

## Review

# Recent Progress on Chelating Reagents in Flotation of Zinc Oxide Ores: A Review

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**Abstract:** Zinc oxide minerals (primarily smithsonite and hemimorphite) are important sources of Zn. Flotation is the most widely used method of enriching zinc oxide minerals for mineral processing. Chelating reagents have received extensive attention for the flotation of zinc oxide ores because of their high selectivity and stability. This paper systematically summarizes the selective separation performance and mechanisms of various chelating reagents as collectors, activators, and depressants in the flotation of zinc oxide ores. The types and mechanisms of chelating reagents in the flotation of zinc oxide ores are discussed, providing new ideas for the development of efficient flotation reagents for zinc oxide ores.

**Keywords:** zinc oxide ores; flotation; chelating reagents; selective separation



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## 1. Introduction

Zinc is widely distributed in nature. It possesses several physical and chemical characteristics, including good electrical and thermal conductivities, corrosion resistance, and ductility. These properties make it suitable for various applications, such as galvanizing processes and alloy production, and as a chemical additive in fields such as medicine, rubber, and paint [1–4]. In recent decades, the global consumption of Zn has significantly increased, making it the fourth most consumed metal after iron, aluminum, and copper [5]. Zn resources are primarily found in sulfide deposits, with sphalerite being the main Zn-bearing mineral. Therefore, the main raw materials used in industrial production are zinc sulfide minerals. However, the continuous consumption of limited zinc sulfide resources has made it difficult to meet the growing demand for Zn. Consequently, the efficient development and utilization of zinc oxide ores have become crucial for supplementing the supply of Zn metal [6].

Several types of zinc-bearing minerals exist in zinc oxide ores, including smithsonite ( $\text{ZnCO}_3$ ), willemite ( $\text{Zn}_2\text{SiO}_4$ ), hemimorphite ( $\text{Zn}_4\text{Si}_2\text{O}_7(\text{OH})_2 \cdot \text{H}_2\text{O}$ ), hydrozincite ( $3\text{Zn}(\text{OH})_2 \cdot 2\text{ZnCO}_3$ ), and zincite ( $\text{ZnO}$ ) [7–9]. The most prevalent and economically valuable among them are smithsonite and hemimorphite. In nature, zinc oxide minerals do not exist alone. The minerals associated with zinc oxide minerals mainly include copper, lead, and iron oxide minerals, such as malachite, cerussite, and limonite. The main gangue minerals are calcite, dolomite, quartz, goethite, and clay minerals (kaolinite, chlorite, mica, etc.). Because of the complex relationship between the ore structure and co-association in zinc oxide ores, the surface properties of the target mineral and gangue are similar (crystal structure, solubility, and hydrophobicity), and they have a fine particle size, severe mud phenomenon, and high soluble salt content, leading to difficulties in Zn recycling [5,7]. Flotation is the main method used to treat zinc oxide ores in the field of mineral processing [10], and the treatment of zinc oxide ores usually includes the following methods:

(1) Sulfidization–xanthate flotation: Sulfidization–xanthate flotation is an effective method for treating zinc oxide ores. It uses a sulfiding agent to pre-sulfurize the surfaces of oxide minerals, covering them with a hydrophobic sulfide film, and then using xanthate as a collector for flotation [11]. However, when sulfidization–xanthate flotation is used to directly separate zinc oxide ores, the flotation index is often not ideal and is difficult to directly apply in industrial production. To improve the flotation efficiency and mineral recovery of sulfidization–xanthate flotation, it is usually necessary to heat and add metal ions for activation [9,12]. Complex procedures, high reagent dosages, and unreliable industrial production indices may result from the additional processing steps [13].

(2) Sulfidization–amine flotation: Sulfidization–amine flotation is the most commonly used flotation technology for zinc oxide ores in industry; it first sulfidizes zinc oxide minerals with sulfidizing reagents ( $\text{Na}_2\text{S}$ ,  $\text{NaHS}$ , etc.) and then uses cationic collectors (such as dodecylamine and octadecylamine) for flotation [14,15]. When using this method, it is necessary to strictly control the dosage of sulfidizing reagents and the pH of the flotation pulp [16]. In addition, there are problems such as high reagent consumption, difficulty in defoaming, sensitivity of amine collectors to pulp, and soluble salts during the flotation process.

(3) Direct flotation via fatty acids: Fatty acids can be used for the direct flotation of zinc oxide minerals. This technology performs well in the flotation of zinc oxide ores containing silicate or muddy gangue, but has poor selectivity for zinc oxide ores containing carbonate gangue [17,18].

(4) Thiol collector flotation: Non-aromatic compounds (thiols) containing thiol functional groups ( $-\text{SH}$ ) were used as collectors for zinc oxide mineral flotation, and ideal flotation results were obtained [19]. Hosseini et al. [9] pointed out that after thiol was adsorbed on the surface of zinc oxide minerals, the  $\text{S}-\text{H}$  bond in thiol broke. The broken H reacted with  $-\text{OH}$  on the surfaces of the minerals to form  $\text{H}_2\text{O}$ , and the broken S formed a  $\text{S}-\text{Zn}$  bond with Zn on the surfaces of the minerals. The S atom is connected to the hydrophobic group. Therefore, the formation of the  $\text{S}-\text{Zn}$  species enhances the hydrophobicity of the mineral surface and realizes the collection of zinc oxide minerals by the thiol collector. However, in the actual flotation process, when thiol is used as a collector to float smithsonite, the flotation recovery obtained is low. In addition, thiol also has the disadvantages of easy volatilization, an unpleasant smell, and a large dosage consumption. The industrial production index is not stable enough, so it is less used in industry.

(5) Chelating reagent flotation: Chelating reagent flotation uses specific chelating reagents as collectors or regulators to achieve efficient mineral separation. Owing to their exceptional selectivity and stability, chelating reagents have been extensively studied as collectors or regulators for the flotation of zinc oxide ores [20,21].

Chelating reagents can interact with metal ions to form stable complexes with ring structures. Chelating reagents generally contain two or more electron-donating groups that combine with metal ions to form cyclic structures called metal chelates [22–25]. The active atoms in the chelating reagents provide electron pairs that interact with the metal ions. These active atoms are often non-metallic elements, mainly O, N, S, and P atoms [22,24]. Electron-donating groups can be classified into acidic and basic groups. Acidic groups can lose protons and coordinate with metal atoms. Common acidic groups include the  $-\text{COOH}$  (carboxylic),  $-\text{SO}_3\text{H}$  (sulfonic),  $-\text{PO}(\text{OH})_2$  (phosphoric),  $-\text{OH}$  (enolic and phenolic),  $=\text{N}-\text{OH}$  (oxime), and  $-\text{SH}$  (thiol) groups. Basic groups contain atoms carrying lone pairs of electrons that can interact with metal cations. Common basic groups include  $-\text{NH}-$  (imino),  $-\text{NH}_2$  (amino),  $-\text{N}=$  (tertiary acyclic or heterocyclic nitrogen),  $=\text{O}$  (carbonyl),  $-\text{O}-$  (ether or ester),  $=\text{N}-\text{OH}$  (oxime),  $-\text{OH}$  (aliphatic alcohol), etc. [24,26].

