

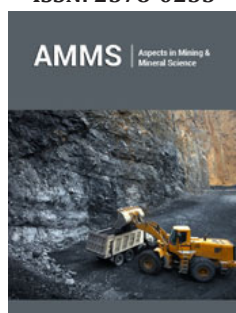
Flotation of Chalcopyrite and Molybdenite by Means of Different Depressants: Review

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Abstract

This review delves into the critical process of separating chalcopyrite and molybdenite, two key minerals in the metal mining industry, through flotation. Effective separation of these minerals is paramount for maximizing copper and molybdenum recovery. The core focus is on the role of depressants in enhancing flotation selectivity. A comprehensive examination of various depressants employed in previous research is conducted to assess their efficacy in discriminating between chalcopyrite and molybdenite. The underlying mechanisms of depressant action, including surface chemistry and flotation kinetics, are explored in detail. Furthermore, the influence of operational parameters such as pH, solids concentration, and depressant combinations on flotation performance is investigated. While traditional inorganic depressants have been utilized for this purpose, they often pose environmental concerns due to their toxicity and limited biodegradability. This review highlights the potential of organic depressants as a more sustainable alternative. Research in recent times has focused on developing organic depressants that effectively separate these valuable sulfides.

However, the optimal conditions for utilizing these novel depressants require further exploration. A crucial aspect of this review is the comparison between organic and inorganic depressants. It sheds light on the advantages of organic depressants, such as their eco-friendliness and potential for improved selectivity. Conversely, the review discusses the limitations of inorganic depressants, including their environmental impact and stricter regulations governing their usage due to environmental concerns imposed by regulatory bodies. By understanding the efficacy and limitations of both organic and inorganic depressants, this review aims to provide valuable insights for optimizing the flotation process for chalcopyrite and molybdenite separation. This knowledge can contribute to improved metal recovery, reduced environmental impact, and compliance with environmental regulations in the mining industry. Many countries strive for optimal metallurgical performance, yet not all possess the necessary knowledge or resources to achieve this objective. This review aims to assist readers in understanding key strategies for implementing environmentally friendly metallurgical processes. China, Chile, Japan, and Mexico have developed a certain expertise in advancing the understanding of green flotation processes.

Keywords: Chalcopyrite; Molybdenite; Flotation; Organic depressants; Inorganic depressants; Collectors; Flotation-conditions; Crystalline-structure

Introduction

The review delves into the realm of mineral processing, introducing a critical technique known as flotation. This method has emerged as a cornerstone in the industry, superseding many traditional concentration processes due to its versatility and effectiveness. The upcoming discussion will position flotation as a selective separation process, capable of discerning and isolating valuable metal components from a matrix of commercially insignificant substances. To provide a foundational understanding, the text will explore the underlying physicochemical principles governing this process. Essentially, flotation leverages the ability of specific compounds to adhere to mineral surfaces, thereby influencing their interaction with water. This differential wettability of minerals is the crux of the separation process. Those minerals with altered surface properties attach to air bubbles, forming a froth that can be skimmed off, while the remaining material settles. The subsequent paragraphs will likely delve deeper into

the specific mechanisms of adsorption and the factors affecting a mineral's wettability [1].

Mineral Classification

Every mineralogical body possesses certain specific characteristics, even when they belong to the same class and share similar chemical compositions. Their behavior can vary significantly in response to certain chemical changes on their surface. These anisotropies depend on various factors, such as the geographical location of the mineral, chemical interactions with the surrounding environment, and pressure and temperature conditions, especially if the mineral is located in the Earth's mantle or crust. As a result, the conditions for the concentration treatment of a mineral body will vary depending on the most suitable beneficiation method [2]. Given that flotation is based on the surface characteristics of the mineral, minerals can be classified into two general categories: hydrophilic and hydrophobic minerals.

Hydrophobic minerals have a very low wettability index due to the lack of polarity in their compounds, thus repelling other polar compounds like water. Common examples of this type of minerals include pure metals that are embedded in other mineral species without any chemical interaction, sulfide minerals, or carbonaceous minerals like graphite. Another important feature of hydrophobic minerals is their aerophilic nature, as they exhibit an exceptional affinity towards gas bubbles, thereby facilitating the flotation process [3]. On the other hand, hydrophilic minerals are the opposite; they have a higher wettability index due to the polar capacity of their surface to interact with other ionic compounds like water. The most common compositions within this category include carbonates, sulfates, silicates, and especially metal oxides. The affinity towards air is inversely related to hydrophobicity; since these minerals tend to dissociate their surface, they are typically aerophobic, making it difficult for them to adhere to gas bubbles [4].

Sulfide flotation

The flotation process is based on the hydrophobic characteristics of the minerals to be concentrated. Sulfide metals are the preferred candidates for this process due to the mineral's chemistry, which favors adsorption onto air bubbles because of the minimal wettability caused by sulfur present on the mineral surface. While flotation of polar mineral species like carbonates and oxides is also common, these systems employ different reagents compared to sulfide mineral flotation to prevent particle wetting. A water-immiscible layer is added to achieve flotation. However, these reagents are more harmful to the environment and costly, so they are not used directly. In contrast, sulfide minerals possess a natural hydrophobicity, making it more feasible to float the desired sulfide without adversely affecting the environment and in a more cost-effective manner [5].

Flotation of bivalent minerals

There are minerals with both hydrophobic and hydrophilic properties, such as fluorite (CaF_2). These properties vary according to the contact angle of water with the surface, the crystal structure,

and the color of the fluorite, which changes based on impurities. Gao and collaborators state that a larger contact angle correlates with higher hydrophobicity and aerophilicity [6].

Bimetallic flotation

Some minerals containing valuable metals are chemically mixed, forming complex crystal structures, which complicates the selective flotation of a metal with higher commercial value compared to the others. To selectively obtain these metals, it is necessary to float some agglomerated species of interest, then depress the ores within the concentrate, and float those of greater economic relevance [7].

