

## Advances in depressants for flotation separation of Cu–Fe sulfide minerals at low alkalinity: A critical review

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# Advances in depressants for flotation separation of Cu–Fe sulfide minerals at low alkalinity: A critical review

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**Abstract:** The flotation separation of Cu–Fe sulfide minerals at low alkalinity can be achieved using selective depressants. In the flotation system of Cu–Fe sulfide minerals, depressants usually preferentially interact with the pyrite surface to render the mineral surface hydrophilic and hinder the adsorption of the collector. This review summarizes the advances in depressants for the flotation separation of Cu–Fe sulfide minerals at low alkalinity. These advances include use of inorganic depressants (oxidants and sulfur–oxygen compounds), natural polysaccharides (starch, dextrin, konjac glucomannan, and galactomannan), modified polymers (carboxymethyl cellulose, polyacrylamide, lignosulfonate, and tricarboxylate sodium starch), organic acids (polyglutamic acid, sodium humate, tannic acid, pyrogallol acid, salicylic acid, and lactic acid), sodium dimethyl dithiocarbamate, and diethylenetriamine. The potential application of specific inorganic and organic depressants in the flotation separation of Cu–Fe sulfide minerals at low alkalinity is reviewed. The advances in the use of organic depressants with respect to the flotation separation of Cu–Fe sulfide minerals are comprehensively detailed. Additionally, the depression performances and mechanisms of different types of organic depressants on mineral surfaces are summarized. Finally, several perspectives on depressants vis-à-vis flotation separation of Cu–Fe sulfide minerals at low alkalinity are proposed.

**Keywords:** Cu–Fe sulfide minerals; flotation separation; selective depressants; depression mechanism

## 1. Introduction

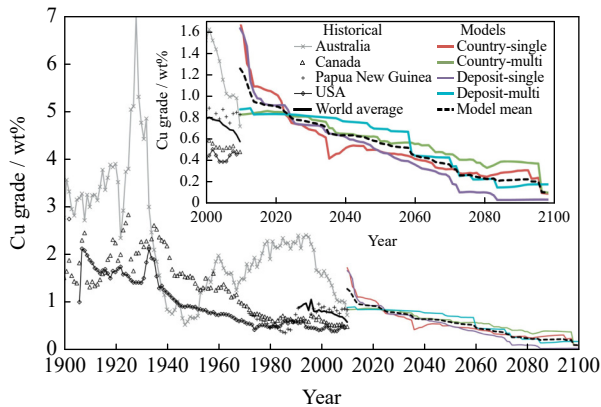
Copper (Cu) is an important nonferrous metal and is used as a raw material in industrial production. It is widely used in electrical and mechanical manufacturing and transportation owing to its satisfactory electrical conductivity and ductility [1–3]. During the mineralization process, copper sulfide minerals are often associated with iron sulfide minerals, forming Cu–Fe sulfide ores that contain copper sulfide and iron sulfide minerals [4–5]. The main copper sulfide minerals in Cu–Fe sulfide ores include chalcopyrite, bornite, and covellite, and the main iron sulfide ones are pyrite, pyrrhotite, and marcasite. Additionally, the gangue minerals primarily comprise quartz, sericite, chlorite, gypsum, other silicates, and carbonates. Currently, in industrial production of plants, the most common flotation separation method for Cu–Fe sulfide minerals is the separation of chalcopyrite from pyrite and pyrrhotite. In the separation process of Cu–Fe sulfide minerals, a large amount of iron sulfide minerals enter the copper concentrate if the iron sulfide minerals are not effectively depressed. This not only deteriorates the quality of the copper concentrate but also increases the smelting difficulty and pro-

duction cost of the subsequent metallurgical stage [6–8]. Additionally, Cu–Fe sulfide minerals contain precious metals such as gold and silver; therefore, it is necessary to consider the comprehensive recovery of high-value components to avoid the loss of precious metals from tailings. Hence, the goal of the flotation separation of Cu–Fe sulfide minerals is to ensure the effective depression of iron sulfide minerals and achieve comprehensive recovery of copper sulfide minerals and associated precious metals. With the economic progress of developing countries, copper demand will remain strong and rise in the coming decades [9–12]. However, over time, copper mining enterprises will deplete high-grade copper resources and aim for low-grade refractory ores, gradually declining the global average grade of copper ores (Fig. 1). This indicates a requirement for the efficient recovery of Cu–Fe sulfide minerals.

The most widely used methods for flotation separation of Cu–Fe sulfide minerals involve high-alkali and cyanide techniques, i.e., using lime and cyanide as depressants for iron sulfide minerals [13–16]. Lime and cyanide possess a strong depression capacity for iron sulfide minerals at low dosage cost, and they can achieve high efficiency of Cu–Fe separa-

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**Fig. 1. Actual historical Cu ore grades for selected countries up to 2010 and projected global ore grades for 2010 onward. Reproduced from *Resour., Conserv. Recycl.*, 83, S. Northey, S. Mohr, G.M. Mudd, Z. Weng, and D. Giurco, *Modelling future copper ore grade decline based on a detailed assessment of copper resources and mining, 190–201*, Copyright 2013, with permission from Elsevier.**

tion. However, they suffer disadvantages in industrial production. In the high-alkali technique, the addition of a large amount of lime as a depressant causes the mineralized froth to be sticky, calcifies gangue minerals to adhere to the pipe surface, and easily depresses precious metals in the high-alkali environment to be lost in the tailings [17–19]. To reduce the pH of the pulp in the subsequent process, pyrite depressed due to lime must be activated by adding a large amount of sulfuric acid; however, the cost of the depression treatment is high. Additionally, water must be recycled during actual production, and the return water that contains lime deteriorates the flotation environment after reuse, which is not conducive to the flotation separation of minerals [20]. Similarly, when pyrite is depressed using cyanide, the associated precious metals are easily dissolved and lost in the pulp, following which the cyanide-depressed pyrite becomes extremely difficult to activate and recover. Additionally, cyanide is highly toxic and poses a threat to flotation operations and the environment [21–23]. Therefore, it is necessary to develop nontoxic alternative depressants that can effectively depress iron sulfide minerals in neutral or low-alkalinity environments to reduce drug consumption, pipeline clogging, precious metal loss, and environmental pollution. Compared with the high-alkali technique, the low-alkali technique offers the advantages of high precious-metal recovery and low environmental impact. Therefore, the low-alkali technique has emerged as a potential direction for future flotation separation of Cu–Fe sulfide minerals.

Depressants used for the flotation separation of Cu–Fe sulfide minerals at low alkalinity usually include inorganic and organic ones. Inorganic depressants (oxidants and sulfur–oxygen compounds) have proved effective in reducing the floatability of pyrite. However, their use is limited because of the associated environmental and economic concerns [24]. Although oxidants and sulfur–oxygen compounds are either nontoxic or have low toxicity, they usually suffer poor depression capacity and require high dosages to

effectively depress iron sulfide minerals. Additionally, use of strong oxidants or reductants may incur additional costs on account of increased requirements for flotation equipment and operations. However, biodegradable organic depressants have a low environmental impact, remarkable depressive ability, and low dosages. In the backdrop of sustainable development and environmental policy requirements, the use of organic depressants to achieve clean mineral separation is on a rise. Compared with inorganic depressants, organic ones are characterized by a wide variety of types and sources and can be designed as per the molecular structures and functional groups of various reagents according to the principles of quantum chemistry to meet the requirements of specific flotation systems. These characteristics afford organic depressants with potential advantages in mineral flotation separation and have become an important direction for the development of depressants. Interaction between organic depressants and mineral surfaces is complicated because of the structural characteristics of the former and the heterogeneity of the latter. Various possible interactions can occur between organic depressants and mineral surfaces, including electrostatic attraction between their charged groups/molecules, hydrogen bonding and hydrophobic interactions, and chemical interactions between anionic groups (e.g., carboxyl or sulfonyl groups) or functional atoms (e.g., N and S atoms) of organic depressants and metal cations on mineral surfaces [25–28]. Fig. 2 shows several interaction mechanisms between organic depressants and mineral surfaces. Recently, several types of organic depressants, such as natural polysaccharides and modified polymers, have proven effective for the flotation separation of Cu–Fe sulfide minerals at low alkalinity [29–30]. Although organic depressants have the potential to partially or completely replace inorganic ones, their industrial applications for the flotation separation of sulfide minerals have rarely been reported. The flotation separation of Cu–Fe sulfide minerals in industrial production is still a high-alkali technique that employs inorganic depressants. The primary reason may be that organic depressants can firmly exist on the pyrite surface, which makes their desorption difficult on the pyrite surface and poses hindrance in achieving effective activation, resulting in the loss of pyrite and precious metals. Therefore, based on the interaction mechanisms between different types of organic depressants and mineral surfaces, it is important to develop organic depressants with satisfactory selectivity and ease of derepression for industrial applications.

