Flotation of smithsonite: A review

Ruofan Sun, Jiushuai Deng

Inner Mongolia Research Institute-CUMTB, Key Laboratory of Separation and Processing of Symbiotic-Associated Mineral Resources in Non-ferrous Metal Industry, Engineering Technology Research Center for Comprehensive Utilization of Rare Earth – Rare Metal – Rare Scattered in Non-ferrous Metal Industry, School of Chemical & Environmental Engineering, China University of Mining & Technology (Beijing), Beijing 100083, China

Corresponding author: dengshuai689@163.com (Jiushuai Deng)

Abstract: Zinc, a high-performance metallic element, is widely used in industries such as transportation, construction, light industry, machinery, and batteries. In recent years, with the continuous development of the world economy and the continuous expansion of zinc application fields, high-grade and easily selected zinc sulfide mineral resouąrces have gradually become depleted. The efficient recovery and utilization of complex and difficult-to-treat zinc oxide resources has gradually attracted attention. Smithsonite, an important zinc oxide mineral resource, has enormous development potential. Scholars have conducted extensive exploration and research from different perspectives to extract high-grade smithsonite and have recognized that flotation is the most important beneficiation method. This paper provides a brief introduction to the interactions between smithsonite and flotation reagents from the perspective of their properties and crystal structures. Based on this, flotation reagents, including collectors, depressants, and auxiliary reagents, are systematically summarized and evaluated. The most challenging flotation case is selected to outline the current status of the smithsonite flotation process. This study aims to provide insights into the development, discovery, and practical application of flotation reagents and processes for smithsonite.

Keywords: smithsonite, flotation, calcite, quartz, surface chemistry

1. Introduction

Zinc, which has the chemical symbol Zn and atomic number 30, is a widely distributed metallic element in nature. Its density is about 7.13 g/cm³, and it is a glossy bluish white metal with a melting point of 419.5 °C and a boiling point of 906 °C. Zn exhibits good ductility, wear and corrosion resistance, castability, and favorable mechanical properties at room temperature. It can be used to fabricate high-performance alloys with various metals. In addition, owing to the easy formation of a protective film on the surface of Zn at room temperature, it is resistant to atmospheric corrosion; therefore, Zn is widely used in the galvanizing industry. Currently, Zn is widely used in industries such as automobiles, construction, household appliances, ships, light industry, machinery, and batteries in the form of zinc plating, zinc-based alloys, and zinc oxide (ZnO) (Thompson, 2006).

Zn is the fourth most widely consumed metal after iron, aluminum, and copper. According to data from the International Lead and Zinc Study Group, global Zn consumption has significantly increased over the past few years. This growth is largely attributed to the growth in demand in the construction industry. Asia, America, and Europe are the main Zn-producing regions, accounting for 54%, 23%, and 17% of global Zn production, respectively (Abkhoshk et al., 2014).

In the past few decades, zinc sulfide (ZnS) ore has been the main source of zinc metal production, with over 85% of the world's Zn originating from ZnS concentrate (Gordon et al., 2003, Balarini et al. 2008; Gilg et al., 2008). Although non-sulfide Zn ores may contain 10%–20% Zn, they have not been extensively mined because of the difficulty in separating them from gangue or the difficulty in enriching them using conventional flotation techniques. In 1996, non-sulfide ores accounted for less than 5% of

global zinc production; however, this proportion is projected to exceed 10% in the near future (Hitzman et al., 2003; Gilg et al. 2008).

ZnO is a potential Zn ore resource, usually occupying a considerable proportion of the weathered surface of lead-zinc deposits. Owing to the low processing efficiency of ZnO ore in the mineral processing industry in the past, a large amount of ZnO ore resources accumulated as solid waste, resulting in the loss of valuable metal, which is not environmentally friendly (Reichert and Borg 2008; Boni et al., 2009; Mondillo et al., 2014). However, with the gradual depletion of easily treatable sulfide ore, the efficient recovery and utilization of ZnO ore has received increasing attention (Shi et al., 2012; Wu et al., 2017; Feng et al., 2023).

ZnO ore has the following characteristics: (1) It consists of various types of ZnO minerals with complex compositions mixed and associated with each other; the embedded particle size is relatively fine, the mud state is severe, and the oxidation rate is high (Jia et al. 2018; Nayak et al., 2021). (2) ZnO minerals have the same carbonate structure as gangue minerals such as calcite and dolomite, and their surface properties are similar (Bulatovic, 2007; Araújo and Lima 2017; Cao et al., 2022). (3) ZnO ore often contains a certain amount of soluble salts, iron oxide, and point soil slime. The dissolution of these soluble gangue minerals contributes to many inevitable ions, reduces the selectivity of flotation reagents, and causes difficulties in mineral enrichment and low recovery rates (Ejtemaei et al., 2012, Shi et al., 2013; Rongdong et al., 2017).

Smithsonite is an important mineral resource with industrial value. In recent years, the efficient development and utilization of smithsonite resources has become one of the hottest topics in the mineral processing industry. This study introduces the physical and chemical properties of smithsonite and systematically summarizes recent developments in flotation reagents and methods for smithsonite. At present, many reagents exhibit good separation ability under laboratory conditions, but there are few examples of industrial applications. Our goal is to track the latest progress in the smithsonite flotation process by summarizing the properties of smithsonite ore and flotation reagents, with the hope of providing guidance for the efficient utilization of smithsonite resources.

2.   Surface properties and crystal structure of smithsonite

2.1. Basic properties of smithsonite

The chemical formula of smithsonite is $ZnCO_3$, with various colors, including white, gray, yellow, blue, green, pink, and brown, as well as white stripes. Smithsonite is located in the oxidation zone of lead-zinc deposits and is formed by the oxidation and decomposition of sphalerite to produce $ZnSO_4$, which is replaced by calcite in the carbonate rock or primary ore. It is a secondary mineral in the oxidation zone that often coexists with minerals such as malachite, azurite, hemimorphite, hydrozincite, galena, and cerusite. Zn in smithsonite is sometimes replaced by iron or manganese, and occasionally by small amounts of magnesium, calcium, cadmium, copper, cobalt, or lead. Similar to most carbonate minerals, smithsonite dissolves in hydrochloric acid to produce bubbles. In the calcite group, smithsonite belongs to a type with higher hardness and higher specific gravity. In nature, Zn-containing minerals are mostly sphalerite, whereas smithsonite is less common.

2.2. Solubility of smithsonite

Smithsonite is a semi soluble mineral with a solubility product constant of 1.46×10^{-10} M, and its solubility increases with increasing pressure and temperature (Farsang et al., 2021). During the flotation process, dissolved mineral species undergo reactions such as hydrolysis, complexation, adsorption, and surface and overall precipitation, which may interfere with the selective interactions between reagents and minerals (Vučinić et al., 2010; Nunes et al., 2011; Sø et al., 2011). The relevant reactions of smithsonite dissolution in aqueous solutions are listed in Table 1 (Charlton and Parkhurst, 2011).

The distribution of smithsonite species based on formulas (1)–(8) and the effect of pH value on the proportion of dissolved sphalerite components in the aqueous solution at 25 °C are shown in Fig. 1. Zn^{2+} is the dominant species in solutions with pH < 8.5, and its content decreases with increasing pH. As the pH value continues to increase, $Zn(OH)_2(aq)$, $Zn(OH)_3^-$, and $Zn(OH)_4^{2-}$ become the dominant species, one after the other.

Table 1. Related reactions and thermodynamic data of dissolution of smithsonite in aqueous solution

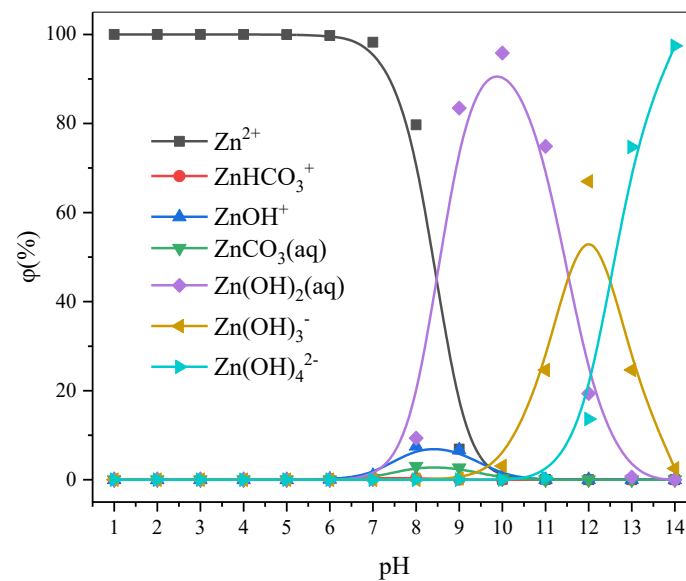| Related chemical reactions	Thermodynamic constant	Title 1	Title 1
(1) $ZnCO_3 \leftrightarrows Zn^{2+} + CO_3^{2-}$	5.30	entry	entry
(2) $CO_3^{2-} + H^+ \leftrightarrows HCO_3^-$	10.33		
(3) $HCO_3^- + H^+ \leftrightarrows H_2CO_3$	6.35		
(4) $Zn^{2+} + OH^- \leftrightarrows ZnOH^+$	5.00		
(5) $Zn^{2+} + 2OH^- \leftrightarrows Zn(OH)_2(aq)$	11.10		
(6) $Zn^{2+} + 3OH^- \leftrightarrows Zn(OH)_3^-$	13.60		
(7) $Zn^{2+} + 4OH^- \leftrightarrows Zn(OH)_4^{2-}$	14.80		
(8) $Zn^{2+} + HCO_3^- \leftrightarrows ZnHCO_3^+$	2.10		