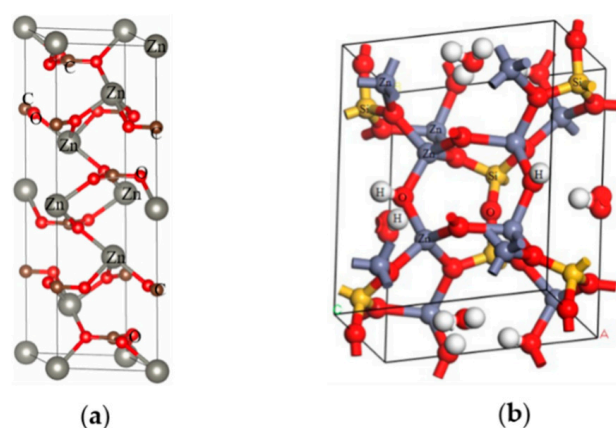
Recently, the development of efficient flotation reagents for oxide minerals has become prevalent in mineral processing. Owing to the greater stability of metal chelates, chelating reagents have been widely investigated as flotation reagents in mineral processing and are considered to have excellent collection and selective properties with enormous potential for applications. For example, hydroxamic acid has been widely applied in the flotation of

oxide minerals such as scheelite, wolframite, and cassiterite [27–29]. Chelating reagents have also been extensively investigated for the flotation of zinc oxide minerals and have achieved significant progress and advancements. For example, hydroxamic acid, phosphate, amide, 8-hydroxyquinoline, and heterocyclic collectors have been widely investigated in the flotation of zinc oxide minerals, and some chelating reagents containing oxime groups, hydroxyl groups, carboxyl groups, and phosphate groups have also been investigated as regulators in the flotation of zinc oxide minerals. However, a systematic introduction to the application and mechanisms of action of chelating reagents in the flotation of zinc oxide minerals has rarely been reported. This article summarizes the selective separation performance and action mechanisms of various chelating reagents in the flotation of typical zinc oxide and gangue minerals, providing new ideas and a theoretical basis for the study and application of chelating reagents in the flotation of zinc oxide ores.

## 2. Crystal Structures and Surface Properties of Typical Zinc Oxide Minerals and Gangue Minerals

### 2.1. Crystal Structures and Surface Properties of Typical Zinc Oxide Minerals

Smithsonite is a typical island carbonate mineral with a trigonal crystal structure. As illustrated in Figure 1a, Zn, in a single smithsonite unit cell, coordinates to O in the surrounding six  $\text{CO}_3^{2-}$  groups to form six-coordinate bonds, whereas C coordinates to O to form three-coordinate bonds. Furthermore, O coordinates to two surrounding Zn atoms and one C to form a three-coordinate structure. The strength of the Zn–O bond in the smithsonite crystal is weaker than that of the C–O bonds in the carbonate groups. As a result, the Zn–O bond is more prone to fracture during crushing and grinding, leading to the exposure of fresh Zn sites on the mineral surface [30,31]. Smithsonite is a semi-soluble mineral with a solubility product constant of  $1.46 \times 10^{-10}$ . Due to the dissolution and hydration of lattice ions, there is a large number of unavoidable ions in the solution, and the dominant components in the solution include  $\text{ZnOH}^+$ ,  $\text{Zn(OH)}_2$ ,  $\text{Zn(OH)}_3^-$ , and  $\text{Zn(OH)}_4^{2-}$  [32–34]. The hydrolysis products can be adsorbed to the mineral surface, thus making the flotation separation of smithsonite and gangue minerals more difficult. Moreover, the smithsonite surface is partially hydroxylated to form zinc hydroxides in alkaline conditions, which hinders the interaction between flotation reagents and active sites on the surfaces of the minerals.



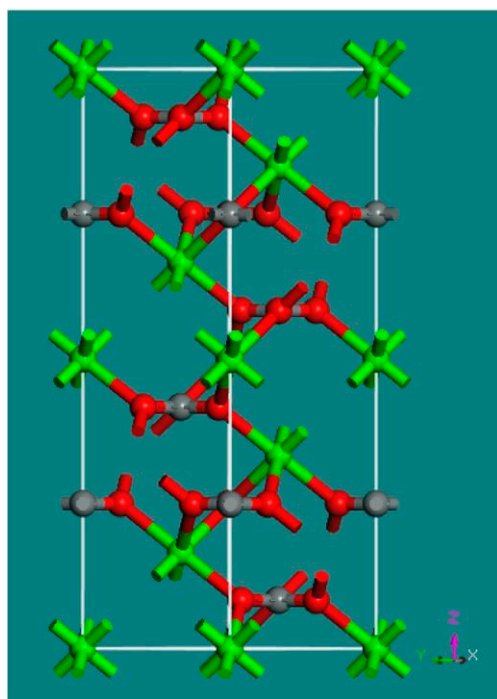
**Figure 1.** (a) Crystal structure of smithsonite [31]; (b) cell model of hemimorphite [35].

Hemimorphite is a complex silicate mineral whose structure is shown in Figure 1b. In the crystal structure of hemimorphite, Zn atoms form new tetrahedra with –OH and three O atoms belonging to the Si–O tetrahedron, resulting in low Zn activity in the lattice [35]. The bonding strength between the Si–O bonds being stronger than that between the Zn–O bonds leads to the breaking of the Zn–O bonds during the crushing and grinding process of hemimorphite. Consequently, the  $\text{SiO}_4^{2-}$  and  $\text{Zn}^{2+}$  chemical bonds are often exposed on the surfaces of minerals. These  $\text{SiO}_4^{2-}$  components often shield the Zn component on

the surface of the hemimorphite, reducing the reactivity of the surface with the flotation reagents and making flotation difficult.

## 2.2. Crystal Structure and Surface Properties of Common Gangue Minerals

Calcite is the most common gangue mineral in zinc oxide ores. It belongs to the trigonal crystal system with the space group symbol R3C and has a closely packed structure. As shown in Figure 2,  $\text{Ca}^{2+}$  ions in the calcite crystal lattice combine with O atoms in the surrounding six  $\text{CO}_3^{2-}$  ions to form an irregular octahedral coordination with a Ca–O bond length of 2.36 Å. The C atom is coordinated with the O atoms to form a structure with a C–O bond length of 1.28 Å [36]. The cleavage planes of calcite are along three groups, namely, the {101}, {211}, and {102} surfaces of the rhombohedral plane, which correspond to the {104}, {018}, and {214} surfaces of the hexagonal cell [37]. The crystal structures and surface properties of the calcite and smithsonite are similar. In pulp solutions, the surfaces of calcite and smithsonite can be hydroxylated and dissolved, affecting the flotation separation of minerals through the release and migration of calcium ions and the heterogeneous coagulation of minerals.



**Figure 2.** Unit cell structure of calcite (Ca = light green, O = red, C = grey) [36].

Quartz is another common gangue mineral in zinc oxide ores. Quartz surfaces possess strong electronegativity, a low isoelectric point, and high hydrophilicity. Quartz does not have a fixed cleavage surface, and researchers typically choose to analyze the structure and surface properties of quartz on the (101), (100), and (001) surfaces. Quartz is composed of Si–O tetrahedrons that form a frame-like crystal structure. Each Si atom is bonded to four O atoms through four single bonds, forming a Si–O tetrahedron [38]. The Si–O bond energy was high, which caused a large number of Si–O bonds in the quartz crystal to break during the crushing and grinding processes, leading to the exposure of  $\text{Si}^{4+}$  and  $\text{O}^{2-}$  ions on the surface. These ions can adsorb  $\text{OH}^-$  and  $\text{H}^+$  in aqueous solutions, resulting in the formation of hydroxylated quartz surfaces (Figure 3) [39–41]. During the flotation process, the Si–O functional group on the quartz surface can react with the hydroxyl complexes of metal ions, causing the metal ions to adsorb onto the quartz surface and form the action sites of the flotation reagents, thereby activating flotation [38,42,43].

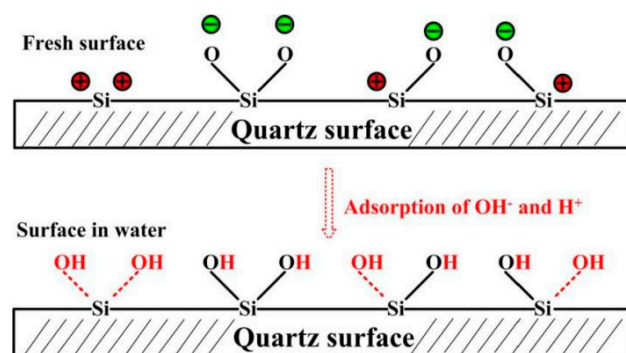


Figure 3. Quartz surface model [41].

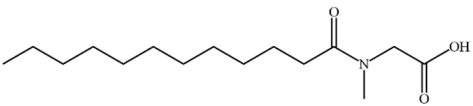
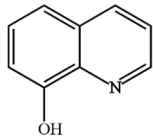
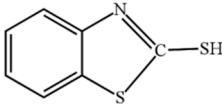
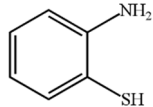
### 3. Chelating Collectors

Based on the different types of electron donor atoms in the chelating collectors, various types of chelating collectors can be distinguished for the flotation of zinc oxide ores. These include O–O, N–O, S–S, and S–N chelating collectors (Table 1).

