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Invited Review

Flotation separation depressants for scheelite and calcium-bearing minerals: A review

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Abstract: Owing to the depletion of wolframite, the focus of tungsten extraction has gradually shifted to scheelite. However, separating the associated minerals (e.g., apatite, fluorite, and calcite) and scheelite is challenging because their surface physicochemical properties are similar to those of scheelite. Fortunately, researchers have made substantial progress in separating the minerals of scheelite by using depressants. This study reviews the application and inhibition mechanism of inorganic depressants in obtaining tungsten from its calcium-bearing minerals. The application of new organic depressants in obtaining tungsten from its calcium-bearing minerals and the associated mechanisms are also summarized. After an objective assessment of inorganic and organic depressants' advantages and disadvantages, possible future research directions for inorganic and organic depressants are proposed. Herein, we provide a theoretical basis for developing scheelite flotation depressants.

Keywords: scheelite; calcium-bearing minerals; flotation; depressant

1. Introduction

Tungsten resources have received considerable research attention because of their strategic importance in the continuous development of the aerospace industry and other advanced technologies. Wolframite and scheelite are the most widely available tungsten minerals. Moreover, wolframite is the preferred mineral for mining tungsten because it contains a higher grade of WO_3 than scheelite, has a relatively simple mineral composition, and is easy to mine [1]. However, the rapid development of cutting-edge technologies, such as aerospace and atomic energy technologies, has increased the consumption of tungsten. Moreover, extensive mining has nearly exhausted the high-grade wolframite resources available in nature. Hence, the utilization of scheelite has become a focal point of research [2–4], explaining the rapid increase in the number of studies on scheelite flotation in recent decades (Fig. 1).

China has abundant scheelite reserves (6,723,800 tons). However, problems, such as low ore grade and numerous fine particles, are encountered during its mining and utilization. Depending on the gangue minerals, the two common types of scheelite are silicate mineral-associated scheelite and calcium-bearing mineral-associated scheelite [4–6]. Separating scheelite from its silicate minerals is easy owing to the substantial difference in the flotation behaviors of scheelite and silicate minerals. However, separating scheelite from its calcium-bearing minerals is difficult owing to their similar physical and chemical properties in scheelite pulp [7–10].

Sodium oleate is a commonly used collector that is used during scheelite flotation; however, its poor selectivity hampers the separation of scheelite and calcium-bearing minerals [11–12]. The use of depressants is necessary for separation of scheelite and calcium-bearing minerals. Scholars systematically studied inorganic depressants such as sodium silicate and found that acidifying sodium silicate can effectively improve its inhibition effect. However, scholars have differing views on the best acidification formula. In addition, scholars found that organic depressants have good prospects for application in the separation of scheelite and calcium-bearing minerals. Moreover, the adsorption mechanism of organic depressants on the surface of calcium-bearing mineral crystals and the related influencing parameters were thoroughly investigated.

Calcium-bearing minerals associated with scheelite ($CaWO_4$) mainly include apatite ($Ca_5(PO_4)_3(F,Cl,OH)$), calcite ($CaCO_3$), and fluorite (CaF_2) [13]. The main reason for the difficulty in separating scheelite from calcium-containing gangue is the complex behavior of these calcium-bearing minerals in the pulp (including interactions between various dissolved ions). The WO_4^{2-}, F^-, and CO_3^{2-} produced owing to the dissolution of calcium-bearing minerals in scheelite pulp are adsorbed on the mineral surface and undergo chemical reactions subsequently, resulting in the mutual transformation

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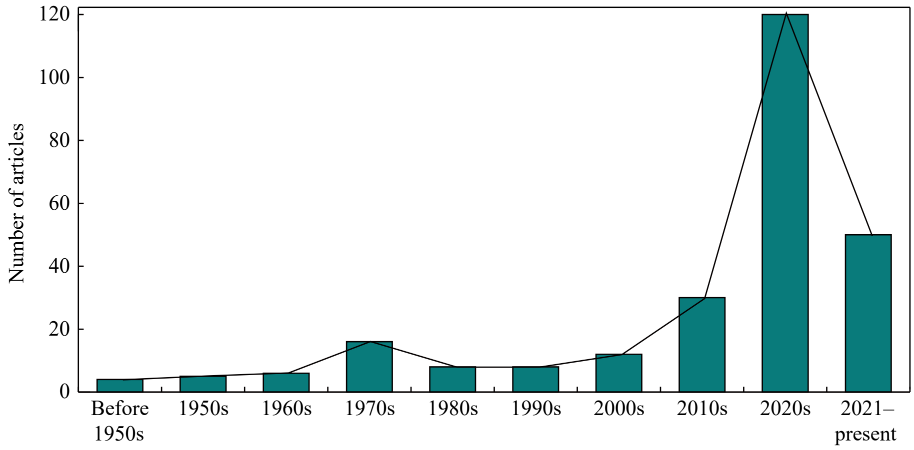


Fig. 1. Articles related to scheelite flotation in recent decades.

of the mineral surface components and changing the properties of the mineral surface as well as making calcium-bearing minerals eventually exhibit similar surface physicochemical properties and floatability [14–16].

Furthermore, dissolved cations (such as Ca^{2+}) in the pulp react with anionic collectors to form precipitates, and the dissolved anions compete with the anionic collectors to be adsorbed on the mineral surface, resulting in reduced scheelite flotation efficiency [17–18].