With the increase in refractory Cu–Fe sulfide ores in industrial production, the problems associated with environmental impact and low comprehensive resource utilization caused by traditional high-alkali techniques are becoming increasingly prominent. Accordingly, development of efficient depressants with low alkalinity has become a focus of research. Currently, extensive research is being conducted on the flotation separation of Cu–Fe sulfide minerals; however, there is a lack of systematic reviews on depressants in the flotation systems of Cu–Fe sulfide minerals at low alkalinity.

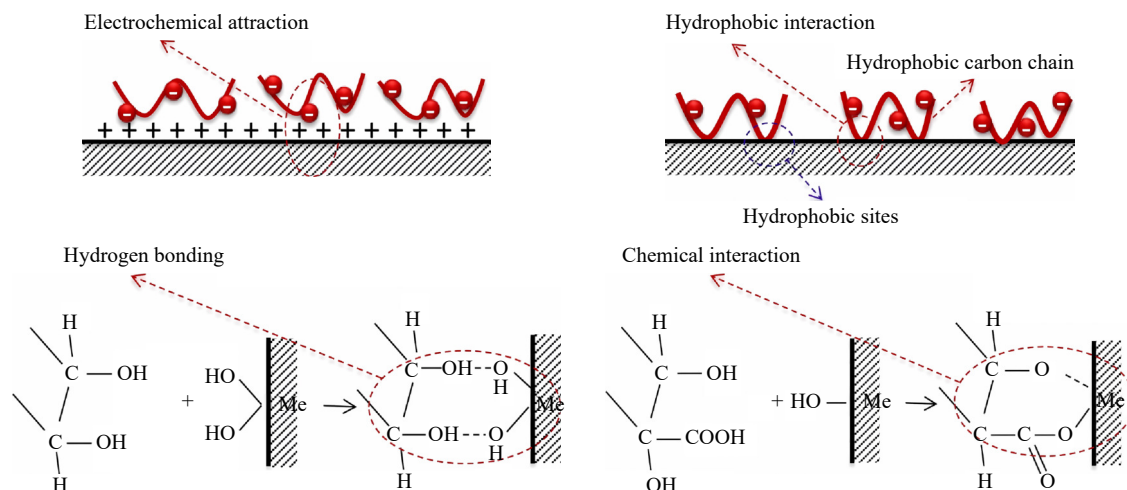


Fig. 2. Possible mechanisms of interaction between organic polymers and mineral surfaces. Reproduced from *Electrochim. Acta*, 174, Y.F. Mu, Y.J. Peng, and R.A. Lauten, *Electrochemistry aspects of pyrite in the presence of potassium amyl xanthate and a lignosulfonate-based biopolymer depressant*, 133–142, Copyright 2015, with permission from Elsevier.

This study compensates for the lack of progress in the application of inorganic and organic depressants in the flotation systems of Cu–Fe sulfide minerals at low alkalinity. The advantages and disadvantages of different depressants and their application challenges in industrial flotation are discussed, along with several perspectives on organic depressants in flotation systems at low alkalinity.

## 2. Issues in the flotation separation of Cu–Fe sulfide minerals

The flotation separation efficiency of sulfide minerals is affected by various factors, including the minerals' crystal characteristics, dissolution, particle size, and composition. The following are the primary issues associated with the flotation separation of Cu–Fe sulfide minerals.

(1) Lattice defects are common in pyrite, and the surface properties of pyrite are complex and variable, considerably changing its floatability during the flotation process [31–33]. Additionally, pyrites from different mining areas or sectors in the same mining area may have completely different floatabilities, limiting the adaptability of simple flotation separation techniques to pyrites with different floatabilities [34].

(2) In the mining and mineral processing stages, the oxidation of Cu–Fe sulfide minerals and dissolution of gangue minerals give rise to several unavoidable ions in the pulp, which affect the flotation separation of the minerals [35–38]. Unavoidable ions affect mineral flotation in several ways, which include the following: they interact with flotation agents and consume the effective content of flotation agents in the pulp; they nonselectively interact with the mineral surface by means of precipitation, thereby affecting the adsorption behavior of flotation reagents on the mineral surface; copper sulfide minerals dissolve and release copper ions into the pulp, which activate iron sulfide minerals, thus further complicating the flotation separation of Cu–Fe sulfide minerals.

(3) Comprehensive recovery of associated gold and silver

should be considered in Cu–Fe sulfide mineral flotation to enrich the precious metals in the copper concentrate. However, high-alkali and cyanide techniques are not conducive to the recovery of precious metals, and minerals having precious metals are easily depressed, resulting in the loss of valuable components [39].

(4) The proportion of low-grade and refractory Cu–Fe sulfide ores gradually increases during industrial production, and thus the mineral composition becomes more complex [40–43]. To liberate copper sulfide minerals, it is necessary to fully fine-grind or supplement the middle ore regrinding process for copper sulfide minerals with a fine distribution size, and more fine-grained minerals enter the flotation system, which considerably increases the difficulty of mineral flotation separation [44].

(5) Depressed iron sulfide minerals must be activated and recovered. Considering the comprehensive use of mineral resources and the recovery of associated precious metals, traditional high-alkali technique employing lime requires the addition of a large amount of sulfuric acid to activate depressed pyrite during flotation thereof. This increases the cost incurred on reagents, and ensuring a continuous supply of sulfuric acid poses a problem for enterprises. Organic reagents, such as pyrite depressants, possess the characteristics of low dosage; however, they often interact with the pyrite surface via stable chemisorption, which is not conducive to the derepression of pyrite. There have been only a few studies on the derepression of pyrite after treatment with organic depressants, which may be limiting the widespread application of organic depressants.

Aiming at solving these problems, researchers conducted a number of studies to achieve flotation separation of Cu–Fe sulfide minerals at low alkalinity, and they developed a series of pyrite depressants. Notably, pyrite depressants, including oxidants, sulfur–oxygen compounds, natural polysaccharides, modified polymers, organic acids, and sodium dimethyl dithiocarbamate, have been employed for the flotation separation of Cu–Fe sulfide minerals at low alkalinity. The depres-

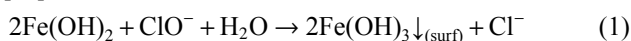
sion mechanisms of pyrite depressants include elimination of the collector or activator adsorbed on the pyrite surface [24–25], removal of active ions on the pyrite surface [24], and adsorption onto the pyrite surface to render the mineral surface hydrophilic and hinder the adsorption of the collector on the pyrite surface [28–30].

### 3. Inorganic depressants

#### 3.1. Oxidants

The oxidation of sulfide mineral surfaces affects the floatability of minerals. Factors that affect the surface oxidation of minerals in the flotation process include flotation reagents, pulp potential, pulp pH, and galvanic corrosion between different minerals or between minerals and the grinding medium during the grinding process [36,45–51]. Pyrite surfaces are more easily oxidized than chalcopyrite ones. The addition of appropriate oxidants can modify the surface components of pyrite to control its surface hydrophobicity and separate chalcopyrite and pyrite [52–53]. After the oxidants interact with the pyrite surface, hydrophilic substances, such as ferric hydroxide and sulfate, are formed on the mineral surface, following which collector adsorption is depressed [54–55].

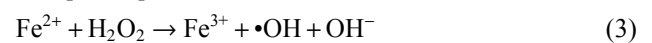
The addition of oxidants to the flotation system modifies the REDOX potential (Eh) of the pulp, which directly affects the balance of hydrophilic and hydrophobic species on the pyrite surface, thus affecting pyrite floatability. Pulp Eh can affect the surface composition of sulfide minerals by means of surface oxidation. Within a certain range of pulp Eh, slight oxidation of sulfide minerals can facilitate the formation of hydrophobic sulfur and the flotation of sulfide minerals [36,56]. However, over a wide range of pulp Eh values, the pyrite surface is more likely to produce hydrophilic metal hydroxides, which depresses the adsorption of xanthate onto the mineral surface [24]. Sodium hypochlorite and ammonium persulfate have been proven to be effective in the depression of pyrite flotation at low alkalinity, and the depression capacity of the oxidants is related to their oxidation [57]. At low alkalinity (pH 7–8), calcium hypochlorite reduces pyrite floatability in two manners [58]. Moreover, calcium hypochlorite exerts a strong oxidation effect on pyrite, resulting in the generation of many hydrophilic ferric hydroxide species on the pyrite surface. Additionally, calcium hypochlorite releases calcium ions into the pulp. During aeration and stirring, the pulp absorbs a certain amount of carbon dioxide from the air and forms carbonate ions. After the reaction between the calcium and carbonate ions, the hydrophilic calcium carbonate precipitates on the pyrite surface. The newly formed ferric hydroxide and calcium carbonate on the pyrite surface enhance the hydrophilicity of the pyrite surface and suppress collector adsorption. The reactions are as follows [58]:



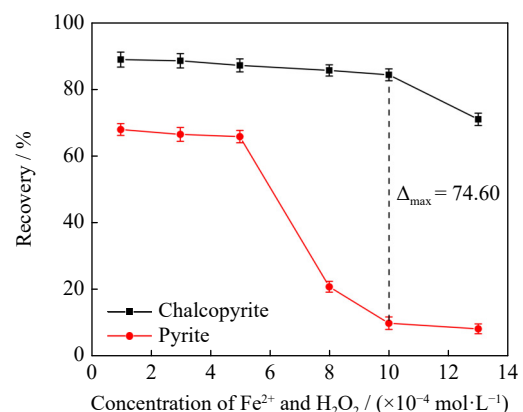
Bai *et al.* [59] supplemented the depression mechanism of

calcium hypochlorite on pyrite surfaces. After treatment with calcium hypochlorite, various hydrophilic species, such as calcium sulfate, calcium hydroxide, and calcium hydroxy, were formed on the pyrite surface; additionally, the contents of hydrophilic species from high to low included calcium hydroxy, iron carbonyl, hematite, calcium sulfate, and calcium carbonate. These newly formed hydrophilic species hindered the adsorption of dioxanthogen on the pyrite surface, resulting in pyrite depression at low alkalinity.