Table 1. Common chelating collectors for zinc oxide minerals.

Type	Name	Mineral	Optimum pH Range	Molecular Structure	Refs.
O–O	Salicylhydroxamic acid	Smithsonite	5–7.5		[44]
	Octyl hydroxamic acid	Smithsonite	7.5–8.5		[45]
	Salicylaldoxime	Smithsonite	7.5–8.5		[46]
	Benzohydroxamic acid	Smithsonite	7–9		[46,47]
	Phenylpropenyl hydroxamic acid	Smithsonite	7		[48]
	Cupferron	Smithsonite	7.5–9		[49]
	Dodecylphosphate	Smithsonite	8–10		[50]
	Di(2-ethylhexyl)phosphoric acid	Hemimorphite	6–10		[51]

Table 1. Cont.

Type	Name	Mineral	Optimum pH Range	Molecular Structure	Refs.
N–O	N-lauroylsarcosinate	Hemimorphite	7		[52–54]
	8-Hydroxyquinoline	Smithsonite	7		[55–57]
S–S	Mercaptobenzothiazole	Smithsonite	<7		[58]
S–N	Aminothiophenol	Smithsonite	–		[59]

### 3.1. O–O Chelating Collectors

Hydroxamic acid is widely used as a chelating collector in the flotation of zinc oxide ores. The  $-\text{C}(\text{O})\text{NHOH}$  group in its molecular structure possesses high coordination activity, providing strong binding to metal ions on mineral surfaces and forming stable chelates, which enable stable adsorption onto mineral surfaces and enhance their hydrophobicity [48,60].

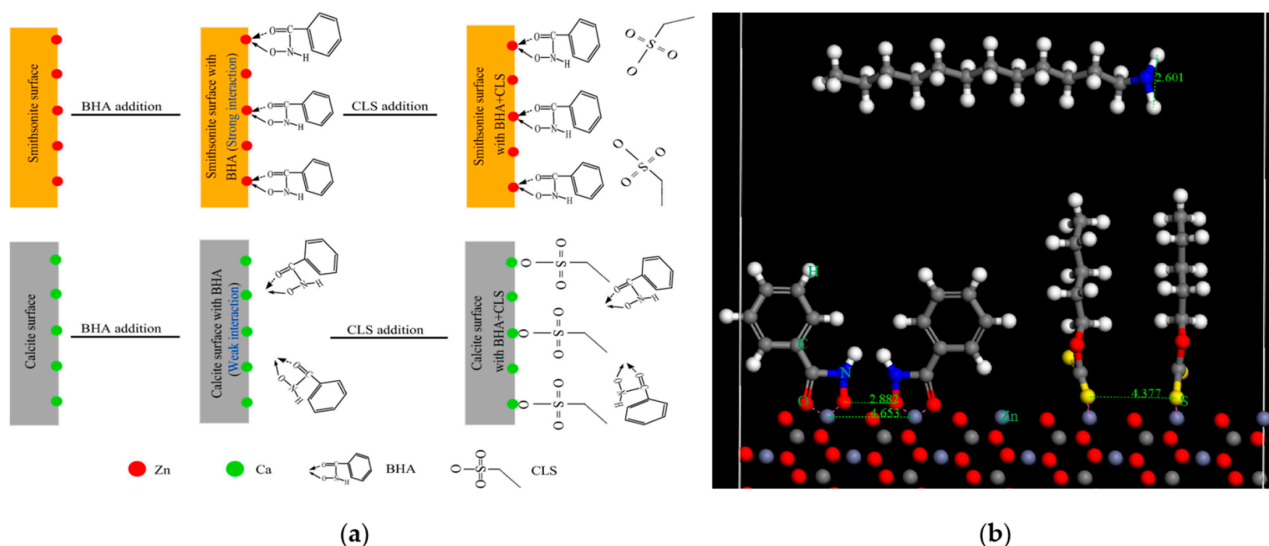
Zhao et al. [44] discovered that using salicylhydroxamic acid as a collector in the flotation of smithsonite resulted in a recovery of over 90% within a pH range of 5–7.5, demonstrating the strong collection ability of salicylhydroxamic acid for smithsonite. The zeta potential and infrared spectral analyses confirmed that salicylhydroxamic acid interacted with the surface of smithsonite through chemical adsorption, that is, the metal ions on the mineral surface formed chemical bonds with the coordination groups in salicylhydroxamic acid, resulting in hydrophobic chelation on the mineral surface. Similarly, He et al. [45] found that octyl hydroxamic acid (salt) is an effective collector for smithsonite, as the N and O atoms in the functional groups interact with the Zn sites on the surface of smithsonite, improving the hydrophobicity of the mineral surface.

Based on the isomerism principle, Zhu et al. [46] studied the collection performance of salicylaldoxime and benzohydroxamic acid on smithsonite. The results of the tests reveal that both salicylaldoxime and benzohydroxamic acid exhibited promising collection performances for smithsonite. When benzohydroxamic acid was employed as the collector, a higher flotation recovery of smithsonite was obtained than that of salicylaldoxime. This suggests that benzohydroxamic acid has a stronger ability to collect smithsonite than salicylaldoxime. To explain the variation in the collection ability of the two reagents, a quantum chemistry method was applied to calculate the net charges of the bonding atoms of the benzohydroxamic acid and salicylaldoxime functional groups with metal ions. The calculation results indicate that the net charge of the bonding atoms between the functional groups in benzohydroxamic acid and the metal ions on the mineral surface was higher than that of the bonding atoms between the functional groups in salicylaldoxime and the metal ions on the mineral surface. Therefore, the reaction between benzohydroxamic acid and the smithsonite surface is stronger than that with salicylaldoxime.

Liu et al. [47] investigated the floatability and separation performance of smithsonite and calcite using benzohydroxamic acid as a collector and calcium lignosulfonate as a depressant, with the collector added first and the depressant added second. As illustrated in Figure 4a, benzohydroxamic acid can bind to the active sites on the surface of smith-



sonite and prevent the interaction between calcium lignosulfonate and Zn sites through spatial steric effects, resulting in a hydrophobic smithsonite surface. Furthermore, benzohydroxamic acid weakly interacts with the calcite surface, leaving enough space for calcium lignosulfonate to attach, resulting in a hydrophilic calcite surface. Wang et al. [61] used molecular dynamics simulation to simulate the chemisorption configuration of benzohydroxamic acid on the surface of smithsonite, as shown in Figure 4b. The distance between adjacent Zn atoms on the cleavage surface (101) of smithsonite crystal is 4.653 Å. Benzohydroxamic acid can be adsorbed onto the surface of smithsonite through chelation between the two O atoms in its head group and the Zn atoms, forming a five-membered ring. The weak interaction between benzohydroxamic acid and the calcite surface may be attributed to the low matching ability between the O–O distance of benzohydroxamic acid and the O–O distance of the carbonate group in calcite [62]. In addition, because  $\text{Zn}^{2+}$  belongs to the transition metal ion and  $\text{Ca}^{2+}$  belongs to the main group metal ion, the stability constant of the Zn-hydroxamate salt formed by the reaction of hydroxamate with  $\text{Zn}^{2+}$  is 7.31 [63], and the stability constant of the Ca-hydroxamate salt formed by the reaction of hydroxamate with  $\text{Ca}^{2+}$  is 2.4 [25]. Therefore, hydroxamate easily interacts with smithsonite containing  $\text{Zn}^{2+}$  on the surface, and the chelate that is formed is more stable [64,65].

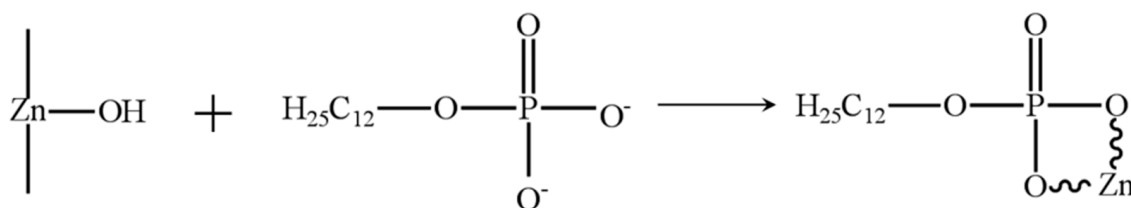


**Figure 4.** (a) Schematic of the interaction of benzohydroxamic acid with mineral surface at pH 8.5 [47]; (b) adsorption configuration and spatial measurement [61].