The crystal structure of minerals leads to differences in mineral surface characteristics and flotation properties [15,19–20]. In the scheelite crystal structure, calcium ions are highly active in the crystal section of scheelite. When scheelite is deconfined along the {101} surface, positively charged Ca^{2+} and negatively charged O^{2-} are formed on the mineral surface. The WO_4 tetrahedra resemble a positive tetrahedral structure, with one O ion on the same level as the Ca ion and the remaining three O ions located below the Ca ion; the Ca ion is prominently positioned and easily chemisorbed on the sodium oleate. Therefore, sodium oleate can quickly react with the Ca ions on the scheelite surface to form calcium carboxylate and precipitate on the scheelite surface [21–24]. By contrast, some reactive oxygen ions on the surface of calcite crystals mask some Ca ions. But the calcite surface has a greater density of calcium ions and more sites compared to the scheelite surface (the numbers of Ca plasmas on the common dissociation surfaces {2134} and {1014} of calcite are 4.98 and 4.95 nm^{-2}, respectively, and those on the dissociation surfaces of scheelite {001}, {101}, and {111} are 3.64, 3.04, and 4.51 nm^{-2}, respectively); therefore, the addition of a small amount of sodium oleate can substantially improve the hydrophobicity of the calcite surface [25–26]. Compared with scheelite and calcite, fluorite has a higher ionic content and is easily hydrated in solution, thereby exhibiting poor floatability. In addition, fluoride ions with large radii in the fluorite molecule have a shielding effect on calcium ions with small radii, hindering the adsorption of oleate ions on the mineral surface and reducing the floatability of fluorite. Similar to calcite, the proportion of calcium ions on the mineral surface of fluorite is higher than that of fluoride ions. Therefore, sodium oleate can also effectively collect fluorite [27–30].

The reasons for the difficulty in separating scheelite and calcium-bearing minerals are as follows: (1) The surfaces of these minerals are subjected to interconversion in the pulp, and the directional regulation of the interconversion of the surface materials of calcium-bearing minerals is the key to separating the scheelite concentrate from the calcium-bearing gangue. (2) The ions dissolved on the surface of calcium-bearing minerals affect the pulp environment by changing the pH of the scheelite pulp and reacting with the reagents, thus influencing the expected flotation of scheelite flotation. (3) Mineral surfaces are difficult to separate because they have similar flotation behavior and identical active particles and crystal structures.

2. Inorganic depressants

In the scheelite flotation process, depressants are highly important to improve the concentrate grade of scheelite. Based on the limited research on the flotation of scheelite, the introduction of inorganic depressants can achieve concentrate enrichment at room temperature. Water glass, phosphate, and high-valence metal ions are the most commonly used inorganic depressants for separating calcium-containing gangue and scheelite. Many studies on inorganic depressants have been carried out.

2.1. Sodium silicate

2.1.1. Sodium silicate

Sodium silicate is a soluble inorganic silicate often used in industrial production as the primary depressant for fluorite, calcite, and apatite [3,9,31–32]. In field production, sodium silicate helps achieve good flotation index, as demonstrated by Martins and Amarante [33] and Ji *et al.* [34]; Martins and Amarante used sodium silicate to suppress fluorite and calcite in the Tarouca tungsten ore, and Ji *et al.* relied on sodium silicate for the secondary enrichment of tungsten in Huangshaoping tailings, which yielded concentrates containing more than 70wt% WO_3. However, sodium silicate must be added in large doses during flotation, which can affect the subsequent process.

The form of sodium silicate in the scheelite pulp is complex and is determined by two key parameters: the pH value of the slurry and the concentration of sodium silicate. Previous studies reported that pH in the range of 7–11 is suitable for scheelite flotation with sodium silicate as the depressant [35–36]. In the above aqueous solution, sodium silicate exists in the forms of silica monomer [37], $Si(OH)_4$, and $SiO(OH)_3^-$ [38–39]. $Si(OH)_4$ and $SiO(OH)_3^-$ combine with exposed calcium ions on the mineral surface to form silicates adsorbed on the mineral surface, increasing their hydrophilicity. Owing to the dense surface density of Ca sites and short Ca–O bonds, calcite, fluorite, and apatite acquire high-energy Ca sites resulting in high silicate adsorption [8,40]. The adsorption of silicates reduces the hydrophobicity of calcium-bearing minerals and hinders the adsorption of collectors, inhibiting calcium-containing minerals such as calcite. Sodium silicate enters an "activated state" at high temperatures. The "activated sodium silicate" in combination with sodium oleate reduces the depression of scheelite while increases the depression of gangue minerals considerably, which is the basis of the Petrov process realization [41].

The suitable sodium silicate concentration is crucial for the flotation separation of scheelite and gangue. As measured using the formation point of calcium silicate precipitation, a low concentration of sodium silicate can properly adjust the pH, improve the floatability of minerals, and promote flotation. Moreover, extremely high concentration of sodium silicate promotes mineral surface precipitation, increases the hydrophilicity of minerals [42].

2.1.2. Modified sodium silicate

The addition of metal ions or sulfuric acid is a standard method for sodium silicate modification. The combination of sodium silicate with metal ions, such as Fe^{2+} and Mg^{2+}, can improve its inhibitory ability [43–44]. Other metal ions have different effects on sodium silicate, and their inhibition properties with respect to sodium silicate are in the following order: $Pb^{2+} > Cu^{2+} > Zn^{2+}$ and $Al^{3+} > Cr^{3+} \geq Fe^{3+}$ [36,45]. Metal ions can be adsorbed on the surface of calcium-bearing minerals and change its surface potential, altering the flotation behavior of sodium silicate on the mineral surface. Moreover, the adsorption of metal ions on the surface of scheelite increases the adsorption of the anion collector, decreasing the adsorption of sodium silicate [46].