Fig. 1. The effect of pH on the dissolved components of smithsonite in aqueous solution

2.3. Electric characteristics of smithsonite

Owing to the dissolution and lattice displacement of minerals in the slurry, the mineral surface may carry a charge in the slurry. Electrostatic interactions between flotation agents and mineral surfaces play an important role in adsorption; therefore, the charge information on mineral surfaces is crucial (Fuerstenau and Pradip, 2005). The isoelectric point (pHIEP) of pure smithsonite is approximately 7.8, and at pH values below pHIEP, the surface of smithsonite is positively charged (Zhang et al., 2022). In the flotation process, adjusting the pH value of the pulp and adopting the appropriate electric flotation reagent are key to obtaining good flotation indices for smithsonite.

Studies have indicated that during the separation process from carbonate flotation, there may be a surface transformation between smithsonite and calcite owing to the interaction between the dissolved substances and mineral surfaces in the flotation system. Surface transformation from calcite to smithsonite occurs at pH < 8.2, whereas surface transformation from smithsonite to calcite occurs at pH > 9.8(Shi, Zhang et al. 2013). This transformation causes difficulties in the flotation of smithsonite and increases the cost of reagents.

2.4. Crystal structure of smithsonite

Smithsonite is a typical carbonate mineral with a triangular structure of spatial group R-3C. Table 2 lists the Mulliken population of each atom in smithsonite. The number of electrons localized on the Zn atom is 10.75, with a charge of +1.25 e, indicating that it is an electron donor. The number of electrons localized on the C atom is 3.34, with a charge of +0.66 e, indicating that it is an electron donor. The number of electrons localized to the O atom is 6.64, with a charge of -0.64 e, indicating that it is an electron acceptor.

Table 2. Mulliken population of each atom in smithsonite

Atom	Atomic orbital population			Total	Charge/e
	s	P1	d		
Zn	0.25	0.50	10.00	7.16	+1.25
C	0.93	2.41	0.00	3.34	+0.66
O	1.79	4.85	0.00	6.64	−0.64

The Zn and C atoms in smithsonite coordinate with the O atoms to form six coordinated Zn-O bonds and carbonate ions, respectively. Table 3 lists the Mulliken population of the chemical bonds in smithsonite. The Zn-O bond population in smithsonite is 0.32, and the bond length is 2.25 Å. The C-O bond population is 0.91, and the bond length is 1.30 Å. These results indicate that the C-O bond in smithsonite is much more stable than the Zn-O bond. Therefore, bond fracture usually occurs at the Zn-O bond during crushing and grinding. This fracture exposes five coordinated Zn atoms on the surface of smithsonite, allowing it to interact with flotation reagents. In the next section, the interaction modes between various flotation reagents and smithsonite are explored in detail.

Table 3. Mulliken population of various chemical bonds in smithsonite crystals

Chemical bond	Bond population	Bond length, Å
Zn-O	0.32	2.25
C-O	0.91	1.30

3. Flotation reagents for smithsonite

The leaching—solvent extraction—electrodeposition process is the most commonly used method for extracting Zn from low-grade ZnO deposits. However, owing to technical and economic limitations, low-grade and complex ZnO ores cannot be extracted directly using metallurgical methods (Ejtemaei et al., 2014). When acid leaching is used to treat low-grade ZnO ores, the leaching solution contains many impurities. These are difficult to remove, and the silicate polymer formed during the leaching process increases the difficulty of solid-liquid separation. Zn can react with alkalis, and alkaline leaching (e.g., ammonia leaching) can be used to treat low-grade ZnO ores; however, the difficulty of extracting zinc ammonia coordination ions is usually a problem (Feng et al., 2023). Therefore, using flotation to separate the gangue minerals in ZnO ores before leaching is crucial for the economical and efficient recovery of Zn from these deposits.

However, because of the ultrafine distribution and corresponding low selectivity of smithsonite in ZnO ores, as well as the fact that ZnO ores usually contain a wide variety of gangue minerals, current beneficiation processes find it difficult to treat smithsonite efficiently. To address these issues, researchers worldwide have extensively studied on flotation reagents and processes for smithsonite. This section presents a detailed list and evaluation of these developments.

3.1. Collector

3.1.1. Amine collectors

Aliphatic amines can form complexes with metal ions such as copper and Zn, and can serve as collectors for ZnO minerals. The famous sulfidizing-amination flotation method involves the use of sodium sulfide to sulfide ZnO minerals, followed by flotation with amine collectors containing 8–18 carbon atoms, such as dodecylamine(Önal, Bulut et al. 2005, Hosseini and Forssberg 2006, Irannajad, Ejtemaei et al. 2009, Chen, Liu et al. 2018). Under high alkaline conditions (pH > 11.5), HS- is the main component of sodium sulfide in the slurry. HS- first interacts with the surface of smithsonite to form a sulfuration surface facial mask, which improves the hydrophobicity of the smithsonite surface, thus making the adsorption of dodecylamine more stable (Marabini et al., 1984, Chen et al., 2018).

Although amine collectors have good adaptability, their efficiency in industrial flotation processes is relatively low. This is primarily because amines are sensitive to fine ore particles (slime), resulting in

excessive foam, high foam viscosity, and high consumption of collectors during flotation. Desliming before flotation can alleviate the foam problem; however, results in the loss of a large amount of Zn-rich slime in the raw ore (Zhang et al., 2019). Navidi Kashani and Rashchi (2008) used sodium sulfide as the sulfidizing agent and primary amine as the capturing agent to obtain zinc concentrate with a zinc grade of 40.7% and a recovery rate of 70% from the Dandy mineral processing plant in northwestern Iran, without desliming.

3.1.2. Xanthate

Xanthate is one of the most important collectors in the flotation of sulfide and oxide minerals (i.e., copper oxide, lead, and Zn minerals) (Janusz et al., 1983; Herrera-Urbina et al., 1999; Hosseini and Forssberg, 2006). Similar to the sulfidizing-amination method, the sulfidizing-xanthate method uses sodium sulfide to pre-sulfurize smithsonite, making its surface exhibit properties similar to those of natural ZnS, which is then activated with copper sulfate, and xanthate is added for flotation. Unlike sulfide minerals, short-chain xanthate is ineffective in the flotation of oxides, whereas zinc oxides can be made to undergo flotation by long-chain xanthate (pentyl or higher) (Pereira and Peres, 2005). The adsorption mechanism of xanthate on the surface of sulfide minerals involves the formation of chemical bonds between xanthate ions and metal atoms. However, for oxides, it is difficult for metal atoms to form chemical bonds with xanthate ions, because the bond between the metal and oxygen is more ionic than that between the metal and sulfur (Helsop and Jones, 1976). Compared with sulfide minerals, the interaction between xanthate and oxidized minerals relies more on electrostatic mechanisms. As electrostatic adsorption is weaker than chemical adsorption bonds, longer hydrocarbon chains are required to form stable hydrophobic films (Naklicki et al., 2002).

Xanthate offers advantages such as high selectivity, controllability, and adaptability to ultrafine smithsonite particles—properties that amine collectors lack (Wu et al., 2017; Jia et al., 2018, Zhang et al., 2022). However, xanthate has certain unavoidable drawbacks. Owing to the limited quantity and stability of ZnS on the surface of smithsonite, the flotation recovery rate of xanthate after sulfurization is low, usually not exceeding 60% (Navidi Kashani and Rashchi 2008; Feng and Wen 2017; Bai et al., 2018; Jia et al., 2018). Önal et al. (2005) used sodium sulfide as the sulfiding agent, and the mixture of potassium pentyl xanthate (KAX) and Aero 407 (mercaptobenzothiazole) as the collector to carry out flotation recovery of valuable metals in lead-zinc oxide ores in Alada region (Kayseri Türkiye), and obtained a lead concentrate with a lead grade of 65.42% and a recovery rate of 77%. Almost all zinc metals are left in tailings and cannot be recovered by flotation.

In addition, when the ore contains gangue minerals such as iron oxide or quartz, the sulfidizing-xanthate method has trouble effectively separating the smithsonite and gangue minerals. This is because xanthate lacks selectivity in flotation of iron and silicate minerals (Rao and Finch 2003; Hosseini et al., 2006).