Hydrogen peroxide is a clean oxidant that can be used for pyrite depression. The Fenton reaction occurs between hydrogen peroxide and pyrite. Ferric ions in pyrite can be employed as catalysts for hydrogen peroxide to decompose it and generate hydroxyl radicals [60]. The reaction is as follows [61–62]:



The oxidation of hydroxyl radicals is stronger than that of hydrogen peroxide, which further facilitates the surface oxidation of pyrite and suppresses the flotation thereof. Khoso *et al.* [63] observed that the adsorption behaviors of xanthate on hydrogen peroxide-treated chalcopyrite and pyrite surfaces were considerably different and that more xanthate was absorbed on the chalcopyrite surface than that on the pyrite surface. Compared with chalcopyrite, pyrite is more easily oxidized; therefore, the flotation of pyrite treated with hydrogen peroxide is more obviously depressed. After treatment with an appropriate concentration of hydrogen peroxide, chalcopyrite and pyrite can be separated via flotation at low alkalinity [63–64]. Ding *et al.* [65] employed Fenton's reagent prepared using hydrogen peroxide and ferrous sulfate to selectively depress pyrite in a chalcopyrite–pyrite flotation system (pH 8). The ideal flotation recoveries of chalcopyrite and pyrite were 84.43% and 9.83%, that is, the maximum difference of flotation recovery between chalcopyrite and pyrite was 74.60% (Fig. 3). After treatment with hydrogen



**Fig. 3.** Flotation recoveries of chalcopyrite and pyrite using Fenton as depressant in the treated acid mine drainage system (mass ratio of  $\text{Fe}^{2+} : \text{H}_2\text{O}_2 = 1:3$ , ethyl xanthate:  $1 \times 10^{-4}$  mol/L, pH 8). Reproduced from *Miner. Eng.*, 187, Z. Ding, Y.X. Bi, J. Li, J.Q. Yuan, H.X. Dai, and S.J. Bai, Flotation separation of chalcopyrite and pyrite via Fenton oxidation modification in a low alkaline acid mine drainage (AMD) system, 107818, Copyright 2022, with permission from Elsevier.

peroxide, the pyrite surface was severely oxidized, generating large amounts of Fe(III)–OOH and Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, whereas only a few oxide/hydroxide species were generated on the chalcopyrite surface. The oxidation effects of hydrogen peroxide on the pyrite and chalcopyrite surfaces were different, and the affinity between the pyrite surface and xanthate was considerably weakened, which is the main reason why hydrogen peroxide can achieve the flotation separation of chalcopyrite from pyrite.

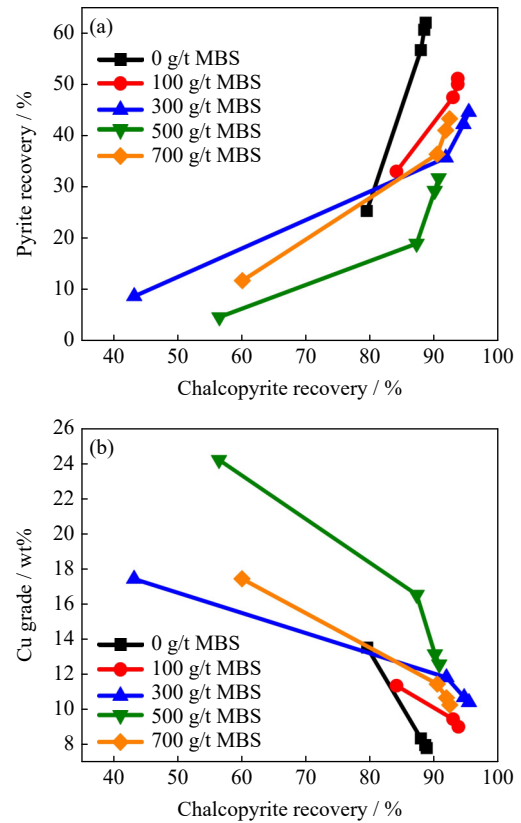
### 3.2. Sulfur–oxygen compounds

The interaction between xanthate and the surface of sulfide minerals is an electrochemical process. Charge transfer occurs between xanthate and sulfide minerals, following which dixanthogens or metal xanthates may be generated. It is generally believed that interaction between xanthate and pyrite surfaces primarily occurs via the formation of a dixanthogen, which is the main species that contributes to the surface hydrophobicity of pyrite [66–68]. Compared with xanthate, sulfite, pyrosulfite, and sulfur dioxide are more easily oxidized on the pyrite surface, which prevents the formation of dixanthogens [69]. Therefore, sulfur–oxygen compounds that contain low-valent sulfur can preferentially undergo oxidation reactions on the pyrite surface, thereby depressing the flotation of pyrite.

Sulfite and sodium sulfide consume dissolved oxygen in the pulp, reducing the pulp potential [70]. Strong competitive adsorption occurs between sodium sulfide and xanthate on the surface of sulfide minerals, which makes it difficult for the collectors to interact with the minerals' surface. Meanwhile, sulfide reagents decrease the potential at the solid–liquid interface, which is not conducive to the formation of hydrophobic dixanthogens [71]. Additionally, sodium sulfide can cause REDOX at low potentials, which prevents oxidation of xanthate to dixanthogen on the surface of sulfide minerals. Furthermore, sulfites may interact with hydrophobic substances on the mineral surface, and the addition of sulfites facilitates the formation of thiosulfate (S<sub>2</sub>O<sub>3</sub><sup>2-</sup>) from elemental sulfur (S<sup>0</sup>), which may be further oxidized to sulfate, reducing the surface hydrophobicity of pyrite [72–74].

Mu and Peng [75] observed that when seawater was used for the flotation of Cu–Fe sulfide minerals (pH 8.5), the addition of an appropriate amount of sodium metabisulfite (MBS) considerably reduced pyrite floatability, whereas chalcopyrite floatability was not notably affected. This may be because the combination of MBS and oxygen in the pulp resulted in the formation of oxidation radicals, which oxidized the high-activity species (Cu(I)–S) on the pyrite surface to form the hydrophilic copper hydroxide or copper sulfate. Additionally, MBS may react with dixanthogen on the pyrite surface to form free xanthate ions, which result in the desorption of dixanthogen from the pyrite surface [72,76]. For an MBS dosage of 500 g/t, the chalcopyrite recovery was 90.80%, whereas that of pyrite decreased to 31.90% (Fig. 4). However, upon increasing the dosage to 700 g/t, the pyrite recovery increased by 10% compared with that at 500 g/t. This may be

because excessive MBS considerably reduced the pulp potential, creating a strong reduction condition conducive to the formation of Cu(I)–S on the pyrite surface, thus reducing the depression capacity of MBS. However, the depression of pyrite using MBS requires a relatively large reagent dosage, the cost of which limits its wide application as a depressant [77].



**Fig. 4.** Effect of MBS dosage on pyrite recovery and copper grade versus chalcopyrite recovery using seawater (pH 8.5). Reproduced from *Miner. Eng.*, 142, Y.F. Mu and Y.J. Peng, The role of sodium metabisulphite in depressing pyrite in chalcopyrite flotation using saline water, 105921, Copyright 2019, with permission from Elsevier.

In summary, oxidants enhance the hydrophilicity of the pyrite surface by modifying the pulp potential and oxidizing the mineral surface to generate the hydrophilic ferric hydroxide. Oxidants that contain calcium species can form calcium sulfate, calcium hydroxyl, and calcium carbonate on the pyrite surface, which further hinders collector adsorption. Sulfur–oxygen compounds that contain low-valent sulfur can consume the dissolved oxygen in the pulp and preferentially undergo oxidation reactions on the pyrite surface, hindering dixanthogen formation, depressing pyrite flotation, and achieving flotation separation of Cu–Fe sulfide minerals at low alkalinity. Table 1 presents the inorganic depressants used for the flotation separation of Cu–Fe sulfide minerals at low alkalinity.