The acidified sodium silicate exhibits a substantial ability to depress gangue in the pulp [35,47]. As shown in Fig. 2, the acidified sodium silicate exhibits extremely strong inhibitory effects in an alkaline environment. The recovery of the calcite treated with acidified sodium silicate is considerably lower than the calcite treated with sodium silicate at 300 mg/L because many silicate colloidal particles are present in the acidic water glass solution when the solution is neutral or weakly alkaline [45,48]. These colloidal particles are highly hydrophilic and have a vital ability to cope with competitive adsorption, allowing them to selectively depress calcium-containing gangue, especially calcite [49–50]. However, different studies used different types of acid to make acidified water glass and used different ratios of acid to sodium carbonate. Therefore, determining the best "acidified water glass formulation" is difficult and has hindered the utilization of acidified water glass in flotation.

2.2. Phosphates

Phosphate depressants, which can form soluble complexes with metal ions such as calcium and magnesium, are widely used in scheelite flotation. Calcium-containing gangue can be considerably depressed using phosphate depressants, such as sodium hexametaphosphate (SHMP, $(NaPO_3)_6$), sodium pyrophosphate (SP, $Na_4P_2O_7$), and sodium tripolyphosphate (STPP, $Na_5P_3O_{10}$). Phosphate depressants are particularly effective in inhibiting calcite; the use of SHMP alone [51] or mixing SHMP with citric acid can substantially improve the efficiency of the separation of scheelite from calcite [52]. In addition, the pretreatment of minerals with sodium tripolyphosphate [53] or modification of minerals with SP and SHMP [54] can improve the grade of scheelite concentrate. Researchers [55–56] strongly demonstrated the feasibility of using polyphosphates at tungsten production sites: the final product with the expected WO_3 content was obtained for different ore properties using phosphate alone or in combination with sodium silicate.

The depressive effect of phosphate on calcium-bearing minerals is only related to the selective dissolution of calci-

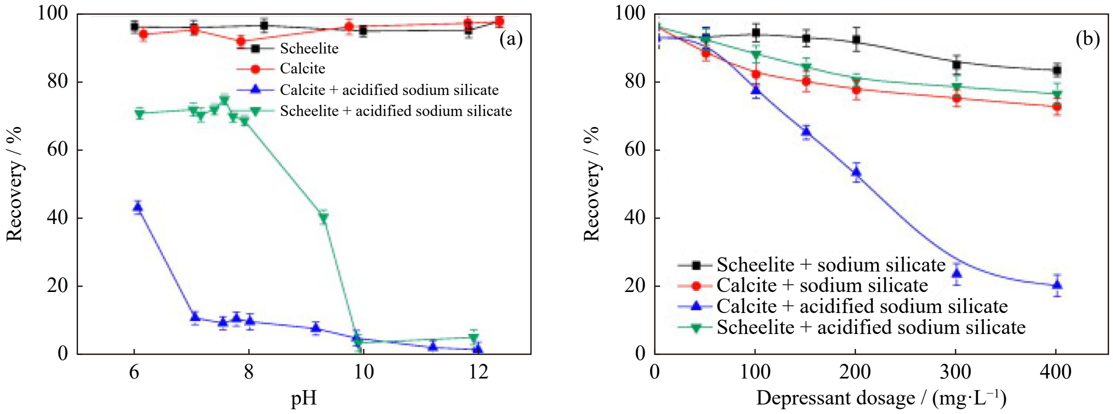


Fig. 2. Effect of pulp pH (a) and agent dosage (b) on the flotation separation of scheelite from calcite by sodium silicate and modified sodium silicate. Reprinted from *Miner. Eng.*, 80, B. Feng, X.P. Luo, J.Q. Wang, and P.C. Wang, The flotation separation of scheelite from calcite using acidified sodium silicate as depressant, 45-49, Copyright 2015, with permission from Elsevier.

um ions by phosphate, which is mainly determined based on the complexing ability of phosphate and the strength of Ca–O bonds on mineral crystals. Calcite has higher calcium ion activity and density on its main dissociation surface than scheelite. Therefore, the calcium ions on the calcite surface are readily dissolved into the slurry with the help of phosphate, preventing the collector from being adsorbed on the calcite surface in the form of calcium oleate [40,54]. As a good dispersant, phosphate (represented by SHMP) can effectively improve the dispersion of minerals as well as the adhesion of reagents and air bubbles to minerals, facilitating the separation of mixed minerals during flotation [57]. Similar to sodium silicate, the amount of phosphate inhibitor should be manageable. High phosphate concentrations inhibit a part of the scheelite flotation and are detrimental to the treatment of tailwater [58–63].

2.3. Summary

Inorganic depressants have played an essential role in the flotation of calcium-bearing minerals and are still the primary depressants used for scheelite recovery from calcium-bearing minerals. The flotation of calcium-bearing gangue using inorganic depressants is related to the dissolution behavior of the reagent in the scheelite pulp, where the dissolved substances, $Si(OH)_4$ and $SiO(OH)_3^-$, of sodium silicate combine with the exposed Ca ions on the mineral surface to create hydrophilic silicates adsorbed on the mineral surface. Phosphate can selectively dissolve Ca ions on the surface of calcite and other minerals, reducing the adsorption of collectors and inhibiting these minerals (Fig. 3).