Polymetallic flotation

In some sulfide mineral deposits, multiple metals are present; the most common example is copper, zinc, and lead deposits. To process such deposits, the three metals are first floated, followed by the depression of one metal. The remaining two are then processed similarly, with one being floated and the other depressed. This process is known as differential flotation. Given the longer duration of this process, it is recommended to design a specific methodology. Moharrami & Abdollahzadeh [8] suggest that in such cases of polymetallic flotation, it is essential to analyze the relationships between parameters such as pH, reagents, preparation time, and particle size [8].

Study of flotation conditions

Studies conducted by Pritzker & Collaborators [9] indicate that the study of Eh-pH diagrams satisfactorily determines the ideal conditions under which sulfide flotation is effective. Other highly recommended techniques include mass balances to determine the correct dosages of collectors and depressants. Stability is analyzed through voltammetry tests and intermittent galvanostatic polarization [9].

External flotation variables

Silva and collaborators identify four key variables during the flotation process: mineral type, reagent concentration, order of reagent addition, and flotation time. In practice, the order and dosage of reagents must be constantly adjusted due to the continuous change in mineral nature. An ideal reagent design is one that can adapt to different circumstances. Techniques such as versatile compound modeling via computational methods are employed, with collectors and some polymeric depressants being the most studied to date [10]. Wang and Xie demonstrated that the grinding methodology and the milling environment directly affect the surface properties and, consequently, the floatability of sulfide minerals through three main aspects: electrochemical interactions, surface morphology, and mechanochemical reactions.

When sulfide minerals come into contact with abrasive grinding media, galvanic cells are formed, leading to redox reactions that alter the surface. The surface roughness has a direct impact on floatability. When sulfides and grinding media are in contact, galvanic cells are formed, and redox reactions occur due to the differences in open-circuit potentials between the sulfide minerals

and the grinding media. These galvanic reactions are controlled by the mixed potential principle. The morphology of the particles and surface roughness, in particular, are heavily dependent on the grinding media and methods. Surface roughness exerts a significant effect on the hydrophobicity of mineral particles [11]. Salazar & Parada [12], in their study of stibnite (Sb_2S_3), found that particle sizes suitable for flotation vary depending on the mineral's hardness and its kinetics with flotation reagents. However, an average range can be established, typically from $70\mu\text{m}$ to $150\mu\text{m}$. If the particle is too fine, the depressant will not function optimally, and the frother will capture both ore and gangue indiscriminately. Conversely, if the particle size is too large, it will be too heavy for the bubble, causing it to burst and leaving the ore in the flotation cell [12].

Bakalarz [13] reports that particle size has a significant impact on tailings volume. If the sulfides of interest cannot be adequately liberated, the reagents cannot interact optimally, resulting in the loss of valuable material and producing a larger mass of tailings, which creates environmental issues. Bakalarz emphasizes the importance of conducting a granulometric analysis to ensure proper sulfide liberation, as each mineral has a different hardness,

requiring distinct grinding conditions [13].

Flotation Reagents

Collector

Each reagent has a specific function, with collectors being the most extensively studied. These reagents coat the sulfide mineral, making it even more hydrophobic and aerophilic. They are organic compounds with two functional groups that serve opposing functions. On one end, they tend to have minimal polarity, reducing surface tension and wettability. The opposite end contains a polar functional group that is affinity-bound to the mineral surface, acting as an anchor to stabilize the interface between the collector and the mineral [14] (Figure 1). The selection of these reagents is based on the mineral with which they will interact. Xanthates are a globally utilized family of reagents due to their effectiveness in floating sulfides and their cost-effectiveness compared to other reagents. However, a limitation of xanthates is their lack of selectivity, which sometimes necessitates the use of specific collectors for certain metals.

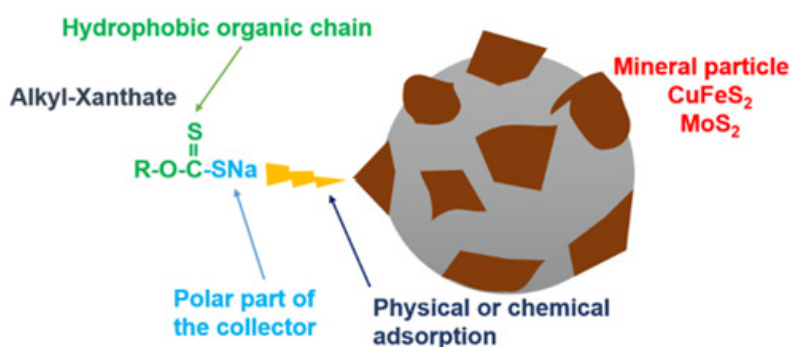


Figure 1: Diagram of the interaction between the collector and the bubble with mineral (Own elaboration).

Gusev & Associates [15] recently studied the use of azo derivatives of pyrocatechol, resorcinol, and salicylic acid as potential replacements for xanthate in the concentration of copper, nickel, and cobalt. They concluded that the selectivity towards these metals increases with the addition of benzene rings in the collectors [15]. Shepeta determined that the high floatability of high molecular weight acids is related to the steric effect and the larger surface area occupied by a molecule at the phase interface. In physisorption, the high floatability of collectors results from a higher rate of propagation on the water surface. The effect of hydrocarbon groups in the side chain on reducing surface tension is two-thirds of the effect of the hydrocarbon groups in the main chain [16].

Depressants

The function of depressants is to suppress the flotation of mineral species that are not of commercial interest, or in the case of polymetallic processes, to depress the metal of lower economic value. These reagents are based on inorganic compounds with partial polarity and have a high affinity for the wettable compounds in the gangue. However, these reagents tend to be harmful to the

environment, as they do not degrade naturally. There are numerous efforts to find organic-based depressants, with the most commonly used being quebracho, starches, thiophenols, and cyanides [17]. Xu and collaborators note that in bimetallic or polymetallic flotation, the suppression of a metal often involves the use of a sulfate of the metal in question. For example, zinc sulfate is used to depress sphalerite, forming more zinc sulfate at the zinc-sulfate interface, thereby achieving suppression. This approach is also applied in chalcopyrite systems using copper sulfate [18].