## 4. Organic depressants

Organic depressants possess the characteristics of biode-

**Table 1. Partial inorganic depressants for flotation separation of Cu–Fe sulfide minerals**

Depressant	Dosage / (g·t <sup>-1</sup> )	pH	Collector	Size / μm	Cu recovery / %	Fe recovery / %	Ref.
Potassium ferrate (K <sub>2</sub> FeO <sub>4</sub> )	250	8	Sodium butyl xanthate (SBX)	75–150	85.48	24.44	[52]
Calcium hypochlorite (Ca(ClO) <sub>2</sub> )	1000	7–8	Butyl xanthate	60–150	>90	19.20	[58]
Hydrogen peroxide (H <sub>2</sub> O <sub>2</sub> )	1360	9	SBX	38–74	>84	<24	[63]
Sodium metabisulfite (Na <sub>2</sub> S <sub>2</sub> O <sub>5</sub> )	500	8.5	Modified thionocarbamate/alkyl mercaptan	D <sub>80</sub> of 106 μm	90.8	31.9	[75]

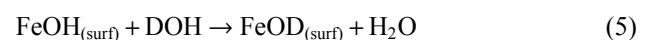
gradability, variety, functional groups, and spatial structure and have garnered considerable interest in the flotation separation of Cu–Fe sulfide minerals at low alkalinity. Organic depressants used for the flotation separation of Cu–Fe sulfide minerals usually have the following characteristics: the structure contains several polar groups with different functions, and the solidophilic groups interact with the pyrite surface to stabilize the presence of organic depressants on the mineral surface, hydrophilic groups, and water molecules that attract each other to facilitate the mineral surface to be hydrophilic.

#### 4.1. Natural polysaccharides

Polysaccharides are natural macromolecular polymers comprising several monosaccharides that can interact with the surface of sulfide minerals in the pulp. Thus, they are considered a promising organic depressant for the flotation separation of sulfide minerals. Studies have been performed on the use of various natural polysaccharides in the flotation separation of Cu–Fe sulfide minerals. However, the interaction mechanism between Cu and Fe sulfide minerals and different types of polysaccharides and the matching relationship between functional groups in polysaccharides and Cu–Fe sulfide minerals have not been systematically summarized. This limits the promotion and application of polysaccharides and the development of novel, high-efficiency polysaccharides as depressants in the flotation separation of Cu–Fe sulfide minerals.

Starch and its derivatives are biodegradable and contain abundant hydrophilic groups in their molecular structures that easily interact with the mineral surface by means of hydrogen bonding [78]. Bulut *et al.* [77] and Han *et al.* [19] observed that in the flotation of chalcopyrite and pyrite (pH 8–9), starch can interact with the pyrite surface and reduce pyrite floatability via chemical adsorption but has a small effect on chalcopyrite floatability. Owing to the macromolecular chain structure of starch, its adsorption covers the active metal sites on the pyrite surface and hinders the interaction between xanthate and the mineral surface. However, in a chalcopyrite–pyrite flotation system, the depression effect of starch on pyrite is not ideal, and thus it is difficult to obtain an ideal separation index via starch dosage adjustment. Therefore, research on starch derivatives and modified starch for the flotation separation of Cu–Fe sulfide minerals has been receiving increasing attention. Furthermore, dextrin is usually obtained via the thermal decomposition of starch and possesses a more branched structure than starch. Similar to

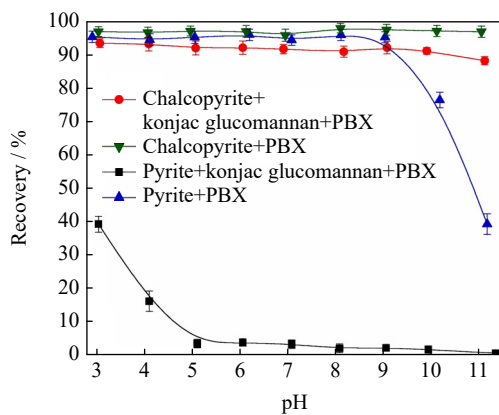
starch, dextrin contains various hydroxyl species that can be adsorbed onto the mineral surface via hydrogen bonding with the metal hydroxides on the surface. Valdivieso *et al.* [79] observed that dextrin was similar to cyanide in terms of depressing pyrite in a low-alkalinity medium (pH 8). Xanthate and dextrin can interact with different sites on the pyrite surface owing to the heterogeneity of the oxidized pyrite surface: The former interacts with the anode site on the unoxidized pyrite surface to generate dixanthogen, whereas the latter interacts with the ferric hydroxide species on the oxidized pyrite surface to cover the hydrophobic dixanthogen on the mineral surface, thereby depressing pyrite flotation. The reactions are as follows (X represents xanthate, D represents dextrin) [79]:



Researchers studied oxidized pyrite surfaces using various methods, including cyclic voltammetry, X-ray photoelectron spectroscopy, infrared spectroscopy, and Raman spectroscopy [80–82]. The formation of hydroxyl compounds with trivalent iron on the oxidized pyrite surface was demonstrated. Todd *et al.* [83] suggested that the hydroxide of trivalent iron (possibly goethite) was the oxidation product of the pyrite surface under alkaline conditions. Liu *et al.* [84] demonstrated that dextrin interacts with ferric hydroxide via chemical adsorption. Bogusz *et al.* [85] observed that dextrin was adsorbed on oxidant-treated pyrite surfaces and that Fe(III)–O/OH species were the adsorption sites of dextrin. Therefore, the adsorption of polysaccharides on the oxidized pyrite surface was ascribed to the interaction between the hydroxyl group in the glucose unit and metal hydroxide on the pyrite surface. Compared with the chalcopyrite crystal structure, the sulfur ions in the pyrite crystal structure are more easily exposed outside the crystal [86]. At low alkalinity, the pyrite surface is more likely than the chalcopyrite surface to undergo an oxidation reaction to generate metal hydroxide sites, which provides conditions for different adsorption behaviors of polysaccharides on the surfaces of pyrite and chalcopyrite.

Konjac glucomannan is a natural neutral polysaccharide extracted from the tubers of konjac, and its main units include mannan and glucose. Liu *et al.* [86] observed that in a chalcopyrite–pyrite flotation system, the pyrite depression capacity of konjac glucomannan was stronger than that of traditional organic depressants (starch, dextrin, and guar

gum). Additionally, the adsorption density of konjac glucomannan on the pyrite surface was considerably higher than that on the chalcopyrite surface, which may result in depression of pyrite flotation by covering the pyrite surface with dixanthogen. Over a wide pH range (5–11), the recovery of pyrite after treatment with konjac glucomannan was less than 5%, whereas the chalcopyrite floatability was not affected (Fig. 5). Konjac glucomannan exists on pyrite surfaces via physical adsorption. Hydrogen bonding and Brønsted acid–base interactions contributed to the adsorption of konjac glucomannan on the pyrite surface. Upon the adsorption of konjac glucomannan on the pyrite surface, the oxidation environment weakened, following which the oxidation of xanthate to dixanthogen on the pyrite surface was hindered, thus increasing the floatability difference between pyrite and chalcopyrite.



**Fig. 5.** Effect of pulp pH on the flotation performances of chalcopyrite and pyrite in different reagent systems at a pH of approximately 7.5 (potassium butyl xanthate (PBX): 9.5 mg/L, konjac glucomannan: 10 mg/L). Reproduced from *Miner. Eng.*, 145, D.Z. Liu, G.F. Zhang, Y.F. Chen, G.H. Huang, and Y.W. Gao, Investigations on the utilization of konjac glucomannan in the flotation separation of chalcopyrite from pyrite, 106098, Copyright 2019, with permission from Elsevier.

Galactomannan is a group of polysaccharides that contain mannose and galactose. On the basis of the mannose-to-galactose ratio, they can be categorized as guar gum, locust bean gum, fenugreek gum, and tara gum. Because galactomannan is rich in hydroxyl groups, it can interact with hydroxylated sulfide mineral surfaces via hydrogen bonding; therefore, it has received considerable attention in the field of flotation separation of sulfide minerals [87].