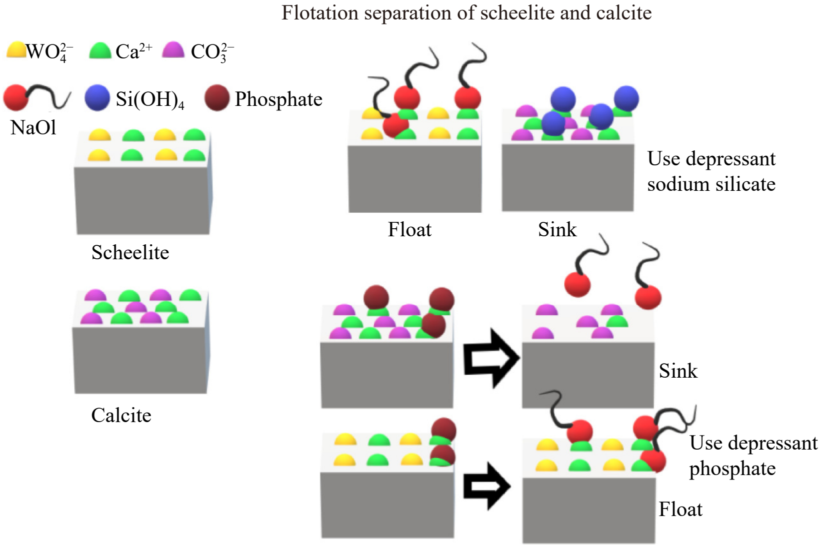


Fig. 3. Schematic of the flotation separation of scheelite and calcite.

The large dosage of traditional inorganic depressants frequently causes inconvenience in actual production of scheelite. Excessive use of sodium silicate leads to the formation of precipitates [64–65], resulting in pipeline blockage and reduced production efficiency. Furthermore, researchers have had to devote considerable efforts to devise follow-up treatments for the wastewater originating from the high-phosphorus beneficiation of the minerals because this wastewater poses a substantial threat to its surrounding water and soil.

3. Organic depressants

To prevent environmental problems arising from the extensive use of inorganic depressants, many researchers focused on organic depressants in recent years. Organic depressants are nontoxic and are easily degraded. Organic depressants are classified as either small molecules or macromolecules.

3.1. Small-molecule depressants

Small-molecule depressants typically have polar groups, such as –OH and –COOH, and the number of polar groups in a small-molecule depressant determines the strength of its depression. For example, depressants with only 1 or 2 polar groups have no depressive effect on fluorite, whereas organic matter with more than three polar groups can effectively depress fluorite. Small-molecule depressants commonly used in calcium-bearing minerals include oxalic acid, citric acid (CA), tartaric acid (TA), and lactic acid.

3.1.1. Oxalic acid

Oxalic acid is a weak dibasic acid that can depress calcium-bearing minerals, such as calcite and fluorite. In the 3-Hydroxy-2-naphthylhydroxamic acid (H_2O_5) system, oxalic acid can selectively depress calcite and fluorite. In its competition with H_2O_5 for the active site (Ca^{2+}) on the surface of calcium-containing gangue, oxalic acid has a greater advantage. This leads to the increased hydrophilicity of calcium-containing gangue that makes flotation difficult [66]. Moreover, oxalic acid is often used to make acidic sodium silicate and is applied in the flotation of scheelite [67–68]. Currently, the mechanism of the deep interaction of oxalic acid with calcium-bearing gangue in scheelite is unclear. Studies found that oxalic acid ($H_2C_2O_4$) reacts with scheelite ($CaWO_4$) to form water-soluble hydrogen aqua oxalato tungstate ($H_2[WO_3(C_2O_4)H_2O]$) and insoluble calcium oxalate monohydrate ($CaC_2O_4 \cdot H_2O$). Furthermore, gangue (oxides of Ca, Mo, Fe, and Mn) in scheelite dissolves in oxalic acid ($H_2C_2O_4$) to form complex oxalate ions [69].

3.1.2. CA

Citric acid is an efficient and selective flotation depressant with good depression of calcite and fluorite and can be used effectively in combination with sodium hexametaphosphate to separate scheelite from calcite [70–72]. Moreover, the selective depression of calcite by CA can be enhanced using Fe ions (Fe^{3+}). The reaction of Fe^{3+} with CA produces iron, which is easily adsorbed on oxygen sites on the calcite surface. Iron citrate is adsorbed on the calcite surface and forms a dense hydrophobic layer, decreasing the floatability of calcite substantially. However, the small amount of iron citrate adsorbed on the scheelite surface does not affect the flotation of scheelite [8].

The depression mechanism of CA on calcium-containing gangue is as follows. In pulp, CA can spontaneously form organic complex CaL^- on the fluorite surface and reduce its hydrophobicity. As shown in Fig. 4, the surface of CA-treated fluorite is rougher than that of scheelite. Thus, the adsorption of CA on the surface of fluorite far exceeds that on the surface of scheelite. Owing to the stimulation of CA, some calcium ions on the fluorite surface are dissolved into the slurry, decreasing the number of calcium ion active sites on the fluorite surface. This decreases the adsorption capacity of the collector on the fluorite surface, leading to a further decrease in fluorite floatability [72].