Frothers

The function of frothers is to provide stability to the bubbles and shield them from disturbances caused by the agitation system and the inclusion of mineral particles. Their chemical composition is usually based on phenolic alcohols, with Methyl Isobutyl Carbinol (MIBC) being the most commonly used in sulfide flotation [19].

pH Regulators

An important parameter is the concentration of hydronium and hydroxyl ions. In highly acidic flotation systems, bubbles tend to burst, although this condition favors mineral floatability.

Conversely, in alkaline systems, bubbles are more stable but do not contribute to the wettability of sulfides. Sulfide flotation systems typically operate in alkaline pH conditions, making NaOH, Na₂CO₃, and CaO commonly used reagents. To regulate excessive alkalinity, HCl or H₂SO₄ is employed [20].

Bioflotation reagents

All the aforementioned reagents entail significant costs on an industrial scale. An improvement being implemented is the use of bacteria that perform the same function as chemical reagents. The interactions between minerals and bacterial cells impact the surface properties of the minerals. Behera and Khalek have determined that the metabolism of bacteria such as *Rhodococcus opacus*, *Rhodococcus ruber*, *Staphylococcus carnosus*, *Stenotrophomonas*, and *Escherichia coli* can function as biocollectors, while cells such as *Acidithiobacillus ferrooxidans*, *Ferropasma acidiphilum*, *Leptospirillum ferrooxidans*, and *Bacillus subtilis* can serve as biodepressants [21,22].

Flotation Kinetics

Wang and colleagues state that the beneficiation process by flotation typically occurs in three sequential stages: collision, attachment, and transport. The collision stage is heavily influenced by the system's hydrodynamics, attachment depends on the interfacial interactions between the bubble and the particle, which are favoured by the hydrophobicity of the mineral surface, and finally, transport depends on the stability of the bubble-particle aggregate. Therefore, flotation will only occur if all three stages are successfully completed [23]. Cheng mentions that the behavior of the metal ion on the mineral surface contrasts significantly with its free form in solution. On the surface, the metal ion is in a semi-restricted state, implying that its properties are strongly influenced by the surface structures and the characteristics of surrounding atoms. It is important to note that the likelihood of interaction between the surface metal ion and collectors is related to the number of available π -electron pairs. The greater the number of these π pairs, the higher the probability of interaction [24].

A useful technique reported by Nakhaei & Collaborators [25] is the monitoring of foam kinetics during the flotation process to determine efficiency. The aspects to evaluate include foam velocity, stability, color, size, and texture. Foams are characterized at specific intervals based on the historical time nature applied to each mineral [25].

Chalcopyrite Flotation

Properties and structure of chalcopyrite

Chalcopyrite is the primary copper ore, with the composition (CuFeS₂). It has a molecular weight of 183.5g/mol, with a stoichiometric composition of 34.6% copper, 30.4% iron, and 34.9% sulfur. It has a characteristic brass-yellow color, occasionally displaying darker shades due to oxides such as (Cu₂SO₃) on its surface. The hardness of this mineral ranges between 3 and 4 on the Mohs scale, with a density of 4.2g/cm³ and a melting point of 880 °C [26]. Chalcopyrite is often found embedded in quartz or magnesium

silicates [27]. Chalcopyrite is present in a myriad of sulfide deposits, particularly in porphyry-type deposits, often in hydrothermal veins or lodes (Figure 2). The most common minerals with which it is usually associated include pyrite, molybdenite, sphalerite, galena, and dolomite [28].

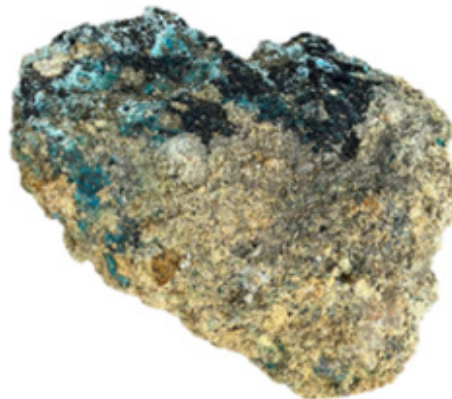


Figure 2: Chalcopyrite (CuFeS₂) from northern Mexico (own photograph).

Crystallographic structure

The crystallographic structure of chalcopyrite is simple tetragonal, with a bond length of 2.30 Å for the Cu-S bond and 2.25 Å for the Fe-S bond [29], (Figure 3).

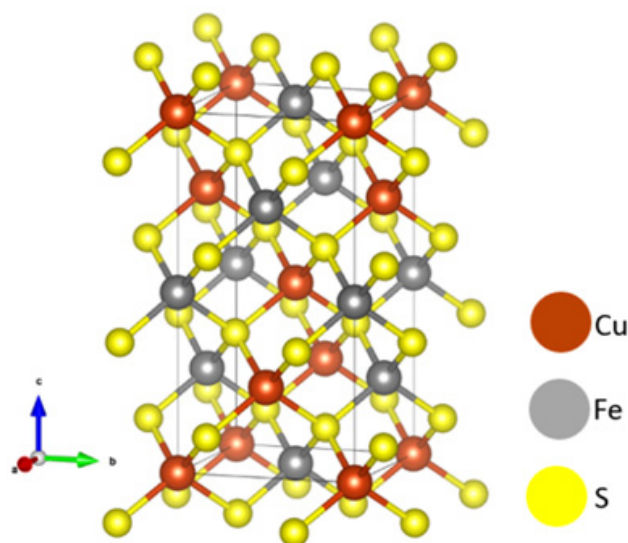


Figure 3: Crystal structure of chalcopyrite [30].

Oxidation of chalcopyrite

As a sulfide, chalcopyrite does not necessarily require a collector coating, as it possesses natural floatability, which can be enhanced by collectors [30]. However, certain factors, such as oxidation, can affect the natural flotation of chalcopyrite [31]. Surface oxidation impacts the efficiency of flotation, making it crucial to evaluate aspects such as the evolution of the mineral surface, the dynamics at the reagent-mineral interface, the oxidation rate, and the compounds derived from the oxidation

process [32]. The natural floatability of chalcopyrite varies depending on the pH level; it significantly decreases under alkaline conditions due to the predominant presence of $(OH)^-$ ions, which form polar compounds with the mineral surface (Figure 4), such

as $Cu(OH)_2$ and $Fe(OH)_3$ [33]. To qualitatively assess the presence of chalcopyrite on the mineral surface, which varies with pH levels, Eh-pH diagrams are used to delineate the boundaries within which various compositions coexist in the Cu-Fe-S system [34].