Guar gum, which is a galactomannan polysaccharide, is a natural polysaccharide extracted from guar beans. The guar gum molecule has a straight-chain structure, and its external active groups can easily approach the mineral surface. Additionally, most active hydroxyl groups in guar gum are located on the outside; therefore, they have a large hydrogen-bonding area and can easily form hydrogen bonds with mineral surfaces. Bicak *et al.* [88] observed that guar gum can considerably depress pyrite flotation at pH 9 and can be adsorbed on the pyrite surface via Brønsted acid–base interactions and hydrogen bonding. Qiu and Sun [89] reported that the addition sequence of guar gum and xanthate affected the

depressive effect of guar gum on pyrite flotation: Upon adding guar gum before xanthate, both were simultaneously adsorbed on the pyrite surface, covering the hydrophobic groups of xanthate, rendering the pyrite surface hydrophilic; when xanthate was added before guar gum, xanthate occupied the active metal sites on the pyrite surface and hindered the adsorption of guar gum, thus weakening the depressive effect of guar gum. However, guar gum can also reduce the floatabilities of chalcopyrite and pyrite. Guo *et al.* [90] showed that in a chalcopyrite–talc flotation system at pH 7, guar gum exhibited a depressive effect on chalcopyrite floatability with increasing dosage. Interestingly, guar gum can be used as a depressant for monoclinic pyrrhotite in the flotation separation of chalcopyrite from monoclinic pyrrhotite at low alkalinity [29]. Using guar gum as a depressant, a copper concentrate with 82.52% recovery and 22.35% grade was obtained at pH 8 [29]. Guar gum interacted with the chalcopyrite surface via weak hydrogen bonding; however, it was adsorbed on the monoclinic pyrrhotite surface via strong chemical adsorption, thus widening the difference in floatability between pyrrhotite and chalcopyrite.

Locust bean gum is a macromolecular polysaccharide with the same monomeric structure as guar and tara gum, but the mannose/galactose ratio is approximately four times higher. Shen *et al.* [91] observed that under low-alkalinity conditions, the addition of locust bean gum depressed pyrite floatability, whereas the depression of chalcopyrite floatability by locust bean gum was negligible. Acid–base interactions, hydrogen bonding, and hydrophobic interactions are considered potential mechanisms for the adsorption of locust bean gum on pyrite surfaces.

Natural polysaccharides such as starch, dextrin, and guar gum are polymers with basic glucose units containing various hydroxyl or carboxyl groups in their molecular structure, which can be adsorbed on mineral surfaces via hydrogen bonding. The abundance of functional groups in polysaccharides, such as hydroxyl or carboxyl, is a key feature behind their capacity to depress the flotation separation of sulfide minerals. Previous studies on polysaccharides as depressants in the flotation separation of Cu–Fe sulfide minerals at low alkalinity noted that polysaccharides often possess a strong chemical affinity for iron hydroxyl or ferric hydroxide species to selectively adsorb onto the pyrite surface, rendering the pyrite surface hydrophilic or hindering collector adsorption on the mineral surface. The precondition for effective depression of polysaccharides is that the pyrite surface must generate iron hydroxyl/ferric hydroxide species via hydroxylation or oxidation, which is difficult to satisfy by the exposed fresh pyrite surface after grinding in the actual flotation process. Therefore, the grinding medium, pulp potential, pulp pH, and aeration affect the degree of oxidation of the pyrite surface and, subsequently, the depression effect of polysaccharides on the flotation separation of Cu–Fe sulfide minerals.

#### 4.2. Modified polymer

Using chemical modification technologies, the functional



groups of natural polysaccharide polymers can be changed, or new functional groups can be introduced to obtain modified polymers that can adapt to specific mineral flotation systems. Carboxymethyl cellulose (CMC) comprises natural cellulose after carboxymethylation. The carboxyl and hydroxyl groups in CMC can interact with metal sites on the pyrite surface. The difference between carboxyl and hydroxyl groups is that the former can interact with both metal cations and metal hydroxyl species on the pyrite surface, but the latter can only react with metal hydroxyl species on the mineral surface via Brønsted acid–base interactions [88]. As a nontoxic and degradable modified polymer, CMC has the potential to replace conventional inorganic depressants in the flotation separation of Cu–Fe sulfide minerals. The interaction mechanism between CMC and the pyrite surface is easily affected by pulp pH. A change in pulp pH can affect the dissociation of carboxyl groups in CMC, the degree of hydroxylation on the pyrite surface, and surface charge, thus affecting the adsorption behavior and the dominant form of CMC on the pyrite surface. Therefore, the CMC depression mechanism on the pyrite surface is related to hydrogen bonding, electrostatic attraction, and Brønsted acid–base interactions; different pH conditions lead to changes in the dominant form of action. Additionally, Bicak *et al.* [88] observed that calcium hydroxyl species were formed on the pyrite surface upon adding calcium ions to the pulp, reducing the electrostatic repulsion between CMC and the pyrite surface and increasing the adsorption capacity of CMC on the pyrite surface. The addition of calcium ions also facilitates the precipitation of calcium hydroxide on the pyrite surface, strengthening the hydrogen bonding between the CMC and hydroxyl groups on the pyrite surface.

Polyacrylamide is a linear polymer. Because polyacrylamide structures contain acrylamide groups, they easily form hydrogen bonds; thus, they exhibit high chemical activity and can be adsorbed onto the mineral surface via electrostatic attraction and hydrogen bonding. Boulton *et al.* [26] observed that multiple functional groups, such as hydroxyl, carboxyl, sulfonyl, and thiourea groups, could be grafted onto the main chain of polyacrylamide to obtain polyacrylamides with different characteristics. The modified polyacrylamide(s) effectively depressed pyrite flotation. Additionally, the interaction of polyacrylamide with pyrite surface promoted mineral surface oxidation. Polypropylene carboxylic acid is a hydrolyzed product of polyacrylamide, which has a strong affinity toward iron sites on the pyrite surface and can be used as a pyrite depressant for the separation of Cu–Fe sulfide minerals [30]. At a pH of 8.16, when polypropylene carboxylic acid was used as a depressant and SBX dosage was 15 mg/L, the flotation recovery of chalcopyrite was 90.88%, and that of pyrite was only 1.29% (Fig. 6).

Lignin is an abundant biopolymer in nature, second only to cellulose [92]. It can be converted into lignosulfonate via sulfonation. Other than the hydroxyl group, the modified lignosulfonate structure contains abundant hydrophilic groups, such as sulfonyl and carboxyl groups [93]. Liu *et al.*

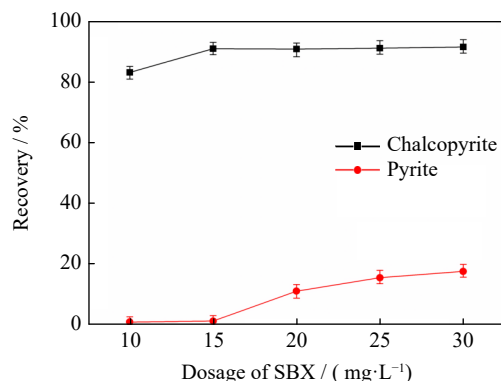


Fig. 6. Effect of SBX dosage on flotation recoveries of pyrite and chalcopyrite (polypropylene carboxylic acid: 60 mg/L; pH: 8.16). Reproduced from *Colloids Surf. A Physicochem. Eng. Aspects*, 620, X. Wang, J. Liu, Y.M. Zhu, and Y.X. Han, Adsorption and depression mechanism of an eco-friendly depressant PCA onto chalcopyrite and pyrite for the efficiency flotation separation, 126574, Copyright 2021, with permission from Elsevier.

[94] observed that in a chalcopyrite–pyrite flotation system under a pH range of 2–12, the addition of lignosulfonate calcium (LSC) depressed the pyrite floatability, whereas the chalcopyrite floatability was not affected, and the separation of chalcopyrite from pyrite was obtained over a wide pH range (Fig. 7). LSC was adsorbed onto the pyrite surface via the interaction of sulfonyl and carboxyl groups with ferric hydroxide species, followed by competitive adsorption between LSC and xanthate, thereby hindering the interaction of xanthate with the pyrite surface.

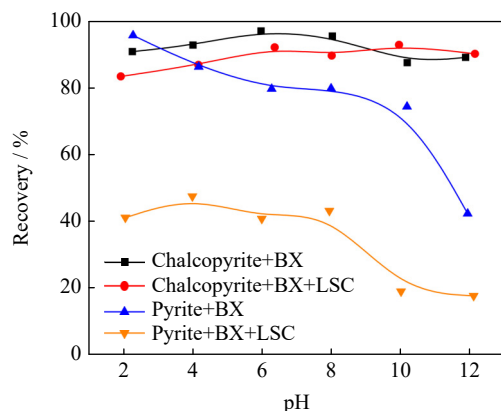


Fig. 7. Effect of pH on flotation recoveries of pyrite and chalcopyrite (butyl xanthate (BX):  $0.1 \times 10^{-3}$  mol/L, LSC: 100 mg/L, 2# oil: 10 mg/L). Reprinted by permission from Springer Nature: *J. Cent. South Univ. Technol.*, Effect of organic depressant lignosulfonate calcium on separation of chalcopyrite from pyrite, R.Q. Liu, W. Sun, Y.H. Hu, and D.Z. Wang, Copyright 2009.