Based on the hydroxylamine method, Zeng et al. [48] synthesized phenylpropene hydroxamic acid using methyl cinnamate, hydroxylamine, and anhydrous ethanol at 50 °C. Flotation separation tests were conducted on smithsonite and calcite, and it was found that, at a pH of 7 and a dosage of 50 mg/L of phenylpropene hydroxamic acid, the recovery of smithsonite reached 90.5%. Furthermore, the artificial mixed ore flotation test resulted in a Zn concentrate with a Zn grade of 35.1% and a Zn recovery of 81.4%. The X-ray photoelectron spectroscopy (XPS) analysis results indicate that phenylpropene hydroxamic acid interacts with the smithsonite surface to form a phenylpropene hydroxamic acid–smithsonite complex. The quantum chemistry calculations further reveal that phenylpropene hydroxamic acid has a higher highest occupied molecular orbital (HOMO) value than benzohydroxamic acid, making it easier for phenylpropene hydroxamic acid to provide electrons when reacting with smithsonite. Additionally, the higher ClogP value of phenylpropene hydroxamic acid compared with benzyl hydroxamic acid suggests that phenylpropene hydroxamic acid possesses better hydrophobic properties, which can effectively improve the surface hydrophobicity of the minerals.

The CF reagent, a metal-chelating collector developed by the Beijing General Research Institute of Mining and Metallurgy, is mainly composed of N-nitroso-N-phenylhydroxylammonium salt and has been applied in the flotation of wolframite and scheelite [66]. Tan et al. [67–69] utilized CF as a collector along with depressants such as sodium hexametaphosphate and a zinc sulfate salted water glass to effectively separate smithsonite from calcite, dolomite, limonite, and quartz through sulfidization–flotation under normal temperature and natural pH conditions. The O– and O= in CF could serve as chelating reagents with metal ions on the surface of smithsonite to form O–O five-membered ring complexes. Furthermore, Zhu et al. [49] found that cupferron exhibited good flotation recovery of smithsonite in both single-mineral and artificial mixed ore flotation tests, resulting in the effective separation of smithsonite from calcite and quartz. The theoretical analysis suggested that cupferron could adhere to the surface of smithsonite the most by forming insoluble Zn salts via the O atoms in the oxime group and the Zn ions on the surface of smithsonite, whereas a small amount of cupferron molecules may be physically adsorbed onto the surface of smithsonite.

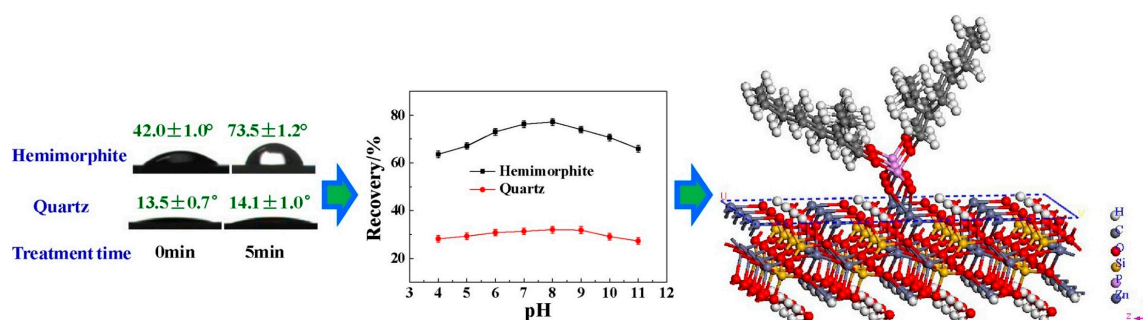
Phosphate groups possess exceptional selective chelating abilities [70–72]. Phosphate esters are anionic surfactants used in industrial production and generally consist of monophosphates, diphosphates, and a small amount of phosphoric acid. Sun et al. [50] discovered that dodecyl phosphate ester potassium demonstrated ideal collection capabilities for smithsonite and could achieve an optimal flotation index for smithsonite under weakly alkaline conditions, with a flotation recovery of 90% under optimal conditions. The infrared spectrum (IR) and XPS analyses demonstrated that dodecyl phosphate ester potassium reacted with Zn atoms on the surface of smithsonite, producing Zn–O bonds by releasing  $H^+$  in –OH, thus existing on the mineral surface through chemical adsorption (Figure 5). Moreover, compared to the common dodecylamine collector, dodecyl phosphate exhibits enhanced selectivity. Dodecylamine adheres to the surfaces of smithsonite and calcite simultaneously, whereas dodecyl phosphate ester potassium preferentially attaches to the surface of smithsonite, providing the potential for the effective separation of smithsonite and gangue minerals [73].



**Figure 5.** Model of dodecyl phosphate ester potassium adsorbed on the surface of smithsonite [50].

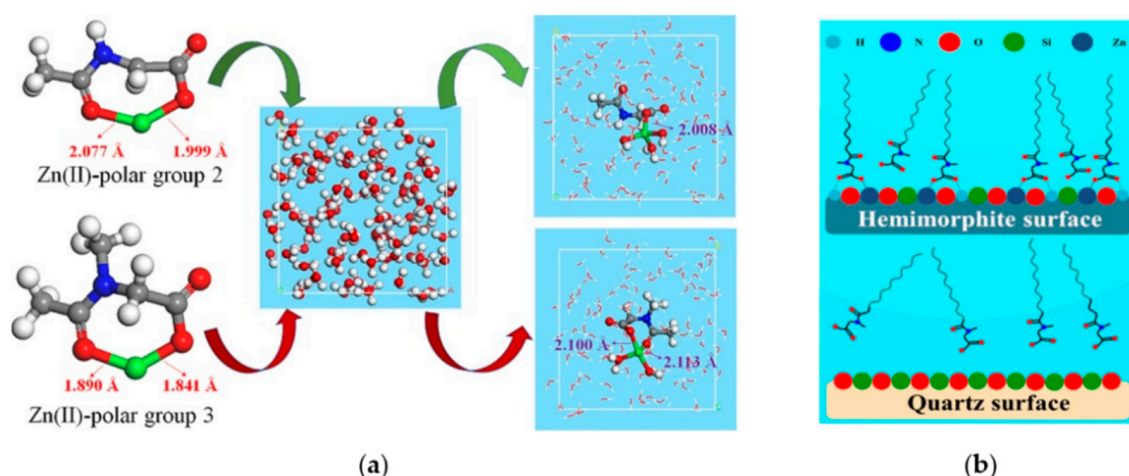
Qin et al. [51] conducted a flotation separation test of hemimorphite ore and quartz using di-(2-ethylhexyl) phosphoric acid as a collector and found that effective separation could be achieved within the pH range of 6–10. The anionic group in di-(2-ethylhexyl) phosphoric acid can interact with the Zn sites on the surface of hemimorphite and form a chemical bond, whereas the adsorption capacity on the surface of quartz is weak, leading to selective adsorption on the surface of the hemimorphite ore and the selective hydrophobic flotation of hemimorphite. Figure 6 shows that di-(2-ethylhexyl) phosphoric acid was chemically adsorbed on the surface of hemimorphite by forming a Zn–O bond between the O atom of the hydroxyl group and the Zn atom on the surface of the hemimorphite, resulting in the generation of a hydrophobic Zn(II)-di-(2-ethylhexyl) phosphoric acid surface complex on the mineral surface. Furthermore, di-(2-ethylhexyl) phosphoric acid reacts weakly with the Si atoms on the quartz surface, enabling the flotation separation of hemimorphite and quartz.





**Figure 6.** Selective flotation separation of hemimorphite from quartz under  $1.0 \times 10^{-4}$  mol L<sup>-1</sup> di-(2-ethylhexyl) phosphoric acid and its hydrophobic mechanism on hemimorphite {1 1 0} surface [51].