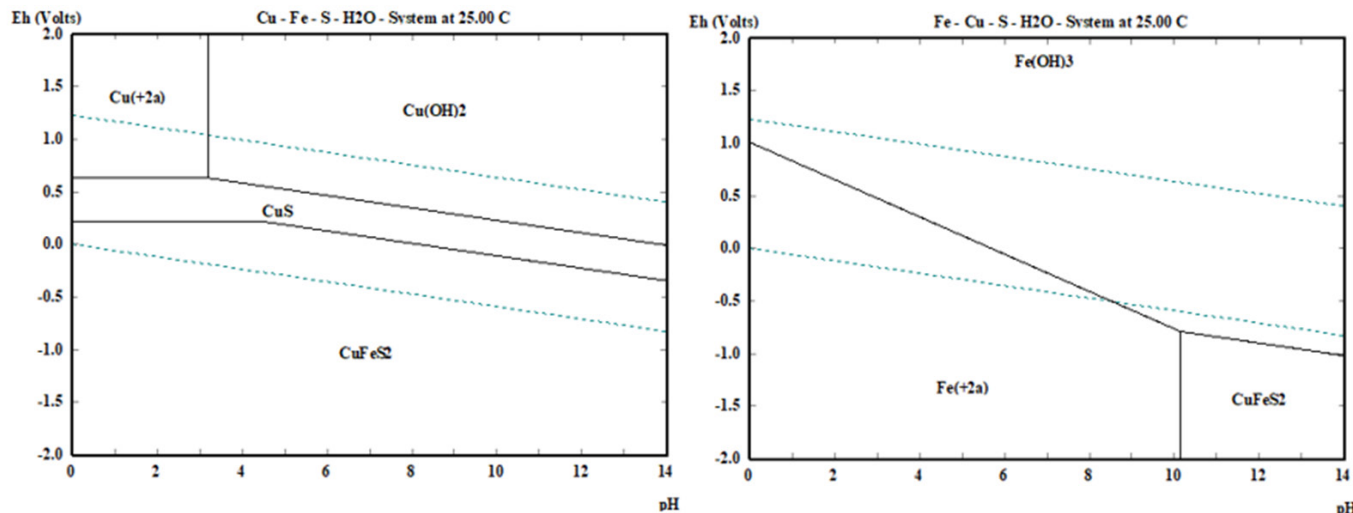


Figure 4: Eh-pH diagram of the Cu-Fe-S system (adapted from [32,34]).

Favorable flotation zone

The favorable flotation zone is found in acidic environments where there is no accumulation of monovalent negative salts. Care must be taken not to over-acidify the solution, as hydronium ions (H_3O^+) could denature the phenolic alcohols in the frothers [35].

Flotation reagents for chalcopyrite







Chalcopyrite exhibits good synergy with anionic collectors from the xanthate, dithiocarbamate, and dithiophosphate families. Since these collector families lack selectivity solely towards chalcopyrite, new molecules have been designed from the molecular base. Innovations such as THA (thiohexanamide) have shown higher recoveries compared to conventional xanthates. Another widely



used collector is IPETC (O-isopropyl-N-ethyl-thionocarbamate) and SIBX (isobutyl xanthate), which are employed to separate chalcopyrite from pyrite [36,37].

Depressants are divided into two families: organic and inorganic. The latter were indiscriminately used before environmental awareness grew, including compounds derived from the CN^- ion such as NaCN or others highly harmful to surrounding substrates like $NaHS_2$. Due to the negative ecological impact, new reagents with equivalent efficiency are being developed, with quebracho, dextrin, and alginate being the most favorable (Table 1). These depressants oxidize the surface of metals other than chalcopyrite, such as galena, making them selective and thereby favoring chalcopyrite recovery [38,39].

Table 1: Literature review of chalcopyrite flotation using various reagent configurations. Note: M. F refers to micro flotation tests.

Author and Year	Title	Conditions		Results
Hornn et al. [40]	Agglomeration-flotation of finely ground chalcopyrite using oil emulsions stabilized by surfactants: Effects of coexisting minerals and ions.	Collector	SDS, KAX	The addition of SDS and KAX emulsifiers in the flotation of chalcopyrite is successful, yielding higher recovery rates compared to when they are not used (97% vs. 68%). The emulsifiers act as stabilizing collectors that expand the particle size range, particularly since the studied size is below the usual range, thus providing a broader working margin for the industrial sector.
		Depressant	CaO	
		Regulator	Sea water	
		Particle size	4.75µm	
		% Solids	30	
		Two emulsifiers (SDS, KAX) are studied with the aim of neutralizing the Ca+ ion, which reduces Cu recovery.		