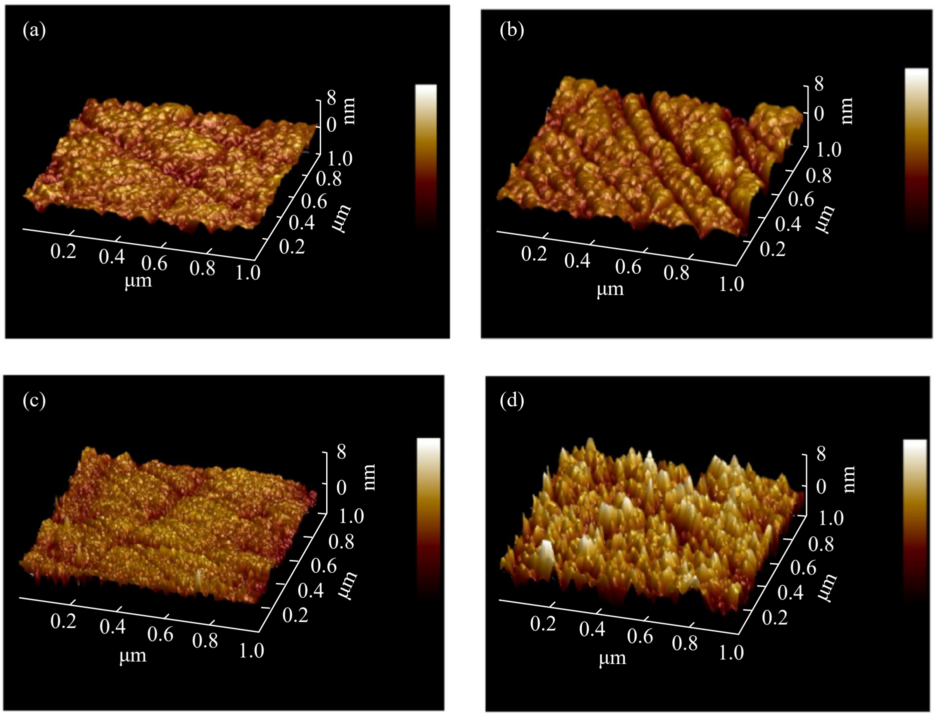


Fig. 4. 3D AFM images of the surface of scheelite (a, c) and fluorite (b, d) before and after reacting with CA. Reprinted from *Miner. Eng.*, 171, L.F. Dong, F. Jiao, W.Q. Qin, and Q. Wei, New insights into the depressive mechanism of citric acid in the selective flotation of scheelite from fluorite, art. No. 107117, Copyright 2021, with permission from Elsevier.

3.1.3. TA

Tartaric acid is a water-soluble, nontoxic, and highly biodegradable carboxylic acid [73] that has a good selective depressive effect on calcite and can effectively separate scheelite from calcite when used in combination with lead complexes of benzohydroxamic acid (Pb–BHA) [74]. Moreover, similar to CA, iron ions (Fe^{3+}) can enhance the selective depression of calcite using TA. The mixed depressant of iron ions (Fe^{3+}) and TA has a substantial coadsorption effect on the calcite surface. The preadsorption of Fe ions improves the adsorption capacity of TA on the calcite surface while hinder the adsorption of the collector sodium oleate (NaOl). The mixed depressant adsorbed on the calcite surface exists mainly in the form of chelate FeL^{2-} [75].

The distance between Ca atoms on the arbitrary dissociation surface of scheelite is 0.3867 nm, and those between Ca atoms on the calcite {104} surfaces are 4.988 and 0.4047 nm. The latter is closer to the distance between two adjacent O atoms (5.311 Å) on the carboxyl group in the TA ion (Fig. 5). Therefore, the Ca sites on the calcite surface are well matched with the carboxyl groups in the TA ion, and TA is preferentially adsorbed on the calcite surface. Moreover, the binding between the O atom in the carboxyl group and the Ca atom on the calcite surface may be bidentate coordination, with one TA ion cooperating with two Ca ions to produce calcium tartrate [74].

3.2. Macromolecular depressants

Macromolecular depressants are organic macromolecular compounds with a molecular weight greater than 10,000,

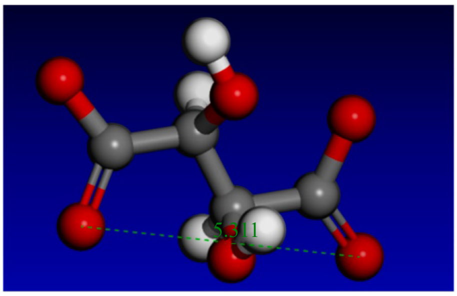


Fig. 5. Molecular diagram of the tartaric acid group [74]. Reprinted from *Colloids Surf. A*, 622, J.H. Fu, H.S. Han, Z. Wei, *et al.*, Selective separation of scheelite from calcite using tartaric acid and Pb–BHA complexes, art. No. 126657, Copyright 2021, with permission from Elsevier.

which is much higher than that of small-molecule depressants. Compared with small-molecule depressants, macromolecular depressants have far greater types and numbers of functional (such as –OH and –COOH) and hydrophilic groups, resulting in a better depressive effect on calcium-containing gangue. Macromolecular depressants used in the flotation of calcium-bearing minerals include tannins, polysaccharides, lignins, and synthetic high-molecular-weight organic compounds.

3.2.1. Tannins

Tannins are water-soluble polyphenols originating from plants, which form complexes with metal ions or precious metal salts in solution. Therefore, they have an inherent advantage in depressing calcium-bearing minerals. Hydrolytic tannins (tannic acids) are strongly inhibitory and can inhibit most calcium-bearing minerals, including scheelite [76–78]. Condensed tannins (quebracho) are marginally less inhibitory than hydrolytic tannins but are highly selective; these tannins have attracted great research attention and are mainly used to inhibit calcium-bearing minerals, such as calcite. Their inhibitory effect on calcite is influenced by factors such as the concentration of the reagent, pH value of the environment, temperature, and order of administration [76,79–81].

Quebracho is a polyphenol (Fig. 6), and its adsorption on the surface of calcium-bearing gangue is based on the phenolic hydroxyl group in its molecules. The chemisorption of quebracho on the surface of calcium-bearing minerals is based on hydrogen bonding (formed between –OH and Ca^{2+} or Ca^{2+} solubles). Moreover, its physical adsorption on the surface of calcium-containing gangue results from the electrostatic attraction between the negatively charged quebracho micelles and the positively charged surface of the calcium-containing gangue [59,76].

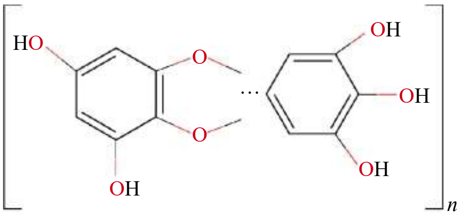


Fig. 6. Structure of quebracho [59].