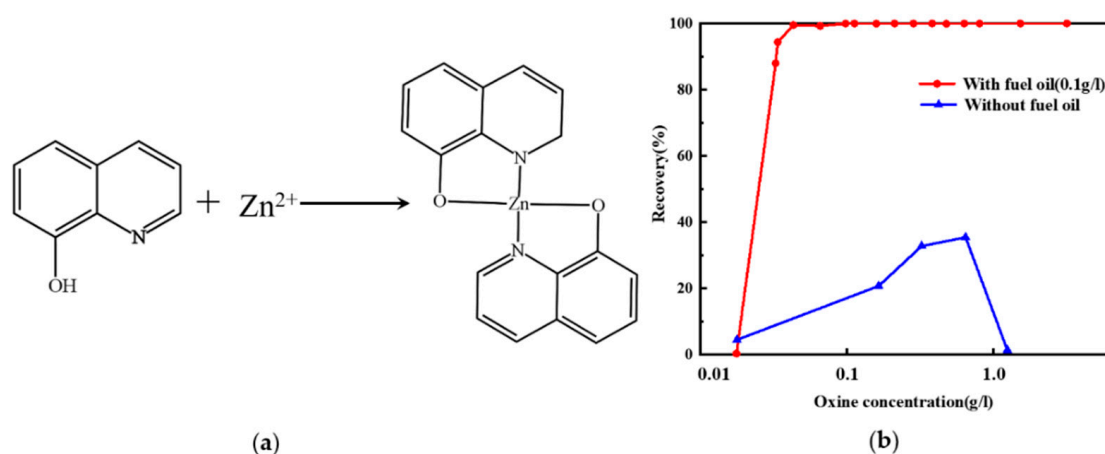
N-lauroylsarcosine is a biosurfactant with amide and carboxyl groups. Because N-lauroylsarcosine can react with heavy metal ions via a complexation reaction, it was used to remove heavy metal ions from wastewater [52]. Based on the relationship between the group bond strength and complexation stability constant, Zhao et al. [53] designed and synthesized N-Lauroylsarcosine and N-dodecylglycine as flotation collectors of zinc oxide minerals using the bond valence model and density functional theory. The flotation results show that both have good collection performances for hemimorphite; however, the collection performance of N-lauroylsarcosine was better than that of N-dodecyl glycine. The mechanisms of action of N-lauroylsarcosine and N-dodecylglycine on the surface of hemimorphite are shown in Figure 7a. The polar groups in N-lauroylsarcosine and N-dodecylglycine can coordinate with the Zn (II) ions on the surface of hemimorphite through carboxyl and carbonyl groups, forming a seven-membered ring chelation in minerals. N-lauroylsarcosine has a better collection performance than N-dodecylglycine because it has two stable Zn (II)–C=O bonds in an aqueous solution, while the Zn (II)–C=O bond in N-dodecylglycine can break in an aqueous solution. Furthermore, Jia et al. [54] studied the adsorption mechanism of N-lauroylsarcosine on hemimorphite and quartz surfaces and found that N-lauroylsarcosine can interact with the Zn and H sites on the surface of hemimorphite to form a stable double-tooth chelation and be adsorbed on the surface of hemimorphite (Figure 7b), which enhances the surface hydrophobicity of hemimorphite and achieves the selective separation of hemimorphite and quartz.



**Figure 7.** (a) Configuration of Zn (II) complexes with N-lauroylsarcosine (group 2) and N-dodecylglycine (group 3) in aqueous solution (O—red; N—blue; C—gray; H—white; and Zn—green) [53]; (b) adsorption model of N-lauroylsarcosine on hemimorphite surface [54].

### 3.2. N–O Chelating Collectors

8-Hydroxyquinoline is a common metal chelating reagent that can react with many metal ions to form water-insoluble precipitates; therefore, it can interact with the surface of metal minerals and change their surface properties [55]. Rinelli et al. [56] used 8-hydroxyquinoline as a collector and found that the floatability of smithsonite was significantly improved under natural pH conditions. As shown in Figure 8, the N and O atoms in 8-hydroxyquinoline can form a five-membered ring chelate with the Zn atoms on the surface of smithsonite. To evaluate the characteristic adsorption of 8-hydroxyquinoline on the surface of smithsonite, Gabriela et al. [57] studied the effects of temperature and reagent concentration on the adsorption rate of 8-hydroxyquinoline on the surface of smithsonite using kinetics and equilibrium adsorption experiments. The results show that the temperature had no significant effect on the reaction rate. In addition, the adsorption activation energy of 8-hydroxyquinoline on the surface of smithsonite showed that the reaction occurred in the diffusion layer at the liquid phase interface.



**Figure 8.** (a) Reaction of 8-hydroxyquinoline with  $Zn^{2+}$  of smithsonite; (b) flotation recovery of smithsonite in Hallimond tube as a function of 8-hydroxyquinoline concentration at pH 7 [56].

Qiu et al. [74] studied a modified alkylamine chelating collector for smithsonite and achieved ideal separation indicators for the industrial production of zinc oxide ores. Alkylamine-chelating collectors have the advantages of good selectivity, strong collection performance, and a low dosage. Their structures contain groups that can chelate with the mineral surface and do not contain other groups that can be hydrated; therefore, they exhibit strong collecting performance. Based on the structural characteristics of zinc oxide minerals, Chen et al. [75] developed a new collector, C08, which could selectively collect zinc oxide minerals. The collector contains chelating functional groups composed of O, N, and P atoms that can strongly chelate Zn ions on the mineral surfaces to promote the hydrophobic flotation of zinc oxide minerals.

### 3.3. S–S and S–N Chelating Collectors

Mercaptobenzothiazole is a heterocyclic compound containing a thiazole ring and a sulfhydryl group that can chelate metal sites on the mineral surface and thus plays a role in collection [25]. Marabini et al. [58] studied the change rule of the floatability of smithsonite and cerussite when 6n-propoxy-mercapto-benzothiazole was used as the collector. The flotation test results show that under alkaline conditions, the collection capacity of 6n-propoxy-mercapto-benzothiazole on cerussite was stronger than that on smithsonite; however, under acidic conditions, the collection capacity of 6n-propoxy-mercapto-benzothiazole on smithsonite was stronger than that on cerussite. Therefore, when 6n-propoxy-mercapto-benzothiazole is used as the collector of lead–zinc oxide minerals, the flotation separation of minerals can be realized by controlling the pH of the pulp to adjust the floatability difference of the lead–zinc oxide minerals. In addition, the selectivity

of aminothiophenol organic collectors for Zn in the flotation of lead–zinc minerals was evaluated using a statistical method. The results show that aminothiophenol had good collecting ability for Zn minerals, with the formation of ionic bonds between Zn and S, and had weak coordination bonds between N and Zn (Figure 9) [59].

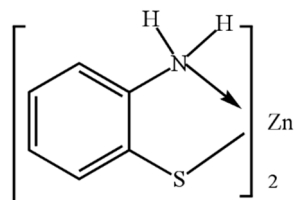


Figure 9. Reaction of aminothiophenol with  $\text{Zn}^{2+}$  of smithsonite [59].

#### 4. Chelating Regulators

##### 4.1. Chelating Activators

Chelating reagents can increase the number of active sites for the physical and chemical adsorption of collectors on mineral surfaces, thereby promoting collector adsorption and enhancing the hydrophobicity of the mineral surfaces [76]. Chelating reagents as activators used in the flotation of zinc oxide minerals can be classified into two categories based on their mechanisms of action. The first category involves the formation of hydrophobic chelates with metal ions on the mineral surface, which are then adsorbed onto the mineral surface, creating preliminary hydrophobic hydration of the mineral and promoting collector adsorption. The O–O and N–O chelating reagents in this category include salicylaldoxime, alpha-benzoic oxime, anthranilic acid, 8-hydroxyquinoline, and  $\alpha$ -nitroso- $\beta$ -naphthol. The second category involves the chelation of metal ions onto the mineral surface to form water-soluble chelates. These chelates enhance the dissolution of metal ions on the mineral surface and promote the multilayer adsorption of collectors onto the mineral surface, thereby activating the mineral. The chelating reagents in this category include ethylenediamine, ethylenediaminetetraacetic acid (EDTA), and xylene orange. Figure 10 provides an overview of various chelating activators used in the flotation of zinc oxide ores.

