of recovery of zinc from these minerals are also dealt with here. The literature indicates that the collector type, sulfidizing agent, pH regulator, depressants and dispersants types, temperature, solid pulp concentration, and desliming are important parameters in the process. The range and optimum values of these parameters, as also the adsorption mechanism, together with the resultant flotation of the zinc oxide minerals reported in the literature are summarized and highlighted in the paper. This review presents a comprehensive scientific guide to the effectiveness of flotation strategy.

Contents

1. Introduction

Zinc enjoys tremendous importance owing to its wide application in industries. It ranks fourth in world metal consumption. Metallic

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zinc is used in the production of alloys and in the process of galvanization which bestows protection to steel structures. It is also present as a chemical additive in rubber and paints [1,2].

At present, zinc is produced from zinc sulfide minerals which are the primary source of zinc, and it is easy to separate the sulfide minerals from the gangue using conventional flotation techniques. As sulfide ores become depleted with the passage of time, the beneficiation of oxidized zinc ores has assumed great importance in recent years. This situation is what drives the urgent need to process these ores in order to produce a marketable product [3,4].

Using the leach/solvent extraction/electrowinning process route is the most common method of extraction of zinc from low-grade zinc oxide deposits. The application of whole-ore-leaching is likely to be uneconomical, and the separation of the acid-consuming gangue minerals prior to leaching is essential to the successful recovery of zinc from these deposits. This offers numerous advantages for leaching reagent consumption, refinery sizing, and site selection, as it could prove to be economically viable to transport zinc concentrate containing high Zn grades. It is technically feasible to separate more than 90% of the acid-consuming gangue minerals from the ROM zinc oxide ores, and to produce a concentrate yielding a zinc grade to the order of 25–35% using the flotation method [5].

There are three basic ore varieties of zinc oxide which are of economic value: (a) hemimorphite (gangue minerals: dolomite, goethite, quartz and kaolinite); (b) smithsonite (gangue minerals: goethite, quartz, calcite, and kaolinite); and (c) willemite (gangue minerals: quartz, barite, goethite, and feldspar) [6].

Flotation is the most commonly used method for beneficiation and pretreatment of oxidized zinc minerals, and there have been extensive investigations conducted on the flotation of zinc oxide ores [3,4,7–13].

Selecting a suitable flotation method greatly depends on the accompanying gangues of the main zinc oxide mineral [3]. Some methods employed for the flotation of the oxide minerals of the base metals have been reported. The most important methods which have long been used are as follows:

(i) Sulfidization using sodium sulfide, and flotation with a cationic collector such as amines [1,3–5,11,12,14–18].
(ii) Using fatty acids [1,3,15,16,19,20].
(iii) Sulfidization and activation using a metal ion and flotation with a sulfydryl collector such as xanthate [13,21–25].
(iv) Other sulfydryl collectors such as mercaptans [23,25–27].
(v) Chelating agents [21,28–31].
(vi) Mixed anionic/cationic collectors such as xanthates with amines [1,10,32,33].

Collector steryl amine acetate works well on smithsonite, but it does not show selectivity toward calamine ores (major zinc bearing mineral hemimorphite). When smithsonite is present in the ore, better results are achieved using a tallow amine emulsion with elevated additions of fuel oil emulsion. Xanthates, thiocarbonates, mercaptans, and dithiocarbamates can collect oxidized zinc minerals [6,34,35]. According to Gaudin (1957), the process is not selective enough for practice, when hexyl or amyl xanthate is used in the collection of smithsonite. Two series of chelating reagents have been synthesized to float smithsonite, but it is difficult to use commercially available chelating reagents on plant scale and, more than this, it is the lack of a long-chain hydrocarbon in the molecule which is the major drawback.