Mu *et al.* [25,95] further decoded the mechanism of the lignosulfonate depression on pyrite surface from an electrochemical perspective. Lignosulfonate can form a Cu-biopolymer complex on a Cu-activated pyrite surface, hindering the electrochemical oxidation of xanthate, thus reducing the hydrophobicity of the pyrite surface. Lignosulfonate can

be adsorbed onto pyrite surface via hydrophobic interactions, electrostatic attraction, hydrogen bonding, or chemical adsorption, which can cover the active sites on the pyrite surface and reduce the ability of the surface to interact with xanthate via REDOX. This may be because lignosulfonate is adsorbed on the pyrite surface and acts as an insulator, increasing the conductivity of the pyrite surface and eliminating the electrochemical REDOX conditions required for dixanthogen formation on the pyrite surface [24]. Additionally, the hydrophilic functional groups of lignosulfonates enhanced the surface hydrophilicity of pyrite, thereby further reducing pyrite floatability. Evidence suggests that lignosulfonate polymers with different molecular weights or different contents of functional groups exert different depression effects on sulfide minerals [95–96]. Lignosulfonate polymers with higher molecular weights and more functional groups exhibit a stronger depression capacity for pyrite flotation.

Compared with natural starch, Fletcher *et al.* [97] observed that starch oxidized using hydrogen oxide at low dosage exhibited better depression performance on Cu-activated pyrite. Oxidation can result in the destruction of the glucose ring structure in natural starch, reduction in the molecular weights of amylose and amylopectin, and increase in the steric freedom of modified starch. Additionally, oxidation can introduce new functional groups, such as carbonyls and carboxyls, into starch, thereby enhancing its adsorption ability onto mineral surfaces. Khoso *et al.* [98] synthesized a modified biopolymer depressant called tricarboxylate sodium starch. Natural starch reacts with hydrogen peroxide to form carboxyl and carbonyl/aldehyde groups. Upon further oxidation, the carbonyl/aldehyde groups are converted into carboxyl groups. Finally, sodium hydroxide is added to convert the free carboxyl groups into sodium carboxyl groups. Tricarboxylate sodium starch can interact with the pyrite surface via chemical adsorption to passivate the pyrite surface and hinder the oxidation of xanthate to dixanthogens, thereby depressing pyrite flotation. The flotation results showed that the floatabilities of pyrite and chalcocopyrite decreased in the pH range of 2–12 after treatment with tricarboxylate sodium starch; however, the depression effect on pyrite was considerably stronger than that on chalcocopyrite (Fig. 8). Tricarboxylate sodium starch can effectively decrease pyrite floatability over a wide pH range. Compared with natural starch, modified starch containing carboxyl and hydroxyl groups exhibited a stronger pyrite depression capacity. Khoso *et al.* [98] reported that tricarboxylate sodium starch, as a polysaccharide depressant, primarily interacts with metal ions or metal hydroxyl species on sulfide mineral surfaces, whereas the pyrite surface has more metal hydroxides than the chalcocopyrite surface, which explains the reason behind tricarboxylate sodium starch being more likely to adsorb on the pyrite surface. Similarly, tricarboxylate sodium starch can be used as a depressant for the flotation separation of chalcocopyrite from pyrrhotite [99]. Under neutral conditions (pH 7), the depression effect of tricarboxylate sodium starch on the pyrrhotite floatability is stronger than that on chalcocopyrite

ite floatability. The adsorption behavior of tricarboxylate sodium starch on chalcocopyrite and pyrrhotite surfaces is dominated by the metal hydroxyl species on the surface. Abundant metal hydroxyl species on a pyrrhotite surface provide active sites for the adsorption of pyrrhotite tricarboxylate sodium starch.

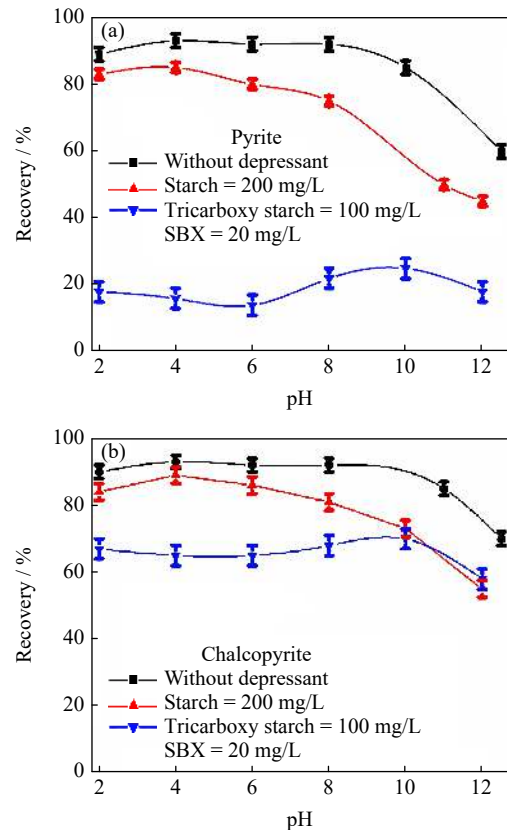
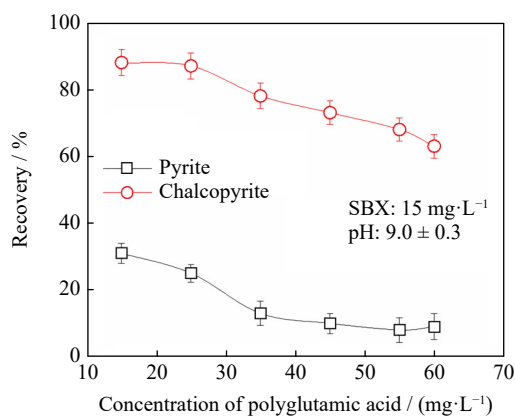


Fig. 8. Effect of pH on the flotation performances of (a) pyrite and (b) chalcocopyrite using starch and tricarboxy starch as depressants. Reproduced from *Sep. Purif. Technol.*, 259, S.A. Khoso, Y.H. Hu, M.J. Tian, Z.Y. Gao, and W. Sun, Evaluation of green synthetic depressants for sulfide flotation: Synthesis, characterization and flotation performance to pyrite and chalcocopyrite, 118138, Copyright 2020, with permission from Elsevier.

### 4.3. Organic acid

Polyglutamic acid is a biodegradable and nontoxic polymer (biopolymer). Khoso *et al.* [100] observed that polyglutamic acid had a stronger affinity toward the pyrite surface than the chalcocopyrite surface (pH range 8–12). Polyglutamic acid was more easily adsorbed onto the pyrite surface, hindering the adsorption of xanthate on the pyrite surface. Polyglutamic acid interacted with the pyrite surface via strong chemical adsorption, whereas it interacted with the chalcocopyrite surface only via weak physical adsorption. At pH 9, an appropriate dosage of polyglutamic acid can control the pyrite recovery to be less than 20% and ensure a chalcocopyrite recovery of more than 85%; i.e., polyglutamic acid was preferentially adsorbed onto the pyrite surface and formed a strong passivation layer, thus reducing pyrite float-

ability (Fig. 9). The difference between the surface adsorption behaviors of polyglutamic acid onto the pyrite and chalcopyrite surfaces was largely determined by the number of metal sites or metal hydroxyl species on the mineral surface and their chemical affinity toward polyglutamic acid; i.e., the iron sites or ferric hydroxide species on the pyrite surface interacted with polyglutamic acid via a strong chemical reaction. However, the chalcopyrite surface was chemically inert to polyglutamic acid; i.e., the copper species on the chalcopyrite surface formed strong chemical interactions with polyglutamic acid with considerable difficulty, following which polyglutamic acid could only undergo weak physical adsorption on the chalcopyrite surface. Another study by Khoso *et al.* [101] demonstrated that lime addition can enhance the depression performance of polyglutamic acid in pyrite flotation and that lime and polyglutamic acid can be adsorbed on the pyrite surface, thus hindering collector adsorption. Therefore, polyglutamic acid possesses considerable potential to reduce lime consumption in the flotation separation of Cu–Fe sulfide minerals.



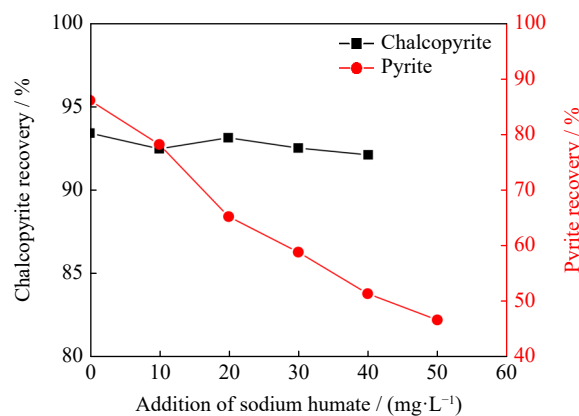
**Fig. 9.** Effect of polyglutamic acid concentration on the flotation recoveries of pyrite and chalcopyrite. Reproduced from *J. Clean. Prod.*, 232, S.A. Khoso, Y.H. Hu, F. Lyu, R.Q. Liu, and W. Sun, Selective separation of chalcopyrite from pyrite with a novel non-hazardous biodegradable depressant, 888–897, Copyright 2019, with permission from Elsevier.