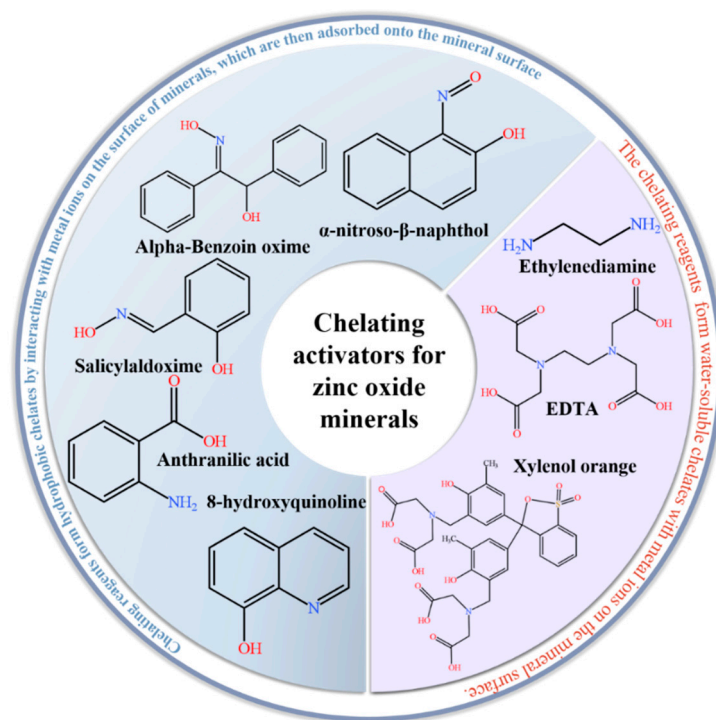
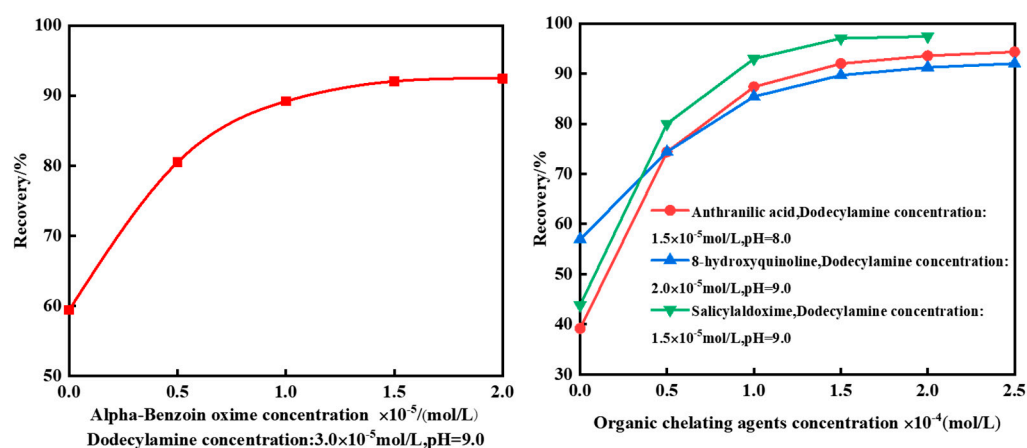


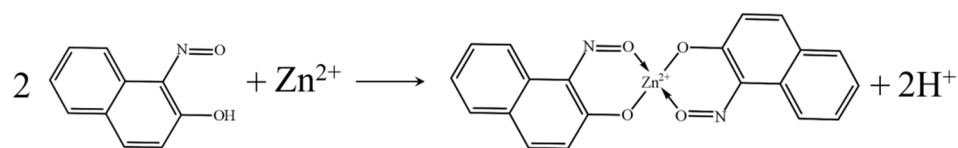
Figure 10. Overview of various chelating activators in the flotation of zinc oxide ores.

Wang et al. [77] studied the activation effects of salicylaldoxime on smithsonite flotation. The results show that smithsonite can be activated by salicylaldoxime without sulfidization, and the flotation of smithsonite can be realized by the direct use of xanthate. The activation effect of salicylaldoxime may occur through the =NOH and -OH groups in its molecular structure and through  $\text{Zn}^{2+}$  on the surface of smithsonite, forming insoluble hydrophobic chelates on the mineral surface. This causes the mineral surface to be initially hydrophobic, destroying the hydration film on the mineral surface, and then promoting the adsorption of xanthate on the mineral surface. Wu et al. [78] studied the activation effects of salicylaldoxime, alpha-benzoic oxime, anthranilic acid, and 8-hydroxyquinoline on the flotation of smithsonite when dodecylamine was used as the collector. The results indicate that the flotation recovery of smithsonite increased with the increasing concentrations of salicylaldoxime, alpha-benzoic oxime, anthranilic acid, and 8-hydroxyquinoline. The four organic chelating reagents activated the flotation of smithsonite (Figure 11). Conversely, the N atom in the chelating activator and the O atom on the hydroxyl group can coordinate with the Zn ion on the surface of smithsonite to form an electrically neutral chelate with a cyclic structure. The chelate is attached to the surface of the mineral, which not only produces preliminary hydrophobic hydration, but also reduces the positive charge on the surface of the mineral, which is beneficial for the adsorption of amine collectors on the surface of smithsonite. Additionally, the chelate formed by the chelating activator on the surface of smithsonite can combine with amine molecules or amine ions through H bonds to promote the adsorption of amine collectors on the surface of smithsonite to achieve the purpose of activating smithsonite flotation.



**Figure 11.** Effect of concentrations of alpha-benzoic oxime, anthranilic acid, 8-hydroxyquinoline, and salicylaldoxime on floatability of smithsonite [78].

$\alpha$ -Nitroso- $\beta$ -naphthol is a chelating reagent with multiple active groups, which can form water-insoluble chelates with  $\text{Cu}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$ , and other metal ions [79]. It was reported that  $\alpha$ -nitroso- $\beta$ -naphthol can be used as an activator in the flotation system of hemimorphite when octadecylamine and benzohydroxamic acid are used as collectors [80]. The activation of  $\alpha$ -nitroso- $\beta$ -naphthol can not only reduce the dosage of flotation reagents, but also promote the flotation separation of target minerals and gangue minerals [78]. It was proven via IR, ultraviolet (UV) spectroscopy, and group electronegativity calculations that  $\alpha$ -nitroso- $\beta$ -naphthol bonds with  $\text{Zn}^{2+}$  on the mineral surface through N and O atoms to form a five-membered ring chelate (Figure 12), which not only enhances the hydrophobicity of the mineral surface, but also promotes the adsorption of the collector on the mineral surface. In addition, the probability of  $\alpha$ -nitroso- $\beta$ -naphthol forming a five-membered ring product with the surface of hemimorphite through N and O atoms in the molecule exceeds the probability of forming other chelates; therefore, it is beneficial to promote the flotation separation of minerals [80,81].



**Figure 12.** Reaction between  $\alpha$ -nitroso- $\beta$ -naphthol and  $\text{Zn}^{2+}$  on the hemimorphite surface [79].