3.1.3. Fatty acids

Fatty acids are classified as anionic or carboxylic oxygen–hydroxyl scavengers. Typical collectors include oleic acid, sodium oleate, synthetic fatty acids, high-fat oils, and some oxidized petroleum derivatives (Kulkarni and Somasundaran, 1980). Unlike xanthate, fatty acid collectors can be used for the flotation of various non-sulfide minerals as well as for reverse flotation to remove carbonates, sulfates, and iron gangue. They are also relatively environmentally friendly (Kupka and Rudolph, 2018). Sodium oleate ($C_{18}H_{33}NaO_2$), a common fatty acid, has considerable advantages such as low cost, easy availability, and strong collection ability, and is widely used in the flotation of various oxidized ores (Gao et al., 2021). Research has shown that sodium oleate has an excellent collection ability for fine-grained smithsonite, but its selectivity is poor. It has difficulty in separating smithsonite and gangue minerals effectively when carbonate- or iron-containing minerals are present in the ZnO ore. Therefore, the applications of and research on fatty acid collectors in ZnO flotation are relatively limited (Liu et al., 2019). In the flotation of smithsonite, the carboxyl groups of sodium oleate chemically adsorb onto Zn^{2+} ions on the mineral surface, forming a hydrophobic zinc oleate complex ($Zn(C_{17}H_{33}COO)_2$). This reaction renders the smithsonite surface hydrophobic, thereby facilitating its selective separation through flotation.
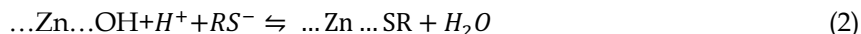
3.1.4. Mercaptans

Mercaptans are a class of non-aromatic compounds containing thiol functional groups (-SH) and are another important thiol scavenger in addition to xanthate and black catching agent. Mercaptan is obtained via a substitution reaction between halogenated alkanes and sodium thiohydride and can be used as a collector for lead oxide, copper, and Zn minerals (Oae 1977; Hosseini et al., 2006).

The hydrolysis reaction of mercaptan in water is shown in formula 1(Dalman and Gorin 1961).

$$RSH + H_2O \leftrightharpoons RS^- + H_3O^+ \tag{1}$$

The hydrolysis product of mercaptan interacts with the -OH group on the surface of smithsonite to form a Zn mercaptan salt and decomposes it into a water molecule. The reaction formula is as follows (Cook and Nixon, 1950):

$$\ldots Zn \ldots OH + H^+ + RS^- \leftrightharpoons \ldots Zn \ldots SR + H_2O \tag{2}$$

Hexadecyl mercaptan ($CH_3[CH_2]_5SH$), with six carbon atoms, has good solubility and can be used as a collector for oxidized minerals such as chalcopyrite, azurite, malachite, smithsonite, and zinc silicate. However, a large amount of hexyl mercaptan is required for flotation of ZnO minerals, which is not economical for large-scale production processes (Hosseini et al., 2006; Ejtemaei et al., 2014).

3.1.5. Chelating agents

Typically, amine and anionic collectors cannot be used simultaneously; however, mixing them can achieve good results in the flotation of ZnO ore. When using a mixture of pentyl xanthate and dodecylamine as collectors, co-adsorption occurs on the surface of smithsonite, which enhances its floatability by enhancing the hydrophobicity of the mineral surface. In the flotation of sphalerite, the optimal amyl xanthate: dodecylamine ratio of the mixed collector is 3:1. The presence of amyl xanthate increases the adsorption capacity of dodecylamine on the mineral surface due to the reduced electrostatic repulsion between the mineral surface and the head-head of the ammonium ions, while the hydrophobic bond between the side tail-tail increases (Hosseini and Forssberg, 2006).

3.2. Depressants

To date, proven effective flotation depressants for smithsonite mainly include inorganic and organic depressants.

3.2.1. Inorganic depressants

3.2.1.1. Water glass

Water glass ($Na_2SiO_3 \cdot xH_2O$) is a series of compounds composed of different proportions of SiO_2 and Na_2O. When the ratio of SiO_2 to Na_2O is greater than 2:1, the water glass forms colloidal silica under high concentration and low pH conditions (Yang, Roonasi et al. 2008). Water glass has a good depression effect on calcite and quartz silicate minerals; however, when gangue minerals are contaminated with Ca^{2+}, Mg^{2+}, or other metal ions, the selectivity of water glass is considerably disturbed (Marinakis and Shergold 1985, Chen and Tang 2020). Additionally, when used as a depressant, waterglass often requires a high dosage, making it difficult to precipitate and filter the concentrate or tailings (Liu, Song et al. 2019).

The results of Yang et al. (2008) indicate that the pH of the solution and the concentration of water glass are key factors determining the type of complex formed on the mineral surface. $Si(OH)_3$ and $Si(OH)_4$ can prevent adsorption of the collector onto the mineral, which may be the main depression mechanism of waterglass (Agar 1984).

3.2.1.2. Acidified water glass

Acidified water glass can be obtained via acid treatment of water glass (Wang, Liu et al. 2021). Compared to regular water glass, acidified water glass exhibits a better selective depression effect on gangue minerals, such as calcite and quartz, which can reduce the amount of reagents used and significantly improve the settling speed of tailings (Feng and Luo 2013, Zhou, Moreno et al. 2013).

The addition of acid promotes the formation of SiO_2 colloids and eliminates Ca^{2+} in the solution through condensation, thereby reducing the adverse effects on flotation (Fuerstenau, Gutierrez et al. 1968, Zhou and Lu 1992). The main problem with acidified water glass is its preparation. Factors such as the type of acid and the ratio of waterglass to acid may affect the selectivity of acidified water glass (Gao, Wang et al. 2021).

3.2.1.3. Sodium hexametaphosphate

The HPO_4^{2-} and $H_2PO_4^-$ anions generated by sodium hexametaphosphate in slurry have strong chelating ability towards metal ions, especially Ca^{2+}(Chen, Ren et al. 2018). When sodium hexametaphosphate is used to depress calcite or dolomite, it can form complexes with Ca2+, increase the hydrophilicity of the gangue mineral surface, prevent the adsorption of collectors on its surface, and thus inhibit the upward movement of calcite or dolomite.

3.2.2. Organic depressants

In recent years, organic depressants have become a research hotspot in the mining industry because of their excellent polymer properties (biodegradability, sustainability, and biocompatibility), high selectivity, and low cost (Lopez Valdivieso et al., 2007 Feng et al. 2018; Zhu et al., 2021). Organic depressants commonly used in the flotation of smithsonite include starch, dextrin, tannins, carboxymethyl cellulose, and calcium lignosulfonate.

3.2.2.1. Starch and dextrin

Starch ($(C_6H_{10}O_5)_n$) is a polymer organic compound with a wide range of sources, low cost, and strong inhibitory effects on barite, mica, sulfides, iron oxide, and calcite (Tian et al. 1997; Ye 1997). Starch may interact with mineral surfaces via hydrogen bonding or electrostatic forces (Afenya, 1982; Qi, 2000; Kaggwa et al., 2005). Our previous research showed that starch may interact strongly with the surface of calcite through O and H atoms in the molecule, forming Ca-O and hydrogen bonds, making the surface of calcite hydrophilic and difficult to recover (Sun et al., 2022).

When starch undergoes decomposition and hydrolysis under the action of heat, acid, or amylase, large molecules of starch are first converted into intermediate substances composed of small molecules, called dextrin (Valdivieso et al., 2004). The structure of dextrin is similar to that of branched starch, but its molecular weight is lower; therefore, dextrin has better solubility than starch (Müller et al., 2001).

3.2.2.2. Tannic acid

Tannic acid is an amorphous polymer that exists in different parts of plants and trees such as seeds, fruits, roots, and bark (Wills and Napiermunn, 1988). Owing to the presence of multiple adjacent hydroxyl groups and its high affinity for some metal ions, tannic acid can be used as a flotation depressant for gangue minerals such as calcite (Nakano et al., 2001, Sengil et al., 2009). Tannic acid mainly interacts with the surface of calcite through chemical adsorption and forms complexes, thereby rendering the mineral surface hydrophilic and exerting depression effects (Kupka and Rudolph, 2017). The molecular structure of tannic acid is shown in Fig. 2.
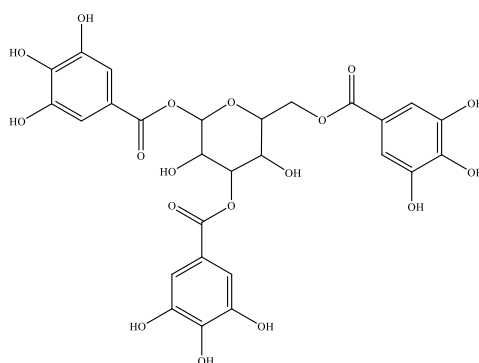

Fig. 2. The molecular structure of tannic acid

3.2.2.3. Carboxymethyl cellulose

Natural cellulose is the most widely distributed and abundant polysaccharide in nature, with a rich source. Current cellulose modification technologies primarily focus on etherification and esterification. Carboxymethylation is a type of etherification technology in which cellulose undergoes carboxymethylation to obtain carboxymethyl cellulose.