3.2.2. Starch

Starch, cellulose, and gum are polysaccharides that are polymerized from sugar units, which are polymer compounds with –COOH, –OH, and ether groups. Although their specific structures differ, these polysaccharides and their processed products are excellent calcium-containing mineral depressants.

Starch is a high molecular polymer composed of glucose units and is a nonionic organic compound with a wide range of applications in the flotation of calcium-bearing minerals. Starch has a depressing effect on calcite and fluorite [82–83]. Dextrin is the product of the first step of the hydrolysis of aqueous starch solution in dilute acid, having a lower relative molecular weight and less depressing efficacy than starch; however, dextrin is more selective [84–85].

The adsorption methods of starch on the surface of calcium-bearing minerals include the following: (1) direct adsorption on the surface of fluorite and calcite through electrostatic interaction or physical bonding and (2) the interaction between the functional group (–OH) and Ca^{2+} to form a stable chemical bond that is adsorbed on the mineral surface. The latter is the primary adsorption type of modified starch on the mineral surface. Furthermore, the –OH in the modified starch consumes less internal electron binding energy compared to starch when interacting with Ca^{2+} on the calcite surface; however, the chemical connections established are more stable than starch [82–85].

3.2.3. Cellulose

Cellulose is a water-insoluble polysaccharide having numerous sources. Because cellulose is insoluble in water, cellulose depressants suitable for flotation, such as carboxymethyl cellulose (CMC), sulfonated cellulose sulfate, and carboxyethyl cellulose, are chemically modified. CMC is commonly used to depress calcite and fluorite, especially calcite, owing to the strong adsorption of CMC on the calcite surface (high adsorption coverage and high density). However, Ca^{2+} on the calcite surface may be partially dissolved in the slurry to build a “bridge” for CMC adsorption on the scheelite surface. Fortunately, this bridge can be blocked by adding an appropriate amount of sodium carbonate [86–88].

As shown in Fig. 7, the zeta potential of the calcite surface underwent a substantial negative shift after the addition of CMC, implying an association between the chemisorption of CMC on the surface of calcium-bearing minerals and the carboxyl group in CMC molecules. Moreover, CMC forms a polymer layer on the mineral surface, making it negatively charged, which may influence the adsorption of anionic collectors and inhibit the flotation of calcium-containing gangue [88–90].

3.2.4. Gum

Recently, gum-based depressants with excellent emulsifying, wetting, and thickening qualities have been frequently employed in various fields and studied extensively in the flotation separation of calcium-bearing minerals. Using the depressant xanthan gum, Dong *et al.* [91] realized the separa-

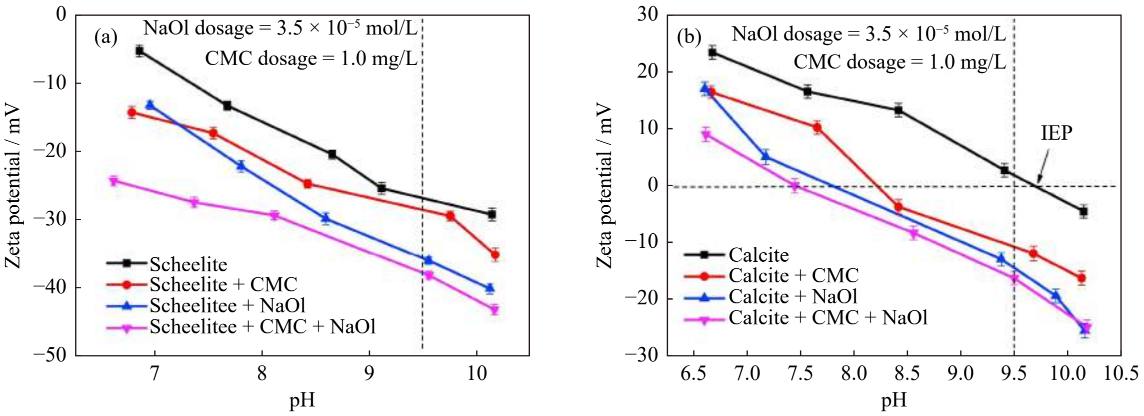
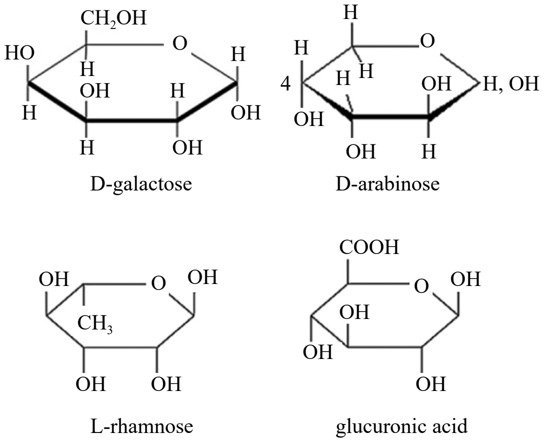


Fig. 7. Effect of different reagents on the zeta potential of scheelite (a) and calcite (b). Reprinted from *Appl. Surf. Sci.*, 463, L. Dong, F. Jiao, W. Qin, H. Zhu, and W. Jia, New insights into the carboxymethyl cellulose adsorption on scheelite and calcite: Adsorption mechanism, AFM imaging and adsorption model, 105-114, Copyright 2019, with permission from Elsevier. IEP—isoelectric point.

tion of scheelite and calcite, and Zhong *et al.* [92] realized the separation of scheelite and apatite. Zhao *et al.* [93] and Zhang *et al.* [94] separated scheelite from talc using sesbania gum and guar gum, respectively. Furthermore, fenugreek gum, saffron gum, tamarind gum, and psyllium gum are excellent calcite depressants. Although gum depressants are not applied to scheelite flotation, they are potential alternative depressants in separating scheelite from calcite [95–100].