After crushing and grinding, the Zn ions exposed on the surface of the smithsonite usually exist in two chemical states: charge-unsaturated  $\text{Zn}^{2+}$  and  $\text{CO}_3^{2-}$  saturated  $\text{Zn}^{2+}$ . Wang et al. [82] and Wu et al. [78] proposed that the activation mechanism of ethylenediamine on smithsonite occurred through two paths. Owing to the high chemical activity of  $\text{Zn}^{2+}$  with an unsaturated charge, it easily reacts with ethylenediamine to form a water-soluble chelate, so that  $\text{Zn}^{2+}$  dissolves from the surface of the mineral, enhancing the negative charge on the surface of smithsonite and thereby facilitating the adsorption of cationic collectors on the surface of the mineral. Conversely, saturated  $\text{Zn}^{2+}$  has weak chemical activity, and the chelate formed after the reaction with ethylenediamine does not easily break away from the mineral surface and enter the liquid phase. The newly formed chelate can interact with the amine collector through H bonding to promote multilayer adsorption of the amine collector on the mineral surface, thereby increasing the adsorption amount of the collector on the mineral surface and realizing smithsonite activation flotation. Zhang et al. [83] studied the effect of ethylenediaminetetraacetic acid disodium calcium on the floatability of smithsonite in a dodecylamine system under different conditions. The results show that ethylenediaminetetraacetic acid disodium calcium could promote the dissolution of  $\text{Zn}^{2+}$  on the surface of smithsonite, reduce the potential on the surface of minerals, enhance the collecting ability of dodecylamine on smithsonite, and improve the flotation recovery of smithsonite. Similarly, Yang et al. [84] found that xylenol orange can form water-soluble chelating ions with Zn ions on the surface of hemimorphite, which promote the multilayer adsorption of amine ions on the surface of hemimorphite to activate its flotation.

#### 4.2. Chelating Depressants

Because of the excellent selectivity of chelating reagents and the high stability of metal chelates formed via complexation with metal ions, chelating reagents with specific structures can be used as depressants for mineral flotation [85,86]. Chelating depressants mainly achieve the selective depression of minerals through three forms of action in the flotation process [87]: (1) chelating depressants interact with activation metal ions in the pulp to form stable chelates, thereby hindering the adsorption of metal ions on the mineral surface and eliminating the activation of activated ions on mineral flotation; (2) chelating depressants interact with the metal ions on the mineral surface to generate hydrophilic products attached to the mineral surface and hinder the adsorption of the collector, thereby enhancing the hydrophilicity of the mineral surface; and (3) chelation depressants react with the activation metal ions on the mineral surface to the pulp, thereby reducing the reactivity of the mineral surface.

Calcite is a typical gangue mineral in the flotation of zinc oxide ores. Because of its similar crystal structure and surface properties of smithsonite, it is difficult to effectively separate smithsonite from calcite during the flotation process, which significantly affects the quality of the Zn concentrate. Phytic acid is an organic phosphate compound that is extracted from plant seeds. Its molecular structure is shown in Figure 13. The carbon ring of a phytic acid molecule contains 12 free hydroxyl groups and six phosphate groups [88]. Therefore, phytic acid exhibits strong chelating ability for multivalent metal ions such as  $\text{Ca}^{2+}$  [89,90]. Chen et al. [91] found that phytic acid, as a depressant, can facilitate the flotation separation of smithsonite and calcite. At a pH value of 9.5, phytic acid can reduce the floatability of calcite from more than 94% to 10% and has little effect on the recovery of smithsonite. The results of the surface analysis show that phytic acid was easily chelated with  $\text{Ca}^{2+}$  exposed and adsorbed on the calcite surface, which hindered the adsorption of the collector on the surface of calcite, whereas only a slight amount of phytic



acid was adsorbed on the smithsonite surface, thus achieving the selective depression of calcite (Figure 13). In addition, based on the difference in the crystal structure, the Zn–O bond length in the smithsonite crystal is 2.11 Å [92], and the Ca–O bond length in the calcite crystal is 2.36 Å [36]. In general, the shorter the bond length, the higher the bond energy. Compared with the Zn–O bond in smithsonite, the Ca–O bond length of calcite is longer, and its stability is lower; therefore, the surface of calcite has higher reactivity, which means it is more likely to chelate with the phosphate group [88]. Similarly, from the perspective of surface solubility, the solubility products of smithsonite and calcite were  $1.46 \times 10^{-10}$  and  $4.96 \times 10^{-9}$ , respectively. The solubility product of calcite is much higher than that of smithsonite, indicating that there are more free metal ions on the calcite surface, providing sufficient active sites for the action of phosphate groups on the calcite surface. In addition, in the smithsonite–calcite flotation system, the pH of the pulp was controlled at approximately 9.5. At this pH range, the calcium component in the pulp solution mainly exists as  $\text{Ca}^{2+}$  and  $\text{CaOH}^+$  [93], whereas the Zn component mainly exists in the form of  $\text{Zn}(\text{OH})_2$  (aq) [94]. Compared to  $\text{Zn}(\text{OH})_2$  (aq), positively charged  $\text{Ca}^{2+}$  and  $\text{CaOH}^+$  are more likely to interact with negatively charged phosphate groups [95].

Organophosphonic acids contain one or more  $\text{PO}(\text{OH})_2$  groups. They are also used in flotation owing to their stable C–P bonds and strong chelation with metal ions. The phosphonic acid groups (directly connected to carbon atoms), including –OH, – $\text{CH}_2$ , and – $\text{COOH}$ , and other groups in organic phosphonates can form three-dimensional bicyclic or polycyclic structures when chelated with  $\text{Ca}^{2+}$  [96]. Chen et al. [97] used amino trimethylene phosphonic acid as a depressant in the flotation system of smithsonite–calcite and found that a large amount of amino trimethylene phosphonic acid can chelate with the  $\text{Ca}^{2+}$  sites on the surface of calcite and be chemically adsorbed on the surface of calcite, thereby depressing the adsorption of sodium oleate on the surface of calcite (Figure 13). In the smithsonite flotation system, the amount of amino trimethylene phosphonic acid adsorbed on the surface of smithsonite was significantly lower than that on the surface of calcite, which almost did not affect the subsequent adsorption of sodium oleate on the surface of smithsonite. Chen et al. [97] believed that, in addition to the difference in the chelating properties of amino trimethylene phosphonic acid on the surface of the two minerals due to the different chemical compositions of the mineral surfaces, the distance between the O–O bond in the  $\text{PO}(\text{OH})_2$  group of amino trimethylene phosphonic acid and the distance of the Ca–Ca bond on the surface of calcite is better than that of the Zn–Zn bond on the surface of smithsonite, that is, the surface structure of calcite makes it easier for amino trimethylene phosphonic acid to chelate with the metal sites on the mineral surface and form a cyclic chelate [98].

Polyepoxysuccinic acid is a biodegradable and low-cost organic acid, and its molecular structure is shown in Figure 13. Liu et al. [99] found that the flotation separation of smithsonite and calcite could be achieved using sodium oleate as the collector and polyepoxysuccinic acid as a depressant. Polyepoxysuccinic acid can react with  $\text{Ca}^{2+}$  on the calcite surface to form a hydrophilic chelate and reduce the adsorption sites of sodium oleate on the calcite surface, thereby enhancing the hydrophobicity of the calcite surface.

Quartz is one of the typical gangues in zinc oxide ores. In the flotation of quartz with sodium oleate as a collector, because of the lack of active sites for sodium oleate on the quartz surface, it is not easy to directly collect quartz with sodium oleate, showing weak floatability. However, owing to the high solubility of smithsonite,  $\text{Zn}^{2+}$  in smithsonite dissolves from the mineral surface to the pulp during the grinding and flotation processes [100]. The interaction between  $\text{Zn}^{2+}$  in the pulp and the quartz surface enhances the reactivity of the quartz surface with the collector, which greatly improves the floatability of quartz and increases the difficulty of flotation separation of smithsonite and quartz. Based on the characteristic that the Zn active sites on the quartz surface can form soluble complexes with chelating reagents, Wang et al. and Zhao et al. [101–103] investigated the selective depression mechanism of 1-hydroxyethylidene-1,1-diphosphonic acid, sodium polyaspartate, and tetrasodium iminodisuccinate on a smithsonite–quartz flotation system when sodium

oleate was used as the collector. The structures of 1-hydroxyethylidene-1,1-diphosphonic acid, sodium polyaspartate, and tetrasodium iminodisuccinate are shown in Figure 14. The results show that 1-hydroxyethylidene-1,1-diphosphonic acid, sodium polyaspartate, and tetrasodium iminodisuccinate could chelate the Zn sites on the surface of quartz and transfer them to the solution, resulting in a decrease in the adsorption of sodium oleate on the surface of quartz, which effectively weakened the floatability of quartz. Because of the different crystal structures of smithsonite and quartz, the chemical environments and reactivities of the Zn sites on the surfaces of the two minerals were different. The reactions of 1-hydroxyethylidene-1,1-diphosphonic acid, sodium polyaspartate, and tetrasodium iminodisuccinate with the Zn sites on the surface of smithsonite were weak. Therefore, they did not have significant effects on the floatability of smithsonite to realize the flotation separation of smithsonite and quartz. The conceivable separation mechanism using chelating depressants is depicted in Figure 14.