Tannic acid is a low-toxicity biodegradable organic acid that can be prepared from *Galla chinensis*. Because tannic acid contains several adjacent hydroxyl groups, it possesses chemical affinity toward metal sites on the surface of sulfide minerals and can generate ring chelates on the surface of sulfide minerals; therefore, it possesses the potential to be a depressant of sulfide minerals [102]. Han *et al.* [103] showed that iron sites on the pyrite surface could bond with the phenolic hydroxyl and carboxyl groups of tannic acid. At a pH of 8, tannic acid can selectively reduce the amount of xanthate adsorbed on the pyrite surface, weakening the floatability of pyrite and resulting in the separation of chalcopyrite from pyrite.

Sodium humate is a macromolecular organic acid salt with multiple functions and is generated from weathered coal, peat, and lignite through a series of complex reactions. Its structure is complex and contains multiple aromatic rings

(benzene rings, fused rings, among others) connected via bridge bonds. Various polar groups exist in the aromatic ring of sodium humate, mainly the carboxyl, phenolic hydroxyl, hydroxyl, methoxy, and quinone groups. Therefore, the reaction of sodium humate with a mineral surface is complex and can result in the formation of metal chelates with metal sites on the mineral surface through multiple groups. The chelating ability of humic acid with ferric ions is stronger than that with copper ions, and the stability constant of the ferric–humic complex is higher than that of the copper–humic one, which provides the conditions for the flotation separation of Cu–Fe sulfide minerals [104]. At a pH of 9.3, sodium humate can react with a pyrite surface and copper ions in the pulp to eliminate the activation of copper ions on the pyrite surface. Sodium humate reacts with ferric and ferrous ions, hindering the hydrolysis of ferric ions, eliminating the hydrophilic ferric hydroxide film on a chalcopyrite surface, and enhancing the reactivity of the chalcopyrite surface [105]. Additionally, sodium humate can stably exist on the pyrite surface because of its strong affinity toward ferric ions. Owing to the strong chemical interaction between sodium humate and the pyrite surface, sodium humate and xanthate undergo competitive adsorption on the pyrite surface, hindering the adsorption of xanthate to achieve the separation of Cu–Fe sulfide minerals. Upon increasing the sodium humate concentration from 0 to 50 mg/L, the chalcopyrite floatability remained unaffected, while the pyrite recovery gradually decreased (Fig. 10). Chen *et al.* [106] observed that a combination of sodium humate and lime could achieve flotation separation of Cu–Fe sulfide minerals in a low-pH medium; additionally, an industrial-scale test was successfully conducted at the Dexing Copper Mine. Importantly, the use of sodium humate reduced the lime dosage, thereby increasing the recoveries of Au, Ag, and Mo in the copper concentrate.

Recently, various small-molecule organic acids have been demonstrated to achieve flotation separation of Cu–Fe sulfide minerals at low alkalinity. Pyrogallol acid is a polysubstituted aryl compound, and the three hydroxyl groups on the

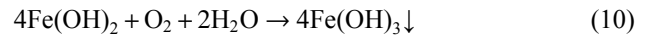
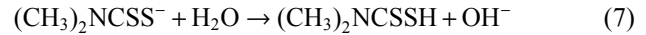
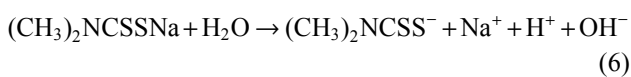


**Fig. 10.** Flotation performances of chalcopyrite and pyrite using sodium humate as a depressant at a pH of 9.5 (butyl xanthate:  $2.5 \times 10^{-5}$  mol/L). Reproduced from *Miner. Eng.*, 24, J.H. Chen, Y.Q. Li, and Y. Chen, Cu–S flotation separation via the combination of sodium humate and lime in a low pH medium, 58–63, Copyright 2010, with permission from Elsevier.

benzene ring have a satisfactory affinity toward metal sites on a mineral surface. It attracted extensive attention in previous studies on the flotation separation of calcium minerals [107–109]. Similarly, pyrogallic acid can interact with pyrite surfaces via chemical adsorption at Fe sites to increase the hydrophilicity of the pyrite surface [110]. Under low-alkali conditions (pH 8), pyrogallic acid can replace lime in the flotation separation of chalcopyrite from pyrite. Based on the affinities between the functional groups of organic depressants and different metal sites on a sulfide mineral surface, Han *et al.* [111] observed that salicylic acid could be adsorbed on the pyrite surface by means of interactions between hydroxyl/carboxyl groups and iron sites, forming rich hydrophilic groups on the pyrite surface. After treatment with an appropriate concentration of salicylic acid, xanthate was barely adsorbed onto pyrite, thus depressing pyrite floatability. Lactic acid is a carboxylic acid that can be produced using biotechnology. A single lactic acid molecule contains hydroxyl and carboxylic groups. Similarly, lactic acid can interact with iron sites on the pyrite surface, hindering xanthate adsorption on the pyrite surface and rendering the surface hydrophilic [112].

#### 4.4. Sodium dimethyl dithiocarbamate

Based on the mirror symmetry rule for the interface between flotation reagents and minerals [113], small-molecule depressants that contain sulfhydryl groups have a strong chemical affinity toward the surface of sulfide minerals and hence can be stably adsorbed onto the surface of sulfide minerals. Additionally, carboxyl and hydroxyl groups can be introduced into small-molecule depressants that contain sulfhydryl groups to enhance their adsorption capacity on mineral surfaces, hindering collector adsorption. Sodium dimethyldithiocarbamate is a straight-chain-chelating agent. The  $-\text{CSS}$  group in sodium dimethyl dithiocarbamate possesses a strong chelating ability with metals and can form water-insoluble complexes [114]. Bai *et al.* [115–116] observed that in a chalcopyrite–pyrite flotation system (pH 8.5), an appropriate amount of sodium dimethyl dithiocarbamate could effectively decrease pyrite floatability but had no considerable effect on chalcopyrite hydrophobicity. The  $\text{CSS}$  groups and N atoms in sodium dimethyl dithiocarbamate can strongly react with the iron sites on the pyrite surface via complexation reactions and form water-insoluble complexes on the mineral surface. Therefore, the affinity of sodium dimethyl dithiocarbamate toward the chalcopyrite surface was weaker than that toward the pyrite surface, which increased the floatability difference between chalcopyrite and pyrite and achieved the selective depression of pyrite. Additionally, after the interaction of sodium dimethyl dithiocarbamate with the pyrite surface, the hydrophilic ferric hydroxide content on the pyrite surface considerably increased, and the difference in floatability between the two minerals further increased. The reactions are as follows [115]:



#### 4.5. Diethylenetriamine

Diethylenetriamine is a chelating agent that binds to various metal ions. Diethylenetriamine contains a pair of amino groups that interact with a mineral surface. Agorhom *et al.* [117] and Ahmadi *et al.* [118] believed that in the flotation of Cu-activated pyrite, diethylenetriamine could react with copper ions on the pyrite surface to form a Cu(I)–diethylenetriamine complex and eliminate the activation of copper ions on pyrite surface. Additionally, diethylenetriamine's ability to react with copper ions to form complexes was stronger than that of xanthate and copper ions to form copper xanthate. The pyrite surface was more easily covered by the newly formed Cu(I)–diethylenetriamine complex, which hindered the electrochemical interaction between xanthate and pyrite surfaces and thus depressed pyrite flotation. However, the use of diethylenetriamine may increase the costs of subsequent treatments. The copper–diethylenetriamine complex produced via the reaction of diethylenetriamine and copper ions is soluble under alkaline conditions, and it is difficult to eliminate the complex from wastewater by means of conventional treatments [119–120]. Additionally, diethylenetriamine is corrosive to metals, and the depression of Cu-activated pyrite usually requires a high dose of diethylenetriamine [118], which is highly toxic. Therefore, in the industrial production of flotation separation of Cu–Fe sulfide minerals, before using organic depressants, one should evaluate their biodegradability, migration rule, and elimination technology and those of metal–organic depressant complexes too in a bid to meet the requirements of environmental protection, pyrite depression, and precious metal recovery. Table 2 presents the organic depressants used for the flotation separation of Cu–Fe sulfide minerals at low alkalinity.