<p>Bilal et al. [41]</p> 	<p>Effects of coarse chalcopyrite on the flotation behavior of fine chalcopyrite.</p>	Collector	KAX	<p>The use of drag particles within the 75µm-38µm range improves the recovery of fine particles by 80% compared to not using coarse drag particles in the froth.</p>
		Depressant	N/A	
		Regulator	N/A	
		Particle size	-74+38µm	
		% Solids	N/A	
		<p>The study focuses on the impact of using coarse particles to drag fine mineral particles, thereby increasing recovery rates.</p>		
<p>Duan et al. [42]</p> 	<p>Investigation of flotation performance and interfacial adsorption mechanism of N-benzoyl-N', N-diethyl thiourea on chalcopyrite and pyrite.</p>	Collector	BDETU	<p>The BDETU collector, with its organic nature specifically synthesized for chalcopyrite, shows satisfactory results compared to its counterpart IPETC. A significant improvement is the selectivity of BDETU for chalcopyrite across different pH levels, unlike the IPETC, which shows decreased recovery at higher pH (96.50% vs. 75.89%, respectively).</p>
		Depressant	N/A	
		Regulator	HCl NaOH	
		Particle size	-74+38µm	
		% Solids	10 M. F	
		<p>The collector IPETC is compared to BDETU under identical conditions, with variations in pH.</p>		
<p>López Reyes [33]</p> 	<p>Flotation of chalcopyrite, pyrite, and molybdenite in porphyry copper ores.</p>	Collector	S-9844	<p>Dextrin as a pyrite depressant shows satisfactory results when low mineral surface oxidation is maintained. With oxidation and at a pH of 8, chalcopyrite flotation increases, and molybdenum recovery is 10% higher compared to other common depressants.</p>
		Depressant	Dextrin	
		Regulator	CaO	
		Particle size	150µm	
		% Solids	30	
		<p>The implementation of dextrin is explored as a new depressant, aiming to achieve higher Cu-Mo recovery rates.</p>		
<p>Chen et al. [27]</p> 	<p>Enhancement of flotation separation of chalcopyrite and magnesium silicate minerals through surface synergy between PAAS and GA.</p>	Collector	PBX	<p>The combination of PAAS and AG depressants demonstrates positive synergy in chalcopyrite flotation, with recovery rates exceeding 70% at alkaline pH levels. The primary gangue minerals depressed by these depressants are talc and magnesium silicates, with a 25% higher depression rate than other depressant mechanisms.</p>
		Depressant	Arabic gum, PAAS	
		Regulator	HCl NaOH	
		Particle size	-74+38µm	
		% Solids	17	
		<p>The use of the gum arabic-PAAS depressant system is investigated to enhance copper recovery.</p>		
<p>Chen et al. [43]</p> 	<p>The role of oxidant in the flotation separation of chalcopyrite and galena using sodium lignosulfonate as a depressant.</p>	Collector	PBX	<p>The separation of galena and chalcopyrite is achieved by adding considerable amounts of Sodium Lignosulfonate (SLS), which depresses galena while having a minimal effect on chalcopyrite depression. CuFeS₂ recoveries reach 82% when the surface is not oxidized.</p>
		Depressant	SLS	
		Regulator	HCl NaOH	
		Particle size	-150+37µm	
		% Solids	5 M. F	
		<p>The interaction between SLS and H₂O₂ presents potential oxidation of a mineral, facilitating separation.</p>		
<p>Liu et al. [44]</p> 	<p>Investigations on the selective flotation of chalcopyrite from talc using gum arabic as a depressant.</p>	Collector	PAX	<p>Chalcopyrite recovery increases to 87.15% using gum arabic as a depressant for other species, primarily talc. Guar gum shows nearly identical chalcopyrite recovery at 87.03%. These gums adsorb onto both talc and chalcopyrite, but the density of gum on the talc surface makes the gum more selective towards talc.</p>
		Depressant	Arabic gum and guar gum	
		Regulator	HCl NaOH	
		Particle size	-74+38µm	
		% Solids	5.71 M. F	
		<p>Chalcopyrite is anchored to talc, and since talc is hydrophobic, new alternatives for selectivity between the two species are studied.</p>		

Zhang et al. [45] 	A novel synthetic polymeric depressant for the flotation separation of chalcopyrite and galena and understanding its interfacial adsorption mechanism.	Collector	IPETC	DTC-PAA successfully depresses galena with selective adsorption on lead, inhibiting the collector's action on the galena itself. The optimal pH is 8, although higher alkalinity levels yield better results than acidic conditions. The difference in recovery between DTC-PAA and $K_2Cr_2O_7$ is minimal, making the latter a viable substitute (96.37% vs. 92.51%).
		Depressant	DTC-PAA	
		Regulator	HCl NaOH	
		Particle size	-74 μ m+38 μ m	
		% Solids	5 M. F	
		$K_2Cr_2O_7$ is used as a depressant, and DTC-PAA, a polyacrylamide with hydrophobic groups, is explored as a potential substitute.		
Cao et al. [46] 	Flotation separation of pyrite and chalcopyrite using potassium permanganate as a depressant.	Collector	SEX	Potassium permanganate is a selective depressant for pyrite, acting as an oxidant. At concentrations of 4×10^{-4} , it selectively depresses pyrite, but at higher doses, it oxidizes chalcopyrite. The ideal pH level for pyrite and chalcopyrite separation is 7; at both alkaline and acidic levels, lower recoveries are observed (pH 7 - 90%, pH 3 - 75%, pH 11 - 76%).
		Depressant	$KMnO_4$	
		Regulator	HCl NaOH	
		Particle size	-74 μ m+38 μ m	
		% Solids	5 M. F	
		The use of $KMnO_4$ as an oxidant for pyrite is analyzed, along with its impact on the oxidation of chalcopyrite.		

Molybdenite Flotation

Properties and structure of molybdenite

Molybdenite is the primary ore of molybdenum, with a composition of MoS_2 . It has a molecular weight of 160.07g/mol, with a stoichiometric chemical composition of 33.3% molybdenum and 66.7% sulfur. Its color is grayish with violet and silver hues, and it has an oily texture due to the sulfur layers in its crystalline structure [40-46]. The hardness of this mineral ranges from 1 to 1.5 on the Mohs scale, and its density is 4.73g/cm³. The melting point is high, reaching temperatures of 1710 °C [28,47]. Like chalcopyrite, molybdenite is commonly found in hydrothermal deposit veins (Figure 5), where it is usually associated in small proportions with other sulfide minerals such as chalcopyrite, pyrite, scheelite, and silicates like talc [28].



Figure 5: Molybdenite (MoS_2) from USA anchored to quartz (image from [48]).

Crystallographic structure

Its crystallographic structure consists of weakly coupled S-Mo-S layers [48]. The Mo-S bond length is 2.42 Å. MoS_2 crystals

are composed of vertically stacked layers that interact weakly and are held together by van der Waals interactions [49], (Figure 6).