Carboxymethyl cellulose is considered an effective inhibitor of silicate and carbonate minerals and can be used to depress gangue minerals such as talc, quartz, and calcite (Jin et al., 2018; Wang et al., 2022). Carboxymethyl cellulose undergoes semi-micelle adsorption on the calcite surface via electrostatic interactions (Qin et al., 2023). Some researchers believe that -COOH in carboxymethyl cellulose may be an active group that depresses gangue minerals (Dong et al. 2019; Xuemin et al., 2020). The molecular structure of carboxymethyl cellulose is shown in Fig. 3 (López-Valdivieso et al., 2017).
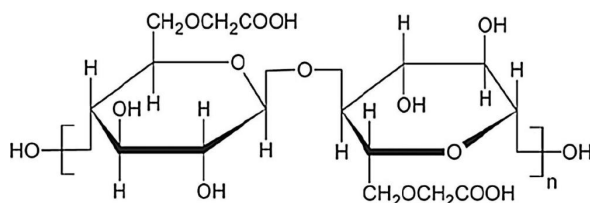

Fig. 3. The molecular structure of carboxymethyl cellulose

3.2.2.4. Calcium lignosulfonate

Calcium lignosulfonate is a multicomponent macromolecular polymer anionic surfactant with an aromatic odor, a molecular weight generally between 800 and 10000, and strong dispersibility, cohesiveness, and chelation. It is usually made from the cooking waste liquor of sulfite pulping and dried by spraying (Aro and Fatehi, 2017). Calcium lignosulfonate can be used as a depressant for minerals such as chalcopyrite, quartz, and calcite (Liu et al., 2009; Liu et al. 2019; Sun et al., 2021). Research has shown that calcium lignosulfonate mainly interacts with cations on mineral surfaces through the sulfonic acid groups in the molecule, forming stable complexes (Sun et al., 2021). The molecular structure of calcium lignosulfonate is shown in Fig. 4.
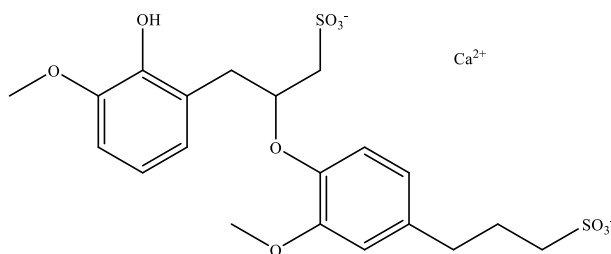

Fig. 3. Molecular structure of calcium lignosulfonate

### 3.2.2.5. Other organic depressants

With the continuous progress in research, more environmentally friendly organic depressants are being developed and applied to the flotation of smithsonite and gangue minerals. Organic reagents used as calcite depressants include Sesbania Gum, Fenugreek gum, flaxseed gum, guar gum, and phytic acid (Luo et al. 2019; Zhou et al., 2021; Chen et al., 2022; Xie et al., 2022; Chen et al., 2023). Organic reagents used as quartz depressants include sodium polyaspartic acid and tetrasodium iminosuccinate (Wang et al., 2022, Zhao et al., 2022). These organic depressants have achieved good experimental results in the laboratory but have not yet been applied in large-scale industrial production.

3.3.   Auxiliary reagents

3.3.1. Sodium sulfide

Sodium sulfide (Na_2S) is one of the most commonly used sulfurizing agents in metal ore flotation processes and is also the most satisfactory sulfurizing agent for smithsonite flotation because it can

significantly increase the pH value of the slurry and is more economical than sodium sulfide hydride (NaHS) (Rausch and Mariacher, 1970; Fuerstenau et al., 1985). Adding an appropriate amount of sodium sulfide during the flotation process to maintain the pH value of the slurry within the range of 10.5–12 is beneficial for the flotation of smithsonite (Marabini et al., 1984; Al, 2005). The chemical formula for the sulfidation of smithsonite is as follows (Wu et al., 2015):

$$ZnCO_3(s) + HS^- \leftrightharpoons ZnS(s) + HCO_3^- \tag{3}$$

$$Zn(OH)_2(s) + HS^- \leftrightharpoons ZnS(s) + H_2O + OH^- \tag{4}$$
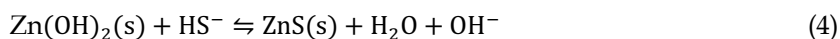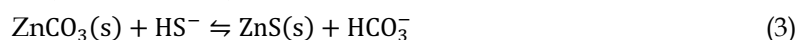
3.3.2. Metal ions

When collectors or depressants exhibit poor selective adsorption on target and gangue minerals, making it difficult to achieve effective flotation, metal ions such as Pb^{2+}, Fe^{2+}, Zn^{2+}, Al^{3+}, and Cu^{2+} are often used as auxiliary reagents to enhance the selectivity of collectors or depressants (Sun et al., 2022; Jin et al., 2023; Zhang et al., 2023). Generally, metal ions mainly affect the effectiveness of flotation reagents in two ways: First, selective pre-adsorption on the mineral surface changes the surface composition of the mineral, providing new active sites for the subsequent adsorption of flotation reagents; second, metal ions react with flotation agents to form a metal ion flotation agent complex, which changes the adsorption mechanism of the collector or depressant on the mineral surface, thereby affecting its selectivity. Research has shown that the addition of Pb^{2+} during smithsonite recovery using the sulfidizing-xanthate method can effectively improve the flotation recovery rate of smithsonite (Zhang et al., 2021; Wang et al., 2023). Pb^{2+} is adsorbed onto the surface of smithsonite through an ion-exchange reaction to form lead sulfide species, increasing the content of sulfide species on the surface of smithsonite and providing new active sites for the adsorption of xanthate on the mineral surface, thereby improving the hydrophobicity of the smithsonite surface. Zhao et al. (2022) found that Cu^{2+} has an activation effect similar to that of Pb^{2+} and that the addition of Cu^{2+} is beneficial for the adsorption of sulfide species on the surface of smithsonite and for improving its floatability.

Xie et al. (2022) used Al^{3+} and guar gum as a mixed depressant to separate smithsonite and calcite in a sodium oleate flotation system. The results indicated that Al^{3+} can enhance the effect of guar gum, increasing the Zn grade in artificially mixed ore concentrates by approximately 10%. This is because the hydrolysis products of Al^{3+}, $Al(OH)_3$ and Al_2O_3, can selectively adsorb on the surface of calcite, reducing the hydrophobicity of the calcite surface and covering the adsorption sites of the sodium oleate collector, thus achieving effective separation of smithsonite and calcite.

3.3.3 Ammonium salt

During the sulfidation process of smithsonite flotation, the difficulty of fully sulfiding the mineral surface leads to low recovery efficiency, which is one of the main problems of the sulfidizing-amination and sulfidizing-xanthate methods. One possible solution for promoting sufficient sulfurization of the smithsonite surface is to increase the sulfurization efficiency by adding surface modifiers. Ammonium ions are among the best candidates this because they have a wide range of sources and relatively low prices (Bai et al., 2020). Ammonium salts are strong electrolytes that dissociate in water. The dissolved ammonium ions interact with smithsonite to form $[Zn(NH_3)_i]^{2+}$ (i = 1, 2, 3, 4) (Bingöl et al., 2005; Ju et al., 2005). These zinc ammonium complex ions are more likely to interact with HS -, resulting in the conversion of more surface smithsonite into ZnS (Bai et al., 2018; Bai et al., 2020). Bai et al. (2018) showed that the use of ammonium chloride to promote sulfidation and xanthate flotation of smithsonite could increase the recovery rate by approximately 17%.

4. Case studies on flotation of smithsonite and gangue minerals

During the flotation recovery of smithsonite, the type of associated gangue minerals often determines the flotation method. Therefore, selecting appropriate flotation reagents for different types of gangue minerals is key to obtaining good flotation indicators. The main gangue minerals in smithsonite deposits include calcite, quartz, limonite, hematite, and dolomite. The presence of calcite, quartz and dolomitemakes efficient recovery of smithsonite particularly difficult.