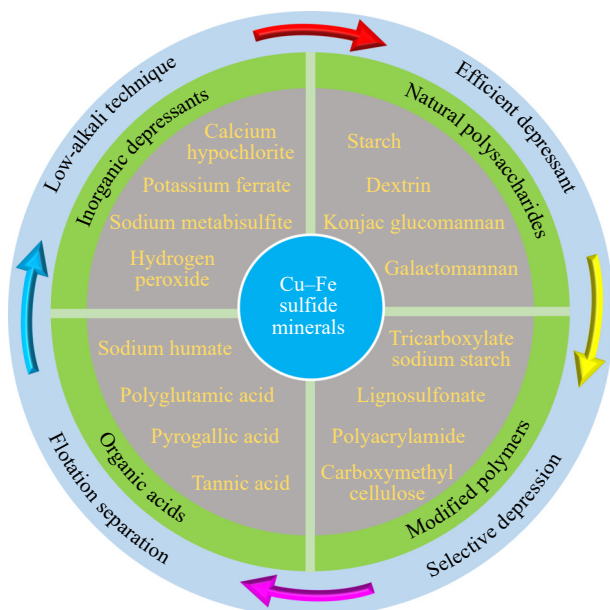
Based on previous studies, Fig. 11 shows a roadmap for advances in depressants for the flotation separation of Cu–Fe sulfide minerals at low alkalinity.

### 5. Action pathways and application challenges of organic depressants

The interaction between organic depressants and mineral surfaces is complex because of the complex structural characteristics of the former and the inhomogeneity of the latter. Organic depressants can interact with mineral surfaces via electrostatic attraction, hydrogen bonding, chemical adsorption, or hydrophobic interactions. The interaction mechanism depends on mineral surface properties and the type of functional group of the organic depressant [26]. In the flotation separation of sulfide minerals, the hydrophobic ability of the mineral surface is determined by the hydrophobic sulfur species, hydrophilic metal hydroxides or metal hydroxyl spe-

**Table 2. Partial organic depressants used for flotation separation of Cu–Fe sulfide minerals**

Depressant	Group	Dosage / (g·t <sup>-1</sup> )	pH	Collector	Size / μm	Cu recovery / %	Fe recovery / %	Ref.
Starch	–OH	400	8	Sodium butyl xanthate	38–74	73.09	26.46	[19]
Konjac glucomannan	–OH	200	9	Potassium butyl xanthate	38–74	>90	<5	[86]
Locust bean gum	–OH	1000	8	Sodium butyl xanthate	38–74	83.02	12.01	[91]
Polypropylene carboxylic acid	–COOH	900	8.16	Sodium butyl xanthate	38–74	90.88	1.29	[30]
Calcium lignosulfonate	–OH; –SO <sub>3</sub> Ca	2000	9–10	Butyl xanthate	<106	80.36	43.07	[94]
Tricarboxylate sodium starch	–OH; –COONa	3000	6	Sodium isobutyl xanthate	38–74	75.36	17.64	[98]
Polyglutamic acid	–COOH; –NH–	700	9	Sodium butyl xanthate	38–74	86.57	14.79	[100]
Sodium humate+ lime	–OH; –COOH; –NH <sub>2</sub>	52.35	—	Butyl xanthate	—	97.26	52.35	[106]
Tannic acid	–OH; –COOH	4000	8	Sodium butyl xanthate	38–74	>90	~5	[103]
Pyrogalllic acid	–OH	1000	8	Sodium butyl xanthate	38–74	76.85	24.95	[110]
Salicylic acid	–OH; –COOH	4000	8	Sodium butyl xanthate	38–74	>90	~3	[111]
Lactic acid	–OH; –COOH	4000	8	Sodium butyl xanthate	38–74	97.06	11.05	[112]
Sodium dimethyl dithiocarbamate	–CSSNa	716	8.5	Butyl xanthate	45–74	84.18	15.47	[116]

**Fig. 11. Roadmap for advances in depressants for the flotation separation of Cu–Fe sulfide minerals at low alkalinity.**

cies, degree of coverage, hydrophilic ability of organic depressants, and collector adsorption amount. The proportion of these components on the surface of the sulfide minerals determines their floatability and separation efficiency of minerals. Based on previous studies, organic depressants in flotation separation of Cu–Fe sulfide minerals at low alkalinity primarily involve the following three pathways.

(1) Pulp composition was regulated to eliminate the activation ions of pyrite. Organic depressants that contain sulfhydryl, carboxyl, hydroxyl, and amine groups can react with the

copper and iron ions in the pulp to eliminate the activation of copper ions on the pyrite surface.

(2) The hydrophilicity of the pyrite surface was enhanced. Organic depressants often exhibit a strong affinity toward ferric hydroxide species on the pyrite surface but a weak affinity toward copper species on the chalcopyrite surface and thus selectively adsorb on the pyrite surface. After the organic depressants were adsorbed on the pyrite surface, the hydrophilic groups of the organic depressants in the solution facilitated the formation of a stable hydrophilic film on the mineral surface.

(3) Covering the pyrite surface hindered the interaction between the collector and mineral surface. The organic depressants with macromolecular chains adsorbed on the pyrite surface occupied the active sites of pyrite and formed a competitive adsorption relationship with the collector, thereby hindering collector adsorption.

However, previous research works and the application of organic depressants in the flotation of sulfide ores have mostly been regarding the removal of gangue and improvement of concentrate grade, whereas the application of organic depressants in the flotation separation of sulfide minerals has rarely been reported. Although organic depressants have the potential to separate Cu–Fe sulfide minerals at low alkalinity, traditional techniques employing lime and cyanide as depressants are still widely used in industrial production. This is primarily because pyrite depressed by organic depressants is difficult to effectively activate and recycle effectively owing to the strong depression capacity of organic depressants. Lime-depressed pyrite was activated by adding an acid. However, organic depressants often chemically react

with metal sites on the pyrite surface to form stable chemical bonds. This makes it difficult for organic depressants adsorbed on the pyrite surface to desorb and achieve effective derepression. Additionally, polymers have abundant groups that can interact with mineral surfaces; therefore, they possess poor selectivity for the flotation separation of sulfide ores. Therefore, to develop organic depressants for the flotation separation of Cu–Fe sulfide minerals, the relationship between the functional groups of organic depressants and metal ions on mineral surfaces should be determined, and the biodegradability, migration rule, and elimination technology of organic depressants and the metal–organic depressant complexes in the flotation system should be evaluated.

## 6. Summary and prospects

Based on the concept of carbon neutrality, future mining industries must meet the requirements of sustainable development to the maximum possible extent, including minimization of energy and water consumption and environmental pollution. Therefore, the design and development of green flotation reagents to reduce the environmental impact of mineral processing are of considerable ecological and economic importance. High-alkali and cyanide techniques for the flotation separation of Cu–Fe sulfide minerals are not conducive to the comprehensive recovery and use of resources, and there is increasingly serious environmental impact on actual production.

Under low-alkalinity conditions, inorganic depressants (oxidants and sulfur–oxygen compounds) can selectively regulate active sites on the pyrite surface, increase the number of hydrophilic species there, or suppress the oxidation of xanthate to dixanthogen. However, practically, high doses of inorganic depressants are usually required to depress pyrite flotation. The cost of reagents and equipment maintenance remains to be obstacles that limit the industrial application of inorganic depressants. Organic depressants for the flotation separation of Cu–Fe sulfide minerals at low alkalinity include natural polysaccharides, modified polymers, organic acids, sodium dimethyl dithiocarbamate, and diethylenetriamine. These organic depressants have been demonstrated to achieve the flotation separation of Cu–Fe sulfide minerals under low alkalinity or neutral conditions and possess the potential to replace traditional inorganic depressants (lime and cyanide). Organic depressants depress pyrite flotation through multiple pathways, including the elimination of activated ions of pyrite, enhancing the hydrophilicity of the pyrite surface, and hindering the interaction of the collector with the pyrite surface. However, the strong depression capacity of organic depressants may result in low selectivity for organic depressants and difficult derepression of depressed pyrite. The recovery of pyrite and precious metals remains a challenge that must be addressed. Organic depressants often interact with the pyrite surface via stable chemisorption, and it is difficult to break the chemical bonds between the organic reagents and metal sites on the pyrite surface.

The results of studies on organic depressants in the flotation separation of Cu–Fe sulfide minerals at low alkalinity are encouraging, and Cu–Fe sulfide minerals can be efficiently separated using specific organic depressants in lab-scale flotation. However, the application of these organic depressants in the industrial flotation of Cu–Fe sulfide minerals suffers various challenges, including high costs and environmental impact. Owing to the complexity of the flotation system and the action mechanism of organic depressants, difficulty in the derepression of pyrite is predictable. Therefore, it is necessary to develop novel organic agents with high depression capacity and easy derepression to achieve efficient and comprehensive use of mineral resources. According to the matching mechanism between the functional groups of organic depressants and mineral surfaces, one should investigate the biodegradability, migration rule, and elimination technology of organic depressants and metal–organic depressant complexes in a flotation system, which is important for research on organic depressants in the flotation separation of Cu–Fe sulfide minerals at low alkalinity.

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## Conflict of Interest

Qicheng Feng and Shuming Wen are editorial board members for this journal and not involved in the editorial review or the decision to publish this article. All authors declare that there is no conflict of interest regarding the publication of this paper.

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