As shown in Fig. 8, the molecules of gum depressants contain many polar groups. The main active groups are carboxyl and hydroxyl groups, and their interaction with the mineral surface includes (1) the chelation of –COOH with Ca^{2+} on the mineral surface and (2) –OH complexation with Ca^{2+} or hydrogen bonding between –OH and Ca^{2+} dissolved products [92,95,101].



D-galactose

D-arabinose

L-rhamnose

glucuronic acid

Fig. 8. Structure of the major polysaccharides in gum arabic [102]. Reprinted from *Colloids Surf. A*, 632, C.H. Zhong, B. Feng, L.Z. Zhang, W.P. Zhang, H.H. Wang, and Z.Y. Gao, Flotation separation of apatite and calcite using gum arabic as a depressant, art. No. 127723, Copyright 2022, with permission from Elsevier.

3.2.5. Lignin

Commonly used lignin inhibitors include humic acid and lignin sulfonates. Humic acid is a weakly acidic polyelectrolyte with a benzene ring, carboxyl, hydroxyl, methoxy, and other reactive groups. Soluble sodium humate and lignin sulfonate are good flotation depressants; the former is formed by the reaction of humic acid with sodium hydroxide solution and the latter by the reaction of lignin with sulfite. Sodium humate and calcium lignosulfonate (CLS) can effectively reduce the hydrophilicity of the calcite surface [103–104]. Sulfonated lignite, a humic acid derivative of lignite, is also an effective calcite depressant [105]. However, the pulp pH affects the inhibitory effect of CLS on scheelite and calcite, and the pulp pH range of 6–9 is the most suitable environment for the inhibitory effect of CLS [89,106–108].

The depressive mechanism of lignin-based reagents with respect to gangue is as follows: (1) The SO_3 group interacts with Ca^{2+} on the gangue surface and is adsorbed on the gangue surface. Alternatively, the dissolved product of –OH and Ca^{2+} undergoes hydrogen bonding and is adsorbed on the gangue surface. (2) The lignin depressant is completely ionized in scheelite pulp to form micelles, which are selectively adsorbed on the gangue surface under the influence of lattice anions on the mineral surface. The adsorption of the depressant on the gangue surface reduces the surface hydrophobicity of the gangue and hinders the adsorption of the collector in the subsequent process [106,109–110].

3.2.6. Synthetic polymer organic compounds

Organic polymer compounds formed from polymeric monomers, such as acrylic acid, acrylate, and acrylamide, are classified as synthetic polymer organic depressants. Common synthetic polymer organic inhibitors include polyacrylic acid, polyacrylamide, and their graft copolymers. Sodium polyacrylate can be uniformly adsorbed on the calcite surface, improving its hydrophilicity. Therefore, adding a small amount of sodium polyacrylate can substantially reduce the recovery of calcite [111]. Moreover, the inhibitory effect of sodium polyacrylate is more potent on fluorite than on scheelite because the absolute value of the adsorption energy of sodium polyacrylate on the surface of fluorite is more than that on the surface of scheelite (the greater the absolute value of the adsorption energy, the stronger the chemical reaction) [112].

The carboxyl group in the polymer depressant molecule reacts with Ca^{2+} on the gangue surface; hence, the depressant is stably adsorbed on the gangue surface. Moreover, the polymer molecules contain many hydrophilic groups, which increase the hydrophilicity and decrease the floatability of the gangue to separate scheelite and calcium-containing gangue.

3.3. Summary

Organic depressants, especially macromolecular depressants, are mostly derived from nature. Therefore, their use places a minimal load on the environment, which is in line with the scientific development concept of "living in harmony with nature." This characteristic gives organic depressants an advantage over inorganic depressants. Moreover, recent findings show that using organic depressants in the processing of calcium-bearing minerals will be future trend (Table 1).

Table 1. Summary of depressants for calcium-bearing gangues

Category	Depressant	Main functional group	Application	Ref.
Inorganic depressants	Sodium silicate	Silicate root	Laboratory, industry	[32–33]
	Sodium hexametaphosphate	Phosphate group	Laboratory	[51]
	Sodium pyrophosphate	Phosphate group	Laboratory	[54]
	Sodium tripolyphosphate	Phosphate group	Laboratory, industry	[54]
Organic depressants	Oxalic acid	Carboxyl group, hydroxyl	Laboratory	[66]
	Citric acid	Carboxyl group, hydroxyl	Laboratory	[72]
	Tartaric acid	Carboxyl group, hydroxyl	Laboratory	[74]
	Diethylenetriaminepentaacetic acid	Carboxyl group, hydroxyl	Laboratory	[113]
	Tanning	Carboxyl group, hydroxyl	Laboratory	[76]
	Sodium alginate	Carboxyl group, hydroxyl	Laboratory	[28]
	Starch	Hydroxyl	Laboratory	[82]
	Carboxymethyl cellulose	Carboxyl group, hydroxyl	Laboratory	[88]
	Xanthan gum, guar gum	Carboxyl group, hydroxyl	Laboratory	[95–100]
	Calcium lignosulfonate	Sulfonic acid group, hydroxyl	Laboratory	[105]
	Sulfonated lignite	Sulfonic acid group	Laboratory	[102]
	Sodium humate	Carboxyl group	Laboratory	[102]
	Sodium polyacrylate	Carboxyl group	Laboratory	[110]