Shi and co-workers [20] used anionic collector for flotation of smithsonite. According to their results, smithsonite showed high floatability using sodium oleate as collector between pH 7.0 and 8.0. By increasing pH, smithsonite flotation recovery decreased from 80% to about 30% at pH 9.5 [20]. They concluded that carbonate ions can affect the zeta potential of smithsonite and its floatability was improved with the pH regulator Na_2CO_3. This was due to the increase of surface cation sites and zinc species in the Stern layer. This phenomena improved the adsorption of oleate ions on the interface at $7.0 < pH < 8.7$ [20].

A mixture of amines and xanthates can also be used as a mixed collector for smithsonite flotation [33]. A new line of collectors [36] has been studied. These collectors are based on xanthated fatty acid (collectors from the DS series (xanthate = 60%, fatty acid = 20%, and fuel oil = 20%)) and xanthated mixtures of fatty acid and amine (DAS series (xanthate = 50%, fatty acid = 20%, amine oxide = 20%, and fuel oil = 10%)). These collectors were tested on a number of lead oxide zinc ores from Egypt, South America, and Canada. The best results were obtained using a collector DAS-2, consisting of xanthated fatty acid + amine. The reagent was prepared by ultrasonic agitation of xanthate (50%), fatty acid (25%), and amine (25%).

With more and more attention being given to zinc oxide flotation in order to increase recoveries of Zn, a review of the zinc oxide flotation literature is presented together with some recent findings. This article gives the overall review of zinc oxide (especially smithsonite) beneficiation by different flotation reagents. The objectives of this investigation are to review zinc oxide flotation and to present a quantitative analysis of published data in this area. The feasibility of considering a surface reaction and reagent effects are also considered.

2. Solution chemistry

Some of zinc oxide minerals such as smithsonite are semi-soluble minerals which may have their surface charge developed by non-stoichiometric dissolution that results in the hydrolysis of the ions released to solution [20]. In the semi-soluble mineral flotation, various ions are hydrolyzed and hydrolysis products of the ions are capable of readsorption onto the mineral surface. Mineral surface charge may be determined by interactions between the ions of the crystal structure and the hydrolysis products [20].

In the zinc sulfide mineral flotation using sulphydryl collectors, large number of xanthate species such as xanthate ion ($ROCS_2$), monothiocarbonate ($ROCOS^-$), xanthic acid ($ROCS_2H$), carbon disulfide (CS_2), and dixanthogen ($ROCS_2S_2COR$) are formed in the flotation [37]. In sphalerite flotation by KAX collector, Zn(OH)AX(s) is the predominant species at pH 8–10 and below pH 8 $Zn(AX)_2(s)$ is predominant [38].

Smithsonite ($ZnCO_3$) being a typical oxide mineral of zinc, is a semi-soluble salt mineral with a solubility product constant of 1.46×10^{-10} M, and it is characterized principally by its ionic bonding and moderate solubility in water [39,40].

In the flotation system, water molecules will chemisorpt on the surface of smithsonite when the smithsonite surface activity in water increases. The high activity to water dipoles is one of the main factors for the low natural floatability of smithsonite compared with zinc sulfide minerals. This process will decrease the probability of effective reagents adsorption on smithsonite surface [3,41].

Solution chemistry of the zinc oxide minerals has been studied by several investigators. The smithsonite dissolution and hydrolysis reactions of Zn^{2+} with equilibrium constants are described below [42–44].

$$ZnCO_3 \Leftrightarrow Zn^{2+} + CO_3^{2-} \tag{1}$$

$$Zn^{2+} + OH \Leftrightarrow ZnOH^{+} \tag{2}$$

$$Zn^{2+} + 2OH \Leftrightarrow Zn(OH)_{2(aq)} \tag{3}$$

$$Zn^{2+} + 3OH \Leftrightarrow Zn(OH)_3 \tag{4}$$

$$Zn^{2+} + 4OH \Leftrightarrow Zn(OH)_4^{2-} \tag{5}$$

Smithsonite solubility as a function of pH is shown in Fig. 1. Smithsonite is a thermodynamically stable solid at pH values less than 7.4. Smithsonite will partially hydroxylate to hydrozincite in pH ranges

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