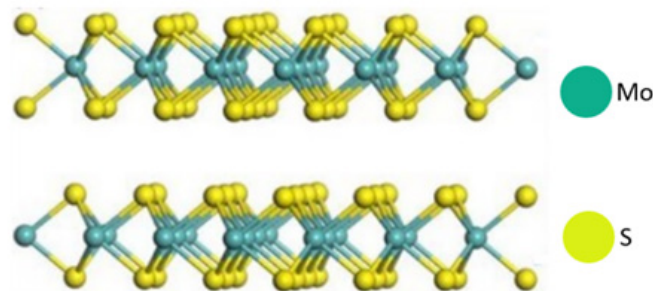


Figure 6: Crystal structure of molybdenite [50].

Molybdenite oxidation

The flotation of molybdenite is influenced by several factors, including mineral anisotropy, degree of liberation, particle size, reagent concentration and permutation, pH, % solids in the cell, and the presence of organic and inorganic oxidizing ions [50,51]. The surface wettability of the edges and base of the mineral is a key factor in understanding the degree of molybdenite oxidation and how it relates to various factors, such as the presence of organic ions released by organic depressants like dextrin or inorganic ions such as Ca^{2+} and Mg^{2+} from silicates in the gangue attached to molybdenite [52], (Figure 7). The optimal flotation of molybdenite depends on the contact angle between the bubble and the mineral itself [53]. Hydrophobic surfaces exhibit a contact angle of 70°, common on the mineral plane, which decreases at the edges with contact angles ranging from 0° to 48°. This is due to the formation of molybdate ions (MoO_4^{2-}) that inhibit flotation by preventing sulfur from contacting the bubbles, similar to what occurs with chalcopyrite [54].

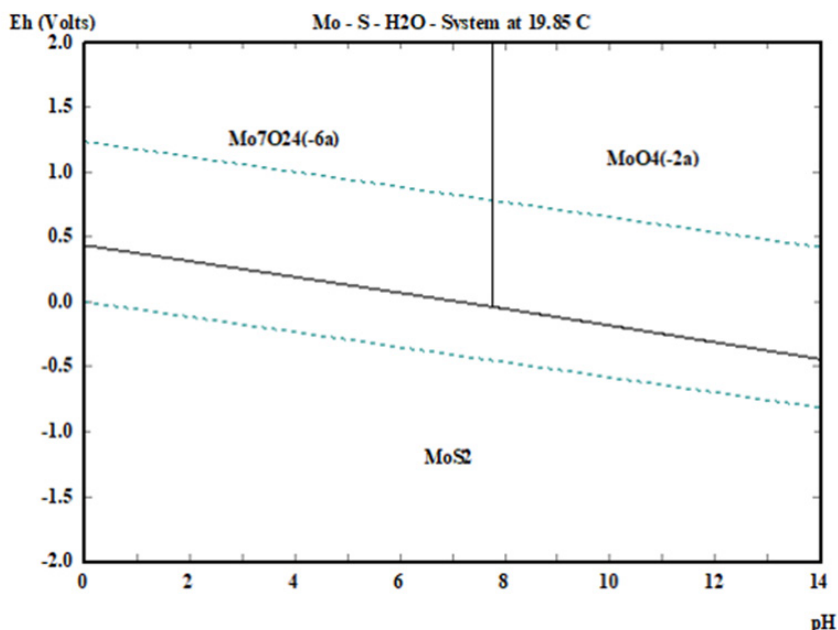


Figure 7: Eh-pH diagram of the Mo-S-H₂O system at 19.85 °C (adapted from [53]).


Favorable flotation zone





The pH levels greatly influence the formation of molybdate ions due to the presence of divalent negative ions (O²⁻) that form oxides on the molybdenite surface layer, thereby disrupting the natural flotation of sulfur with the bubble [55]. Molybdate ions form at alkaline pH levels of 8 and above, according to the Eh-pH diagram of the Mo-S-H₂O system at temperatures of 19.85 °C reported by Liu et al. and Aracena et al. in recent years. Therefore, it is feasible to float molybdenite during the chalcopyrite cleaning stage under acidic conditions [53,56].





Molybdenite flotation reagents

The reagents used for molybdenite flotation are varied but not diverse. Typically, molybdenite is extracted through differential flotation, so the rougher flotation is very similar to that of chalcopyrite, but the reagents vary depending on the mineralogical origin. When molybdenite is associated with species rich in divalent ions like Ca²⁺ and Mg²⁺, collectors such as mercaptans, xanthogen formates, xanthic esters, thionocarbamates, dithiophosphates, and dithiophosphinates are primarily used [57]. In the case of organic depressants, starch, dextrin, guar gum, and humic acids are employed, which oxidize the non-commercially valuable surfaces by forming oxides and hydroxides through ionic exchange redox reactions. For inorganic depressants, Ca(OH)₂, Mg(OH)₂, and Al(NO₃)₃ are used [58], (Table 2).

Table 2: Literature review of molybdenite flotation using various reagent configurations. Note: M. F refers to micro flotation tests.

Author and Year	Title	Conditions		Results
Quing et al. [59] 	An effective method to improve the flotation recovery of fine molybdenite from finely disseminated molybdenum ore	Collector	OAF Kerosene	The flotation product using kerosene resulted in Mo recoveries of less than 48%, with a concentration of 20%, leading to a loss of approximately 52% in the tailings. On the other hand, the agglomerating oil concentrate showed results with a 25.17% concentration and a 71.9% Mo recovery. The OAF demonstrated a 24.63% higher efficiency compared to kerosene.
		Depressant	Na ₂ SO ₃ Na ₂ S ₂ O ₄ C ₂ H ₃ NaO ₂ S	
		Regulator	CaO	
		Particle size	74µm 25µm	
		% Solids	30	
		The impact of particle size was compared, focusing on kerosene (74µm) and agglomerating oils (25µm).		