4.1. Flotation of smithsonite and calcite

The flotation of smithsonite and calcite has always been one of the important challenges faced by the mineral processing industry, mainly because they have similar surface properties, including floatability, solubility, and Zeta potential, which leads to difficulties in flotation of smithsonite and calcite. In addition, Ca^{2+} dissolved on the surface of the calcite solution in the slurry preferentially adsorbs onto the surface of smithsonite, hindering the adsorption of collectors on its surface and worsening the flotation recovery of smithsonite, which further increases the difficulty of separating the two minerals (Chen et al., 2019). Currently, the sulfidizing-xanthate method is the main method for the flotation recovery of ZnO minerals. However, the main problem with this method is the low sulfurization efficiency of smithsonite, which leads to unsatisfactory recovery rates (Feng and Wen, 2017; Feng et al., 2023). To address this issue, researchers have used metal ions such as Cu^{2+} and Pb^{2+} to enhance the vulcanization efficiency of the vulcanizing agent (Zhang et al., 2021; Wang et al., 2023). In addition, studies have shown that increasing the slurry temperature to 30–40 ℃ during flotation is beneficial for the sulfurization flotation of smithsonite, as the sulfurization process on the surface of smithsonite is an endothermic reaction (Ejtemaei et al., 2011).

Sodium oleate has excellent collection ability for fine-grained smithsonite, but its selectivity is poor, especially in the presence of calcite in ZnO ore. It is difficult to effectively separate smithsonite from gangue minerals (Liu et al., 2019). With the continuous deepening of research, various highly selective macromolecular organic compounds have been developed as calcite depressants in sodium oleate flotation systems, such as guar gum, phytic acid, flaxseed gum, gourd gum, and polyepoxysuccinic acid (Luo et al., 2019; Liu et al., 2021; Zhou et al., 2021; Chen et al., 2022; Yang et al., 2022). These organic compounds have achieved good sorting results in the laboratory but have not yet been widely applied in large-scale industrial production.

4.2. Flotation of smithsonite and quartz

Quartz is one of the main vein minerals in natural diamond Zn deposits and has good hydrophobicity. Unlike with calcite, fatty acid anionic collectors such as sodium oleate are not easily adsorbed onto the surface of quartz because quartz exhibits a negative charge over a wide pH range and lacks active sites (Ejtemaeia et al., 2012). Therefore, sodium oleate is a suitable collector for the flotation of smithsonite and quartz.

The main difficulty in separating smithsonite from quartz is that quartz is easily activated by high-valence metal ions such as Pb^{2+}, Cu^{2+}, and Zn^{2+}(Deng, Hu et al. 2018). During the grinding or flotation process, a large amount of Zn^{2+} is released from the surface of smithsonite, causing quartz to be activated and float upward into the concentrate, hindering the separation of the two minerals. Common quartz depressants such as water glass have trouble being effective on Zn^{2+} activated quartz. Therefore, when using sodium oleate as a collector, more selective inhibitors should be used to recover smithsonite (Ejtemaei et al., 2012). Starch and calcium lignosulfonate have been proven to be effective reagents for passivating quartz and achieving the effective recovery of smithsonite (Liu et al., 2019; Wang et al., 2020).

4.3. Flotation of smithsonite and dolomite

Similar to calcite, dolomite and smithsonite are both carbonate minerals with similar physical and chemical properties. The adsorption principle of reagents on mineral surfaces is similar, which leads to the difficulty in separating smithsonite and dolomite in the practical process of flotation of zinc oxide ore using sulfidizing-xanthate or sulfidizing-amination methods. The phenomenon of low grade and recovery rate of zinc oxide concentrate is commonly observed.

Therefore, seeking effective selective depressants is a key means to improve the flotation efficiency of smithsonite and dolomite. At present, depressants such as sodium hexametaphosphate, sodium polyaspartic acid, and phosphoryl carboxyl copolymer have shown efficacy in separating smithsonite and dolomite (Wang et al., 2022; Zhao et al., 2022; Guan et al., 2024). However, research in this field is still limited and further screening of potential flotation agents is needed to expand them to industrial production.

4.4. Types and dosage recommendations of flotation reagents

Table 4 summarizes the recommended reagent combinations and mechanisms for different gangue mineral flotation systems:

Table 4. Recommended reagent combinations and dosage ranges for smithsonite and different gangue minerals in flotation

Gangue Mineral	Collector (Type and Dosage)	Depressant (Type and Dosage)	Auxiliary Reagent (Type and Dosage)	Key Mechanism of Action
Calcite	KAX (200-400 mg/L) DDA (50-150 mg/L) Sodium Oleate (60-100 mg/L)	Guar Gum (15-20 mg/L) Phytic Acid (50-70 mg/L) Polyepoxysuccinic Acid (20-30 mg/L)	Pb^{2+} (50-100 mg/L) Na_2S (800-1200 mg/L)	Pb^{2+} enhances sulfide surface active sites; guar gum selectively covers calcite surface via Ca-O bonds.
Quartz	Sodium Oleate (60-100 mg/L)	Calcium Lignosulfonate (40-80 mg/L) Starch (200-400 mg/L)	/	Calcium lignosulfonate complexes metal ions on quartz surface via sulfonate groups.
Dolomite	Mixed Amines (DDA+KAX, 150-300 mg/L) Sodium Oleate (60-100 mg/L)	Phosphorylated Carboxylic Copolymer (5-10 mg/L) Sodium Hexametaphosphate (60-100 mg/L)	Na_2S (1000-1500 mg/L)	Phosphorylated copolymer competitively adsorbs on dolomite surface via carboxylic groups.

4.5. Examples of flotation results

Table 5 presents a summary of flotation data from key research cases in the paper, covering different gangue combinations and reagent systems.

4.6. Process optimization recommendations

4.6.1 Dosage Optimization

(1) Sodium sulfide (Na_2S) dosage should be adjusted based on the oxidation rate of the ore. For highly oxidized ores (ZnO > 50%), the upper dosage limit (1200-1500 g/t) is recommended.
(2) Excessive concentrations of metal ions (e.g., Pb^{2+}, Cu^{2+}) may lead to over-activation of gangue minerals. Optimization is recommended through Zeta potential monitoring.

4.6.2 Process Synergy

(1) Temperature Effect: Heating the slurry to 35–40°C can enhance the sulfide reaction rate, increasing recovery by 10–15%.
(2) Integrated Process: For ultra-fine ores (-20 μm > 30%), a combined "flotation-magnetic separation-leaching" process can achieve a total recovery of up to 90%.

4.6.3 Environmental and Economic Considerations

(1) Natural organic depressants (e.g., guar gum, tannic acid) are 15-20% cheaper than inorganic reagents and are biodegradable.
(2) Partial substitution of sodium sulfide with ammonium chloride (NH_4Cl) can reduce reagent costs by 10-15%.

Table 5. Summary of flotation data for smithsonite with different gangue minerals

Ore Type	Reagent Combination	Zinc Grade (%)	Recovery (%)	Reference
Smithsonite-Calcite	Sodium Oleate + Phytic Acid	45.23	85.67	Chen et al. (2022)
	Sodium Oleate + Guar Gum + Al^{3+}	36.72	87.63	Xie et al. (2022)
Smithsonite-Quartz	Sodium Oleate + Calcium Lignosulfonate	46.62	85.82	Liu et al. (2019)
	Sodium Oleate + sodium polyaspartate	47.08	85.26	Zhao et al. (2022)
Smithsonite-Dolomite	Sodium Oleate + Phosphorylated Carboxylic Copolymer	36.36	88.36	Guan et al. (2024)
	Benzohydroxamic Acid/Sodium Oleate Mixed Collector + Sodium Hexametaphosphate	>38	>85	Wang et al. (2022)

5. Conclusions

Smithsonite is an important ZnO mineral resource with industrial value, and its efficient development and utilization are receiving increasing attention. However, owing to the low selectivity, fine particle-size distribution, and complex mineral properties of smithsonite, efficient treatment is difficult using the current beneficiation process. To solve these problems, researchers worldwide have made considerable efforts, mainly by improving the floatability of smithsonite and developing highly selective flotation depressants.

The sulfidizing-xanthate method, which has high selectivity for ZnO minerals, is currently the most commonly used flotation method for smithsonite. The main drawback of this method is its unsatisfactory flotation recovery rate. To address this issue, researchers have improved the floatability of smithsonite by adding metal ions such as Pb^{2+} and Cu^{2+} to enhance the sulfurization effect or increase the flotation temperature. However, when gangue minerals such as iron oxide or quartz are present in the ore, it is difficult to separate smithsonite from the gangue minerals effectively.

Fatty acids are relatively environmentally friendly collectors with excellent collection ability for oxidized minerals such as smithsonite, but their selectivity is poor. This problem can be alleviated by developing new highly selective inhibitors combined with fatty acids. Among them, green and natural organic depressants have shown the greatest potential for development.

Notably, there are various types and properties of organic depressants, and their interaction mechanisms with mineral surfaces are more complex than those of inorganic reagents. Therefore, it is necessary to conduct in-depth research on the differences in surface properties between smithsonite and gangue minerals, starting from the surface properties, crystal structure, and coordination effects of the minerals. Studying the mechanisms and physicochemical properties of organic depressants containing different chemical groups forming ligands on mineral surfaces to screen for organic depressants with high flotation performance, further improve their theory, and enhance their applicability will become one of the main objectives of flotation research on smithsonite.

the Hohhot-Baotou-Ordos National Independent Innovation Demonstration Zone and Major Project of Ordos Iconic Innovation Team (2023XM06/202204).