The method of adsorption of organic depressants on mineral surfaces includes chemisorption and physical adsorption. The chemical action of organic depressants on the surface of calcium-bearing minerals can be attributed to the chelation of the active sites exposed on the mineral surface using the functional groups in the depressant molecules. Examples of chelation include chelating reactions between carboxyl groups in the depressant molecule and calcium or magnesium atoms on the surface of the mineral lattice as well as hydrogen bonding between hydroxyl groups in the molecule and dissolution products ($Ca(OH)^+$) of calcium atoms. As shown in Fig. 9, locust bean gum (LBG) molecules are adsorbed on the dolomite surface via the complexation reaction between the carboxyl group in the molecule and Mg atoms on the dolomite surface. A small proportion of the LBG molecules are adsorbed on the dolomite surface via the hydrogen bonding between the hydroxyl group and Ca atoms on the dolomite surface. Physical adsorption mainly occurs through electrostatic attraction and physical bonding, and this type of adsorption is present in the adsorption of some organic agents.

The mode of coordination between these functional groups and the Ca (Mg) site is yet to be discovered. Identifying a specific coordination model between them can facilit-

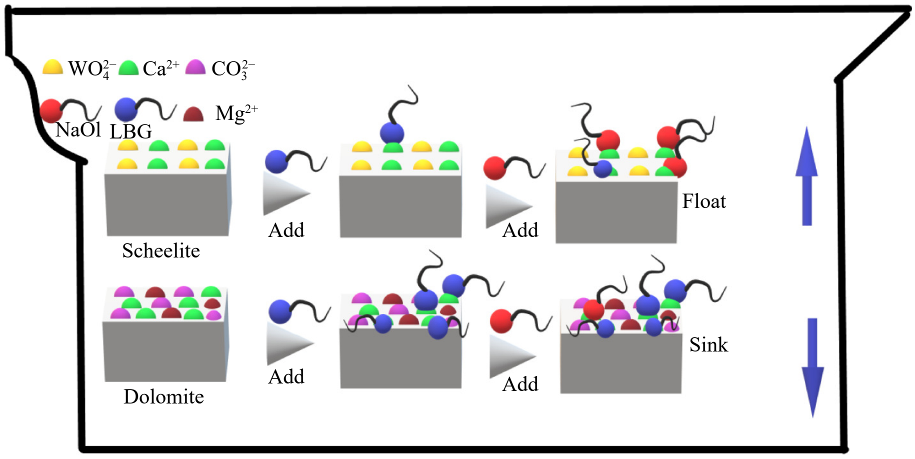


Fig. 9. Adsorption model of LBG for the flotation separation of scheelite and dolomite.

ate the design and synthesis of new organic depressants with great selectivity.

4. Outlook

(1) The application of depressants in combination is an important research direction. The combined use of inorganic and organic depressants for the inhibition of calcium-containing gangue is unknown. The effect of different ratios of agents, the order of addition, the type of agent, the structure of organic depressants (such as location and the number of functional groups), and other factors on the combination of agents and the separation mechanism is unknown and requires numerous experiments for verification.

(2) From the point of view of microcrystal structure, the factors affecting the influence of depressant functional groups at Ca sites on the surface of mineral crystals are worth exploring. Some of these factors are the type and number of atoms that react with the Ca site in the functional group, the binding mode of atoms with the Ca atom on the crystal surface, and the distance between the acting atoms in the functional group. This research direction is of great importance for developing new depressants, especially organic depressants.

5. Conclusions

(1) The consumption of scheelite, which is a strategic resource, increases yearly; however, its deposit grade gradually decreases. Flotation is the primary method to enrich scheelite, especially low-grade scheelite. However, the enrichment of scheelite via flotation is still a challenge owing to the presence of gangue, such as calcite and fluorite. The use of selective depressants is an effective way to overcome this challenge.

(2) Sodium silicate and phosphate are the widely used depressants with respect to the flotation separation of scheelite from the calcium-bearing gangue. However, owing to the decrease in scheelite grade, the dosage of sodium silicate needs to be increased to ensure a high scheelite grade, aggravating the negative impact of sodium silicate on the process operation and environment. Lower use of acidified sodium silicate has better inhibition, therefore, research on the modification of sodium silicate must be deepened to obtain the most suitable acidified water glass formula. Alternatively, using a combination of organic depressants can reduce the usage of inorganic depressants while maintaining the concentrate quality.

(3) Organic depressants are widely sourced, low-polluting, and easily degradable. Their development has resulted in the efficient flotation separation of scheelite from calcium-bearing gangue minerals to a certain extent. The main functional groups of organic depressants are carboxyl and hydroxyl groups. Carboxyl or hydroxyl group and Ca sites (Mg sites) undergo chemical chelation so that the organic agent is adsorbed on the gangue surface, resulting in its hydrophilicity and sinking. Hence, a systematic study of these functional groups and the chelation mechanism at the active sites on the mineral lattice surface can provide new ideas for the design and synthesis of new agents to depress calcium-bearing gangue. In addition, enhancement in the application scope or inhibition performance of some organic depressants after modification warrants further investigation.

(4) The Chinese government has incorporated “mining recovery rate, beneficiation recovery rate, and comprehensive utilization rate” into the development of the mineral resources standard system and continues to insist on “green mines.” Tungsten is an indispensable and poorly substitutable mineral needed in major strategic emerging industries in China; therefore, improving the recovery and comprehensive utilization rates of tungsten ore under the ambit of green mine development will become the focus of future studies. On this basis, inorganic depressants with serious environmental load will eventually be replaced by organic depressants with excellent flotation performance and environmental friendliness. Hence, the research and development of organic depressants will be the main task of scholars at this stage.

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Conflict of Interest

Bo Feng is a youth editorial board member for this journal and was not involved in the editorial review or the decision to publish this article. The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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