Li et al. [60] 	Polyethylene oxide-assisted separation of molybdenite from quartz by flotation	Collector	Kerosene	The use of Polyethylene Oxide (PEO) enhances the flotation of fine Mo particles down to 10µm within a pH range of 7-9. Recovery reaches 86% with PEO, compared to 56.5% without it, using 200ppm of kerosene. The presence of quartz in the concentrates drastically decreases when PEO is used as a flocculant depressant.
		Depressant	PEO	
		Regulator	HCl NaOH	
		Particle size	<20µm	
		% Solids	5 M. F	
		The research investigated the efficiency of PEO as a flocculant for fine quartz.		
He et al. [61] 	Improvement of fine molybdenite flotation using a combination of aliphatic hydrocarbon oil and polycyclic aromatic hydrocarbon	Collector	Kerosene	The highest recoveries were achieved with larger particles (-180+150µm) using kerosene and Aliphatic Hydrocarbon (PAH), reaching 93%. The next best recovery was 91% with slightly smaller particles, while particles -74 +45 µm and those smaller than 45µm showed lower recoveries of 83% and 79%, respectively. Without PAH, recoveries decreased by 5% when using only kerosene, indicating that PAH does not effectively mitigate the inefficiency with fines. The pH during these tests was maintained at 6.5.
		Depressant	PAH	
		Regulator	HCl NaOH	
		Particle size	-180+150µm	
			-150+74µm	
			-74+45µm	
% Solids	4 M. F			
This study focuses on the implementation of PAH as a secondary collector alongside kerosene				
Gao y Pan [62] 	Understanding the froth flotation mechanism of molybdenite using oily collectors from the perspective of liquid film thinning and rupture	Collector	Kerosene Dodecane	Kerosene maintains better stability of the Thin Liquid Film (TLF) than dodecane. This is due to a better dispersion of droplets, averaging 2.70 µm in size, on the flat surface and edges of molybdenite. The contact angle of kerosene is higher than that of dodecane, at 80° and 75° respectively.
		Depressant	N/A	
		Regulator	NaCl	
		Drop size	$\bar{X}=2.70\mu\text{m}$	
		% Solids	N/A	
		In this study, the effect of insoluble oily collectors on the thinning and rupture of TLFs (thin liquid films) between air bubbles and surfaces was investigated.		
Ramírez et al. [63] 	Use of "oily bubbles" and dispersants in the flotation of molybdenite in freshwater and seawater	Collector	Kerosene	Tests were conducted with seawater and freshwater solutions with the addition of kerosene and their respective dispersants. The best recoveries (96%) were obtained with freshwater and kerosene at a pH of 10. On the other hand, seawater solutions with kerosene showed lower results with 83%, and without the collector, 76%. As the pH becomes more alkaline, recoveries in seawater decrease significantly, reaching as low as 22%.
		Depressant	SHMP Na_2SiO_3	
		Regulator	NaOH CaO	
		Particle size	100µm	
		% Solids	10 M. F	
		This work tested the effect of oily bubbles and dispersants (SHMP and Na_2SiO_3) on the flotation of molybdenite in seawater under alkaline conditions.		

Zhong et al. [64] 	Flotation separation of molybdenite and talc using xanthan gum	Collector	PBX	Without PBX or XG, the recoveries of MoS ₂ and MgO are 88.5% and 89.05%, respectively. Xanthan gum has the capacity to depress both talc and molybdenum completely if no collector is used. PBX has no selectivity toward silicates, completely depressing talc while activating molybdenite with 95.15% recovery. The pH working range is broad, covering levels from 3 to 11.
		Depressant	XG	
		Regulator	NaOH HCl	
		Particle size	-150+37µm	
		% Solids	5 M. F	
		This study explores the depressant effect of Xanthan Gum (XG) on the flotation of molybdenite and talc, using Potassium Butyl Xanthate (PBX) as the collector.		
Echeverry et al. [65] 	Depressant effect of an anionic polyacrylamide on molybdenite flotation and the importance of polymer anionicity	Collector	N/A	Unsheared LPAM has the strongest depressant effect on MoS ₂ flotation, with a 50% recovery, followed by moderately sheared LPAM with 55% recovery. In contrast, strongly sheared LPAM shows no effect on molybdenite flotation, maintaining a 95% recovery.
		Depressant	LPAM	
		Regulator	NaOH HCl	
		Particle size	- 150+45µm	
		% Solids	10 M. F	
		This work presents the depressant effect of an 8.15% anionic degree polyacrylamide (LPAM) on molybdenite flotation.		
Chen et al. [66] 	Depression of molybdenite flotation by sodium metabisulfite in freshwater and seawater	Collector	Diesel	The depression of MoS ₂ was more effective with 53µm particles, recovering 35% of molybdenite with a metabisulfite dosage above 2mmol/L, while with 106µm particles at the same MBS concentration, recovery was 90%. The pH was kept constant at 7.5. The depression was caused by the adsorption and oxidation of sulfites on the mineral edges, forming sulfates. In seawater, MBS had no effect.
		Depressant	MBS	
		Regulator	NaOH	
		Particle size	106 y 53µm	
		% Solids	6.66	
		In this study, molybdenite flotation was conducted in the absence and presence of MBS in deionized water and seawater to determine the depressant role of MBS.		
Tang et al. [67] 	Reverse flotation separation of talc from molybdenite without depressant addition: Effect of surface oxidation by thermal pretreatment	Collector	Kerosene PBX	It is feasible to carry out reverse flotation of MoS ₂ with talc, as thermal treatment does not affect talc's floatability but does impact molybdenite. The working pH was maintained at 6. MoS ₂ and MgO recoveries without thermal treatment were 90.12% and 83.43%, respectively. MoS ₂ floatability decreases as the temperature increases, with metal recovery dropping to 11.36% at 400 °C and further to 10.64% at 450 °C.
		Depressant	N/A	
		Regulator	NaOH HCl	
		Particle size	-74µm+38µm	
		% Solids	5.7 M. F	
		The impact of thermal pretreatment was analyzed to reduce the floatability of molybdenite and separate it from talc.		