References

ABKHOSHK, E., E. JORJANI, M. S. AL-HARAHSHEH, F. RASHCHI, M. NAAZERI, 2014. *Review of the hydrometallurgical processing of non-sulfide zinc ores*. Hydrometallurgy 149: 153-167.

AFENYA, P. M., 1982. *Adsorption of xanthate and starch on synthetic graphite*. International Journal of Mineral Processing 9(4): 303-319.

AGAR, G. E., 1984. *Scheelite flotation process*. US.

AL, F., 2005. *Sulphidization flotation for recovery of lead and zinc from oxide-sulfide ores*. Trans. Nonferrous Met. Soc. China 005: 015.

ARAÚJO, A. C. A., R. M. F. LIMA, 2017. *Influence of cations Ca^{2+}, Mg^{2+} and Zn^{2+} on the flotation and surface charge of smithsonite and dolomite with sodium oleate and sodium silicate*. International Journal of Mineral Processing 167: 35-41.

ARO, T., P. FATEHI, 2017. *Production and Application of Lignosulfonates and Sulfonated Lignin*. ChemSusChem 10(9): 1861-1877.

BAI, S., C. LI, X. FU, Z. DING, S. WEN, 2018. *Promoting sulfidation of smithsonite by zinc sulfide species increase with addition of ammonium chloride and its effect on flotation performance*. Minerals Engineering 125: 190-199.

BAI, S., P. YU, Z. DING, C. LI, Y. XIAN, S. WEN, 2020. *Ammonium chloride catalyze sulfidation mechanism of smithsonite surface: Visual MINTEQ models, ToF-SIMS and DFT studies*. Minerals Engineering 146: 106115.

BALARINI, J. C., L. D. O. POLLI, T. L. S. MIRANDA, R. M. Z. D. CASTRO, A. SALUM, 2008. *Importance of roasted sulphide concentrates characterization in the hydrometallurgical extraction of zinc.* Minerals Engineering 21(1): 100-110.

BINGÖL, D., M. CANBAZOĞLU, S. AYDOĞAN, 2005. *Dissolution kinetics of malachite in ammonia/ammonium carbonate leaching.* Hydrometallurgy 76(1): 55-62.

BONI, M., P. R. SCHMIDT, J. R. DE WET, J. D. SINGLETON, G. BALASSONE, N. MONDILLO, 2009. Mineralogical signature of nonsulfide zinc ores at Accha, Peru: A key for recovery. International Journal of Mineral Processing 93(3): 267-277.

BULATOVIC, S. M., 2007. *Handbook of Flotation Reagents*, Handbook of Flotation Reagents.

CAO, Q., H. ZOU, D. LIU, S. WEN, X. CHEN, 2022. *Flotation separation of smithsonite from calcite using an amino-acid collector*. Separation and Purification Technology 281: 119980.

CHARLTON, S. R., D. L. PARKHURST, 2011. *Modules based on the geochemical model PHREEQC for use in scripting and programming languages.* Computers & Geosciences 37(10): 1653-1663.

CHEN, Y., X. GUO, Y. CHEN, 2022. *Using phytic acid as a depressant for the selective flotation separation of smithsonite from calcite.* Separation and Purification Technology 302: 122104.

CHEN, Y., X. GUO, Y. CHEN, 2023. *Adsorption study of sesbania gum onto calcite surface: Implications for smithsonite-calcite flotation separation*. Colloids and Surfaces A: Physicochemical and Engineering Aspects 676: 132174.

CHEN, Y., M. LIU, J. CHEN, Y. LI, C. ZHAO, X. MU, 2018. *A density functional based tight binding, DFTB+ study on the sulfidization-amine flotation mechanism of smithsonite*. Applied Surface Science 458: 454-463.

CHEN, Y. AND X. TANG, 2020. *Selective flotation separation of smithsonite from calcite by application of amino trimethylene phosphonic acid as depressant*. Applied Surface Science 512: 145663.

CHEN, Y., G. ZHANG, M. WANG, Q. SHI, D. LIU, Q. LI, 2019. *Utilization of sodium carbonate to eliminate the adverse effect of Ca2+ on smithsonite sulphidisation flotation*. Minerals Engineering 132: 121-125.

CHEN, Z., Z. REN, H. GAO, R. ZHENG, Y. JIN, C. NIU, 2018. *Flotation studies of fluorite and barite with sodium petroleum sulfonate and sodium hexametaphosphate.* Journal of Materials Research and Technology.

COOK, M. A., J. C. NIXON, 1950. *The Theory of Water-Repellent Films on Solids Formed by Adsorption from Aqueous Solutions of Heteropolar Compounds*. The Journal of Physical and Colloid Chemistry 54(4): 445-459.

DALMAN, G., G. GORIN, 1961. *Ionization Constant of Hexanethiol from Solubility Measurements*. The Journal of Organic Chemistry 26(11): 4682-4684.

DENG, R., Y. HU, J. KU, Y. MA, Z. YANG, 2018. *Ion migration law in flotation pulp and its influence on the separation of smithsonite and quartz.* Separation Science and Technology 53(5): 833-841.

DONG, L., F. JIAO, W. QIN, H. ZHU, W. JIA, 2019. *New insights into the carboxymethyl cellulose adsorption on scheelite and calcite: adsorption mechanism, AFM imaging and adsorption model*. Applied Surface Science 463: 105-114.

EJTEMAEI, M., M. GHARABAGHI, M. IRANNAJAD, 2014. *A review of zinc oxide mineral beneficiation using flotation method.* Advances in Colloid and Interface Science 206: 68-78.

EJTEMAEI, M., M. IRANNAJAD, M. GHARABAGHI, 2011. *Influence of important factors on flotation of zinc oxide mineral using cationic, anionic and mixed, cationic/anionic collectors.* Minerals Engineering 24(13): 1402-1408.

EJTEMAEI, M., M. IRANNAJAD, M. GHARABAGHI, 2012. *Role of dissolved mineral species in selective flotation of smithsonite from quartz using oleate as collector.* International Journal of Mineral Processing 114-117: 40-47.

EJTEMAEIA, M., M. IRANNAJADA, M. GHARABAGHI, 2012. *Role of dissolved mineral species in selective flotation of smithsonite from quartz using oleate as collector.* International Journal of Mineral Processing 114-117(8): 40-47.

FARSANG, S., M. LOUVEL, A. D. ROSA, M. AMBOAGE, S. ANZELLINI, R. N. WIDMER, S. A. T. REDFERN, 2021. *Effect of salinity, pressure and temperature on the solubility of smithsonite, ZnCO3 and Zn complexation in crustal and upper mantle hydrothermal fluids.* Chemical Geology 578: 120320.

FENG, B., X.-P. LUO, 2013. *The solution chemistry of carbonate and implications for pyrite flotation.* Minerals Engineering 53: 181-183.

FENG, B., J. PENG, W. ZHANG, X. NING, Y. GUO, W. ZHANG, 2018. *Use of locust bean gum in flotation separation of chalcopyrite and talc.* Minerals Engineering 122: 79-83.

FENG, Q., M. WANG, G. ZHANG, W. ZHAO, G. HAN, 2023. *Enhanced adsorption of sulfide and xanthate on smithsonite surfaces by lead activation and implications for flotation intensification.* Separation and Purification Technology 307: 122772.

FENG, Q., S. WEN, 2017. *Formation of zinc sulfide species on smithsonite surfaces and its response to flotation performance.* Journal of Alloys and Compounds 709: 602-608.

FUERSTENAU, D. W., PRADIP, 2005. *Zeta potentials in the flotation of oxide and silicate minerals.* Advances in Colloid and Interface Science 114-115: 9-26.

FUERSTENAU, M., G. GUTIERREZ, D. ELGILLANI, 1968. *The influence of sodium silicate in nonmetallic flotation systems.*

FUERSTENAU, M. C., J. D. MILLER, M. C. KUHN, 1985. *Chemistry of flotation.* American Institute of Mining, Metallurgical, and Petroleum Engineers.

G. RINELLI, A. M. M. 1973. *Flotation of zinc and lead oxide–sulphide ores with chelating agents.* X International Mineral Processing Congress. London, 493-521.

GAO, Z., C. WANG, W. SUN, Y. GAO, P. B. KOWALCZUK, 2021. *Froth flotation of fluorite: A review.* Advances in Colloid and Interface Science 290: 102382.

GILG, H. A., M. BONI, N. J. COOK, 2008. *A Special Issue devoted to Nonsulfide Zn–Pb Deposits.* Ore Geology Reviews 33(2): 115-116.

GORDON, R. B., T. E. GRAEDEL, M. BERTRAM, K. FUSE, R. LIFSET, H. RECHBERGER, S. SPATARI, 2003. *The characterization of technological zinc cycles.* Resources, Conservation and Recycling 39(2): 107-135.