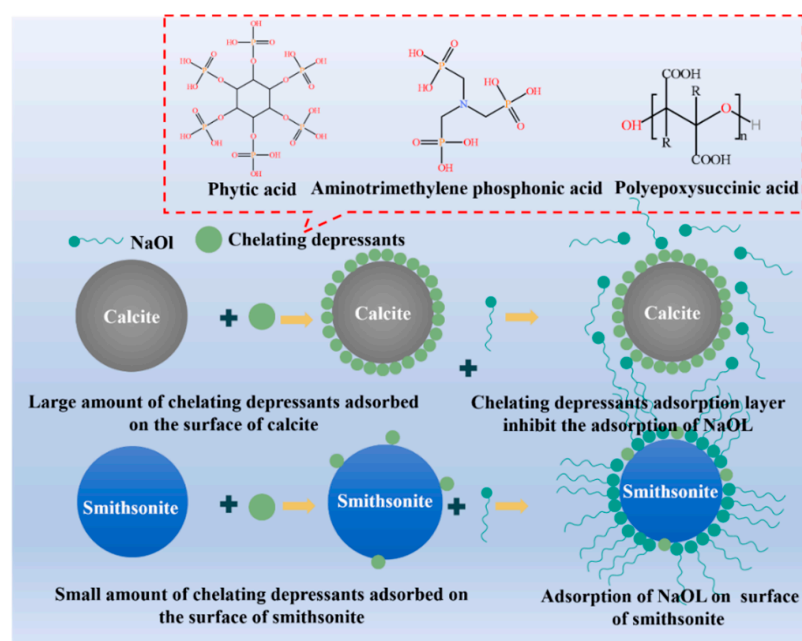


Figure 13. Structure of chelating depressants and its interaction model with smithsonite and calcite [90,97,99].

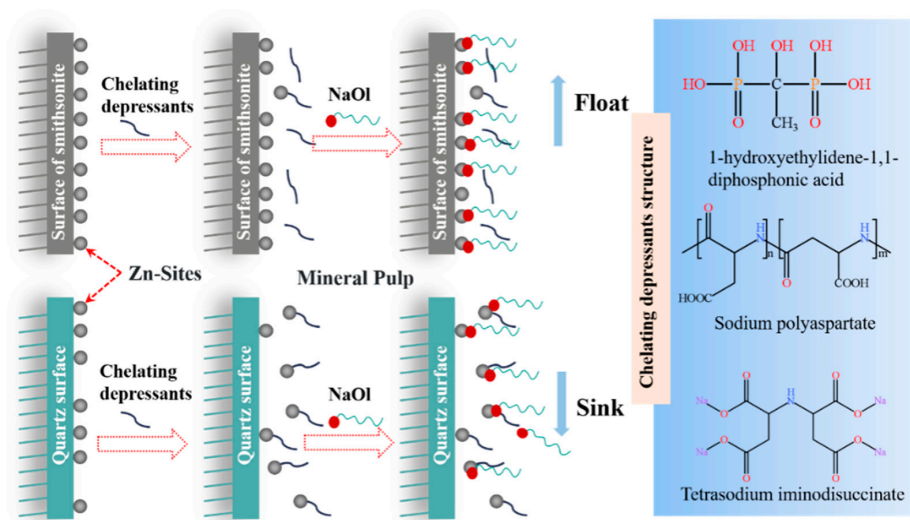


Figure 14. Structure of chelating depressants and its interaction model with smithsonite and quartz [101–103].

## 5. Conclusions and Outlook

Flotation is an effective and economical method for the treatment of zinc oxide ores. However, it is difficult to achieve the efficient flotation recovery of zinc oxide minerals in industrial production because of the difficulty of the flotation of zinc oxide minerals and the difficulty of mineral separation owing to the similar surface properties of the target minerals and gangue minerals. Recently, the development of novel high-selectivity zinc oxide flotation reagents has become a research hotspot. Various chelating reagents have been used in the flotation of zinc oxide minerals, effectively promoting the progress of zinc oxide ore flotation technology. In this study, combined with the crystal structure and surface properties of typical zinc oxide and gangue minerals, the research progress on chelating reagents and mechanisms in zinc oxide ore flotation is reviewed. The conclusions are as follows:

(1) When chelating reagents are used as collectors for zinc oxide minerals, the molecular structure usually includes polar chelating groups composed of O, N, P, and S and hydrophobic non-polar hydrocarbon groups. In the flotation process of zinc oxide minerals, chelating collectors can react with  $\text{Zn}^{2+}$  on the surface of zinc oxide minerals to form hydrophobic chelates, thereby improving the surface floatability. The pH range of 5–10 is optimum for the interaction of the chelating collector with the zinc oxide mineral surface. In this pH range, the main components on the surfaces of smithsonite and hemimorphite are  $\text{Zn}^{2+}$  and  $\text{ZnOH}^+$ , which can provide sufficient active sites for the adsorption of chelating collectors on the mineral surface. Pulp pH can affect the chemical state of the active site on the zinc oxide mineral surface and gangue surface, and then affect the reaction between the mineral surface and chelating reagents. Therefore, the selectivity of the chelating reagent can be enhanced via pH adjustment, and the flotation separation of zinc oxide minerals and gangue can be realized. In addition, the collection capacity of chelating reagent is also related to the chelating group activity, the hydrophobic chain length, and other factors.

(2) Chelating activators are commonly used in the flotation of zinc oxide ores when amine cations are used as collectors. In addition to the chelating group, the structure of the chelating activator usually contains a benzene ring or a shorter alkyl group. It primarily activates zinc oxide minerals by initially enhancing the hydrophobicity of the zinc oxide mineral surface and promoting the dissolution of the mineral surface.

(3) Chelating depressants used in the flotation of zinc oxide ores are mostly derived from scale depressants in the field of environmental protection. The molecular structure of chelating depressants usually contains polar functional groups ( $-\text{PO}(\text{OH})_2$ ,  $-\text{COOH}$ , etc.) that can chelate metal ions on the mineral surface, and the hydrophilic groups ( $-\text{OH}$ , etc.) in chelating depressants can enhance the mineral surface's hydrophilic property. In addition, chelating depressants can achieve the selective depression of gangue by adsorbing onto the surface of gangue to hinder the adsorption of collectors and dissolve the active ions on gangue surface to reduce their reactivity with collectors.

The use of chelating reagents in the flotation of zinc oxide ores is encouraging, and ideal flotation results have been obtained in laboratory flotation tests. However, the application of these new chelating reagents for the flotation of zinc oxide ores in industrial production faces many challenges, including flotation index, cost, and environmental pressure. Further research should be carried out on the combination of different chelating reagents, and the combination of new chelating reagents and traditional reagents. Examples include the combination of chelating collectors with traditional collectors such as xanthate, dodecylamine, and sodium oleate, and the combination of chelating depressants/activators and inorganic depressants/activators. In addition, it is necessary to further investigate the chelating effect of chelating groups on minerals with similar physical and chemical surface properties to better understand the interaction mechanism between chelating reagents and mineral surfaces. Understanding the chelation effect between the chelating group of the reagent and the metal ions on the surface of the mineral can provide theoretical guidance for the selection or design of new selective collectors or depressants/activators for zinc oxide ores.

**Author Contributions:** Z.S.: Data Curation, Formal Analysis, Investigation, Methodology, Software, Visualization, Writing—Original Draft, and Writing—Review and Editing. S.W.: Investigation, Methodology, Project Administration, Resources, Supervision, Validation, and Writing—Review and Editing. G.H.: Conceptualization, Data Curation, Formal Analysis, Funding Acquisition, Investigation, Methodology, Project Administration, Resources, Supervision, Validation, and Writing—Review and Editing. Q.F.: Formal Analysis, Funding Acquisition, Investigation, Methodology, Project Administration, Resources, Supervision, Validation, Visualization, and Writing—Review and Editing. All authors have read and agreed to the published version of the manuscript.

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