GUAN, Z., R. LIAO, Y. ZHANG, Q. FENG, S. WEN, 2024. *Experimental and simulation study on the flotation separation of smithsonite from dolomite using phosphoryl carboxyl copolymer as a novel depressant.* Separation and Purification Technology 346: 127488.

HELSOP, R.B., JONES, K., 1976. *Inorganic chemistry: A Guide to Advanced Study*, Elsevier Publishing Company.

HERRERA-URBINA, R., F. J. SOTILLO, D. W. FUERSTENAU, 1999. *Effect of sodium sulfide additions on the pulp potential and amyl xanthate flotation of cerussite and galena.* International Journal of Mineral Processing 55(3): 157-170.

HITZMAN, M. W., N. A. REYNOLDS, D. F. SANGSTER, C. R. ALLEN, C. E. CARMAN, 2003. *Classification, Genesis, and Exploration Guides for Nonsulfide Zinc Deposits.* Economic Geology 98(4): 685-714.

HOSSEINI, S., H., FORSSBERG, E., 2006. *Smithsonite flotation using potassium amyl xanthate and hexylmercaptan.* Mineral Processing & Extractive Metallurgy, 115(2), 107-112.

HOSSEINI, S. H., E. FORSSBERG, 2006. *Adsorption studies of smithsonite flotation using dodecylamine and oleic acid.* Minerals & Metallurgical Processing, 23(2), 87-96.

IRANNAJAD, M., M. EJTEMAEI, M. GHARABAGHI, 2009. *The effect of reagents on selective flotation of smithsonite–calcite–quartz.* Minerals Engineering 22(9): 766-771.

JANUSZ, W., M. SZYMULA, J. SZCZYPA, 1983. *Flotation of synthetic zinc carbonate using potassium ethylxanthate.* International Journal of Mineral Processing 11(2): 79-88.

JIA, K., Q. FENG, G. ZHANG, W. JI, W. ZHANG, B. YANG, 2018. *The role of S(II) and Pb(II) in xanthate flotation of smithsonite: Surface properties and mechanism.* Applied Surface Science 442: 92-100.

JIN, D., R. SUN, G. WANG, J. DENG, X. ZHANG, 2023. *Flotation separation of fluorite and calcite using anhydrous glucose and aluminum sulfate as a combined depressant.* Applied Surface Science 624: 157089.

JIN, S., Q. SHI, Q. LI, L. OU, K. OUYANG, 2018. *Effect of calcium ionic concentrations on the adsorption of carboxymethyl cellulose onto talc surface: Flotation, adsorption and AFM imaging study.* Powder Technology 331: 155-161.

JU, S., T. MOTANG, Y. SHENGHAI, L. YINGNIAN, 2005. *Dissolution kinetics of smithsonite ore in ammonium chloride solution.* Hydrometallurgy 80(1: 67-74.

KAGGWA, G. B., S. FROEBE, L. HUYNH, J. RALSTON, K. BREMMELL, 2005. *Morphology of adsorbed polymers and solid surface wettability.* Langmuir the Acs Journal of Surfaces & Colloids 21(10): 4695-4704.

KULKARNI, R. D., P. SOMASUNDARAN, 1980. *Flotation chemistry of hematite/oleate system.* Colloids & Surfaces 1(3-4): 387-405.

KUPKA, N., M. RUDOLPH, 2018. *Froth flotation of scheelite – A review.* International Journal of Mining Science and Technology 28(3): 373-384.

LIU, C., S. SONG, H. LI, Y. LI, G. AI, 2019. *Elimination of the adverse effect of calcite slimes on the sulfidization flotation of malachite in the presence of water glass.* Colloids and Surfaces A: Physicochemical and Engineering Aspects 563: 324-329.

LIU, C., X. WANG, S. YANG, Z. REN, C. LI, Z. HU, 2021. *Utilization of polyepoxysuccinic acid as a green depressant for the flotation separation of smithsonite from calcite.* Minerals Engineering 168: 106933.

LIU, C., G. ZHU, S. SONG, H. LI, 2019. *Flotation separation of smithsonite from quartz using calcium lignosulphonate as a depressant and sodium oleate as a collector.* Minerals Engineering 131: 385-391.

LIU, R.-Q., W. SUN, Y.-H. HU, D.-Z. WANG, 2009. *Effect of organic depressant lignosulfonate calcium on separation of chalcopyrite from pyrite.* Journal of Central South University of Technology 16(5): 753-757.

LÓPEZ-VALDIVIESO, A., L. A. LOZANO-LEDESMA, A. ROBLEDO-CABRERA, O. A. OROZCO-NAVARRO, 2017. *Carboxymethylcellulose, CMC as PbS depressant in the processing of Pb-Cu bulk concentrates. Adsorption and floatability studies.* Minerals Engineering 112: 77-83.

LOPEZ VALDIVIESO, A., A. A. SÁNCHEZ LÓPEZ, S. SONG, H. A. GARCÍA MARTÍNEZ, S. LICÓN ALMADA, 2007. *Dextrin as a Regulator for the Selective Flotation of Chalcopyrite, Galena and Pyrite.* Canadian Metallurgical Quarterly 46(3): 301-309.

LUO, Y., G. ZHANG, C. LI, Q. MAI, H. LIU, H. ZHOU, Q. SHI, 2019. *Flotation separation of smithsonite from calcite using a new depressant fenugreek gum.* Colloids and Surfaces A: Physicochemical and Engineering Aspects 582: 123794.

NAKLICKI, M.L., RAO, S.R., GOMEZ, J.A, 2002. *Flotation and surface analysis of the nickel, II oxide/amyl xanthate system.* International Journal of Mineral Processing, 65(2), 73-82.

MARABINI, A. M., V. ALESSE, F. GARBASSI, 1984. *Role of sodium sulphide, xanthate and amine in flotation of lead- zinc oxidized ores.*

MARINAKIS, K. I., H. L. SHERGOLD, 1985. *Influence of sodium silicate addition on the adsorption of oleic acid by fluorite, calcite and barite.* International Journal of Mineral Processing 14(3): 177-193.

MONDILLO, N., M. BONI, G. BALASSONE, M. JOACHIMSKI, A. MORMONE, 2014. *The Jabali nonsulfide Zn–Pb–Ag deposit, western Yemen.* Ore Geology Reviews 61: 248-267.

MÜLLER, P., E. WEBER, C. HELBIG, H. BALDAUF, 2001. *Tethering of long-chain amino acids to a rigid aromatic core - A new type of preorganized surfactants acting as flotative agents.* Journal of Surfactants and Detergents 4(4: 407-414.

NAKANO, Y., K. TAKESHITA, T. TSUTSUMI, 2001. *Adsorption mechanism of hexavalent chromium by redox within condensed-tannin gel.* Water Research 35(2): 496-500.

NAVIDI KASHANI, A. H., F. RASHCHI, 2008. *Separation of oxidized zinc minerals from tailings: Influence of flotation reagents.* Minerals Engineering 21(12): 967-972.

NAYAK, A., M. S. JENA, N. R. MANDRE, 2021. *Beneficiation of Lead-Zinc Ores – A Review.* Mineral Processing and Extractive Metallurgy Review: 1-20.

NUNES, A. P. L., A. E. C. PERES, A. C. DE ARAUJO, G. E. S. VALADÃO, 2011. *Electrokinetic properties of wavellite and its floatability with cationic and anionic collectors.* Journal of Colloid and Interface Science 361(2): 632-638.

OAE, S., 1977. *Organic chemistry of sulfur.* Chemistry International Newsmagazine for Iupac 37(5-6): 47-48.

ÖNAL, G., G. BULUT, A. GÜL, O. KANGAL, K. T. PEREK, F. ARSLAN, 2005. *Flotation of Aladag oxide lead–zinc ores.* Minerals Engineering 18(2): 279-282.

PEREIRA, C. A., A. PERES, 2005. *Reagents in calamine zinc ores flotation.* Minerals Engineering 18(2: 275-277.

QI, L., 2000. *The adsorption of polysaccharides onto mineral surfaces: an acid/base interaction*. International Journal of Mineral Processing. 60(3), 229-245.

QIN, W., J. HU, H. ZHU, F. JIAO, W. JIA, J. HAN, C. CHEN, 2023. *Effect of depressants on flotation separation of magnesite from dolomite and calcite*. International Journal of Mining Science and Technology 33(1): 83-91.

RAO, S. R., J. A. FINCH, 2003. *Base metal oxide flotation using long chain xanthates*. 69(1-4): 251-258.

RAUSCH, R. D., B. C. MARIACHER, 1970. *Mining and concentrating of lead and Zinc*.

REICHERT, J., G. BORG, 2008. N*umerical simulation and a geochemical model of supergene carbonate-hosted non-sulphide zinc deposits*. Ore Geology Reviews 33(2): 134-151.

DENG, R., HU, Y., KU, J., , MA, Y., YANG, Z., 2018. *Ion migration law in flotation pulp and its influence on the separation of smithsonite and quartz*. Separation Science & Technology. 53(5), 833-841.

HOSSEINI, F., 2006. *Flotation behaviour of oxide zinc ore from Angooran deposit, Iran in the presence of cationic/anionic and mixed, cationic/anionic collectors*. Eur. J. Miner. Process. Environ. Protect. 6.

SENGIL, I. A., M. OEZACAR, H. TUERKMENLER, 2009. *Kinetic and isotherm studies of Cu(II) biosorption onto valonia tannin resin*. Journal of Hazardous Materials 162(2-3): 1046-1052.

SHI, Q., Q. FENG, G. ZHANG, H. DENG, 2012. *Electrokinetic properties of smithsonite and its floatability with anionic collector*. Colloids and Surfaces A: Physicochemical and Engineering Aspects 410: 178-183.

SHI, Q., G. ZHANG, Q. FENG, H. DENG, 2013. *Effect of solution chemistry on the flotation system of smithsonite and calcite*. International Journal of Mineral Processing 119: 34-39.

SØ, H. U., D. POSTMA, R. JAKOBSEN, F. LARSEN, 2011. *Sorption of phosphate onto calcite; results from batch experiments and surface complexation modeling*. Geochimica et Cosmochimica Acta 75(10: 2911-2923.

SUN, H., F. NIU AND J. ZHANG, 2021. *Investigation on the flotation separation of smithsonite from calcite using calcium lignosulphonate as depressant*. Colloids and Surfaces A: Physicochemical and Engineering Aspects 630: 127571.

SUN, R., D. LIU, X. TIAN, Q. ZUO, D. WANG, S. WEN, 2022. *The role of copper ion and soluble starch used as a combined depressant in the flotation separation of fluorite from calcite: New insights on the application of modified starch in mineral processing*. Minerals Engineering 181: 107550.

THOMPSON, M., 2006. Base Metals Handbook.

TIAN, X., X. ZHANG, L. LI, D. WANG, 1997. *Room temperature cleaner flotation technique for scheelite rough concentrate*, Transactions of Nonferrous Metals Society of China, 7(2): 21-25.

VALDIVIESO, A. L., T. C. CERVANTES, S. SONG, A. R. CABRERA, J. S. LASKOWSKI, 2004. *Dextrin as a non-toxic depressant for pyrite in flotation with xanthates as collector*. Minerals Engineering 17(9-10): 1001-1006.

VUČINIĆ, D. R., D. S. RADULOVIĆ, S. Đ. DEUŠIĆ, 2010. *Electrokinetic properties of hydroxyapatite under flotation conditions*. Journal of Colloid and Interface Science 343(1: 239-245.

WANG, C., R. LIU, Q. ZHAI, M. WU, N. JING, F. XIE, W. SUN, 2022. *Influence of calcium and ferric ions on the depression of chalcopyrite by CMC: Flotation performance and adsorption mechanism study*. Minerals Engineering 184: 107667.

WANG, D. Q., D. LIU, Y. B. MAO, R. F. SUN, R. T. LIU, S. M. WEN, 2021. *Effect of Fluoride Ion on the Separation of Fluorite from Calcite Using Flotation with Acidified Water Glass*. Minerals 11(11).

WANG, L., L. SHEN, W. SUN, X. ZHANG, Y. ZHANG, Y. WANG, 2022. *Selective flotation separation of smithsonite from dolomite by using sodium hexametaphosphate as a depressant*. Colloids and Surfaces A: Physicochemical and Engineering Aspects 651: 129621.

WANG, L., W. ZHOU, S. SONG, H. GAO, G. AI, 2020. *Selective separation of hematite from quartz with sodium oleate collector and calcium lignosulphonate depressant*. Journal of Molecular Liquids 322: 114502.

WANG, M., G. ZHANG, L. ZHAO, Y. CHEN, D. LIU, C. LI, 2022. *Application of eco-friendly tetrasodium iminodisuccinate for separation of smithsonite from zinc ions activated quartz*. Minerals Engineering 181: 107545.

WANG, M., W. ZHAO, G. HAN, Q. FENG, 2023. *Utilization of lead ions to improve surface hydrophobicity and flotation recovery of sulfidized smithsonite*. Colloids and Surfaces A: Physicochemical and Engineering Aspects 663: 131126.

WILLS, B. A., T. NAPIER-MUNN, 1988. *Mineral processing technology: an introduction to the practical aspects of ore tretment and mineral recovery*. Elsevier Science & Technology Books.

WU, D., W. MA, S. WEN, S. BAI, J. DENG, Q. YIN, 2017. *Contribution of ammonium ions to sulfidation-flotation of smithsonite*. Journal of the Taiwan Institute of Chemical Engineers 78: 20-26.

WU, D., W. MA, S. WEN, J. DENG, S. BAI, 2017. *Enhancing the sulfidation of smithsonite by superficial dissolution with a novel complexing agent*. Minerals Engineering 114: 1-7.

WU, D., S. WEN, J. DENG, J. LIU, Y. MAO, 2015. *Study on the sulfidation behavior of smithsonite*. Applied Surface Science 329: 315-320.

XIE, X., B. LI, R. XIE, X. TONG, Y. LI, S. ZHANG, J. LI, Q. SONG, 2022. *Al³⁺ enhanced the depressant of guar gum on the flotation separation of smithsonite from calcite*. Journal of Molecular Liquids 368: 120759.

XUEMIN, Q., Y. HONGYING, C. GUOBAO, Z. SHUIPING, C. CHUANGKAI, L. BIBO, 2020. *Inhibited mechanism of carboxymethyl cellulose as a galena depressant in chalcopyrite and galena separation flotation*. Minerals Engineering 150: 106273.

YANG, D., B. LI, D. FENG, X. XIE, F. MO, X. TONG, Q. SONG, 2022. *Flotation separation of smithsonite from calcite with guar gum as depressant*. Colloids and Surfaces A: Physicochemical and Engineering Aspects 650: 129562.

YANG, X., P. ROONASI, A. HOLMGREN, 2008. *A study of sodium silicate in aqueous solution and sorbed by synthetic magnetite using in situ ATR-FTIR spectroscopy*. Journal of Colloid & Interface Science 328(1): 41-47.

YE, L., 1997. *A study on the adsorption properties of dextrin on barite and fluorite surface and interaction mechanism*. Journal of Chinese Ceramic Society

ZHANG, S., S. WEN, Y. XIAN, G. LIANG, M. LI, 2021. *Pb ion Pre-Modification enhances the sulfidization and floatability of smithsonite*. Minerals Engineering 170: 107003.

ZHANG, S., S. WEN, Y. XIAN, L. ZHAO, Q. FENG, S. BAI, G. HAN, J. LANG, 2019. *Lead ion modification and its enhancement for xanthate adsorption on smithsonite surface*. Applied Surface Science 498: 143801.

ZHANG, S., Y. XIAN, S. WEN AND G. LIANG, 2022. *Enhancement of xanthate adsorption on lead-modified and sulfurized smithsonite surface in the presence of ammonia*. Minerals Engineering 189: 107872.

ZHANG, X., J. DENG, Y. WANG, S. LI, H. ZHAO, C. LIU, Z. MA, Z. SUN, 2023. *Adsorption characteristics of Pb(II) ions on sulfidized hemimorphite surface under ammonium sulfate system*. International Journal of Mining Science and Technology 33(4): 511-518.

ZHAO, L., G. ZHANG, M. WANG, S. ZHENG, B. LI, 2022. *Selective separation of smithsonite from quartz by using sodium polyaspartate as a depressant*. Colloids and Surfaces A: Physicochemical and Engineering Aspects 644: 128840.

ZHAO, W., B. YANG, D. LIU, Q. FENG, 2022. *Effect of copper ions on sulfidization flotation of smithsonite: Surface properties and adsorption mechanism*. Colloids and Surfaces A: Physicochemical and Engineering Aspects 650: 129515.

ZHOU, H., Z. YANG, Y. ZHANG, F. XIE, X. LUO, 2021. *Flotation separation of smithsonite from calcite by using flaxseed gum as depressant*. Minerals Engineering 167: 106904.

ZHOU, Q. AND S. LU, 1992. *Acidized sodium silicate - an effective modifier in fluorite flotation*. Minerals Engineering 5(3): 435-444.

ZHOU, W., J. MORENO, R. TORRES, H. VALLE, S. SONG, 2013. *Flotation of fluorite from ores by using acidized water glass as depressant*. Minerals Engineering 45: 142-145.

ZHU, W., J. PAN, X. YU, G. HE, T. LIU, 2021. *The flotation separation of fluorite from calcite using hydroxypropyl starch as a depressant*. Colloids and Surfaces A Physicochemical and Engineering Aspects 616(98): 126168.