Chalcopyrite and Molybdenite Separation Techniques

In major molybdenite deposits, it is common to find chalcopyrite to varying degrees, as 50% of molybdenum reserves are associated

with porphyry copper sulfide deposits [59-67]. Given that both sulfides have very similar characteristics, it is challenging to achieve separation based on their initial properties [68]. Generally, in the flotation process of molybdenite and the production of Cu-

Mo concentrates, substances such as alkaline sulfides, reagents, cyanides, oxidizers, and sometimes thermal treatment are used to reduce the presence of copper sulfide minerals. The feed of both sulfides usually has a molybdenum content ranging from 0.2% to 1%. Using conventional reagents, the effectiveness of molybdenite recovery in a single rougher flotation stage ranges between 40% and 90%, with concentrates containing between 5% and 10% molybdenum.

However, it has been observed that by using ozone conditioning to reduce the presence of copper, separation can be improved. The additional use of ozone in subsequent flotation stages results in molybdenum concentrates containing up to 52% molybdenum and with a lower copper content [69]. A contemporary recovery technique involves High-Gradient Magnetic Separation (HGMS), which was used to separate chalcopyrite from a fine copper-molybdenum concentrate. The result showed a copper recovery rate of up to 65% and 92% for molybdenum. Like ozone conditioning, it drastically reduces the indiscriminate use of reagents while improving plant efficiency [70].

The development of oxidizing agents such as H_2O_2 for the selective flotation of chalcopyrite and molybdenite systems has been studied. The target mineral for oxidation is chalcopyrite. A drawback is the high consumption of the oxidizing agent required to match the recovery rate of depressants like $NaHS_2$. Ferric sulfate ion ($FeSO_4$) improves the performance of peroxide by reducing its consumption rate. The compounds formed on the surface of chalcopyrite, such as CuO , $Cu(OH)_2$, $FeOOH$, and $Fe_2(SO_4)_3$, give the surface a lower wettability index, favoring the separation of molybdenite. Recovery rates were 92.3% for molybdenum and 6% for copper under $NaHS_2$ depression, and 91.7% and 9.5%,


respectively, with peroxide treatment. Given the similarity, it is feasible to implement peroxide as a chalcopyrite depressant [71]. Another more practical separation method involves determining certain reagent permutations that promote different behavior between the sulfides, thus obtaining a heterogeneous system without affecting the recovery of both minerals. Depressants play a crucial role in the separation of chalcopyrite and molybdenite, as they achieve the aforementioned objective. The most historically used depressant is sodium hydrosulfide ($NaHS_2$) [72].




An interesting system where sodium hydrosulfide can be applied is through a seawater system, aiming to oxidize and consequently depress chalcopyrite. While chalcopyrite oxidation does occur, it results in partial molybdenite depression. Significant dilution of seawater can weaken its buffering effect on pH and significantly raise flotation pH after $NaHS_2$ addition, leading to the formation of $Mg(OH)_2$ and $CaCO_3$ precipitates that depress molybdenite. This is why this system has not been fully exploited yet [73]. $NaHS_2$ emits toxic vapors like H_2S , making its use highly restricted by environmental associations, leading to the search for its replacement with an organic depressant that interacts similarly with molybdenite. Sodium metasilicate (Na_2SO_3) depresses chalcopyrite depending on its concentration and promotes molybdenite flotation [74].




Sustainable Flotation Reagents for Chalcopyrite and Molybdenite




For these reasons, the substitution of inorganic depressants with organic compounds that have equal or better performance than their predecessors are being pursued. Below is a bibliographic review of the organic depressants implemented throughout the development of new alternatives [75-84], (Table 3).

Table 3: Literature review of molybdenite and chalcopyrite flotation using various reagent configurations. Note: M. F refers to micro flotation tests.

Author and Year	Title	Conditions		Results
Yuan et al. [75] 	Characteristics and Adsorption Mechanisms of O-Carboxymethyl Chitosan on Chalcopyrite and Molybdenite.	Electrolyte	KCl	At pH levels above 3, molybdenite exhibits high electronegativity due to the formation of MoS_2 -chitosan interaction products ($HMoO_4^-$ and MoO_4^{2-}). These compounds are not removed by washing, unlike chalcopyrite, where mechanical action can eliminate them. Characterizations (FTIR, XPS) indicate chitosan adsorption on molybdenite at acidic pH (>3), enabling the separation of both sulfides by depressing MoS_2 .
		Depressant	O-CMC	
		Regulator	KOH HCl	
		Particle size	<37 μ m	
		% Solids	5	
		This study focuses on the adsorption capacity of a chitosan derivative on the surface of both minerals and its impact on the adsorption of the collector.		

Wang et al. [76] 	Adsorption Performance and Mechanism of Galactomannan, an Eco-Friendly and Effective Depressant, in the Flotation Separation of Chalcopyrite and Molybdenite.	Collector	SBX	Molybdenite recovery decreases as the dosage of GM increases, while chalcopyrite recovery shows minimal changes. At 10% GM, Mo recovery is 30%, and Cu recovery is 88%; at 20% GM, Mo recovery drops to 7%, and Cu remains at 89%. The adsorption between chalcopyrite and GM is chemical, while the adsorption between molybdenite and GM is physical, leading to preferential coating of the MoS ₂ surface, thereby depressing it.
		Depressant	GM	
		Regulator	NaOH HCl	
		Particle size	38-74µm	
		% Solids	5 M. F	
		In this work, a highly effective new depressant, Galactomannan (GM), was applied to separate chalcopyrite from molybdenite using Sodium Butyl Xanthate (SBX) as a collector.		
Yang et al. [77] 	Selective Depression of Molybdenite Using a New Eco-Friendly Depressant in a Cu-Mo Sulfide Flotation System.	Collector	SBX Kerosene	MoS ₂ recovery without pectin shows high levels of 86%, which decreases to 60% with pectin at pH 6 and further declines in alkaline conditions. At pH 9, recovery drops to 23%, and at pH 12, it reaches 11%. With kerosene and pectin, similar recoveries are achieved, with the highest recovery of 40%, increasing with kerosene dosage. Chalcopyrite recovery shows minimal changes, around 90% at all pH levels with pectin, except at pH 12 without depressant, where it drops to 60%.
		Depressant	Pectin	
		Regulator	NaOH HCl	
		Particle size	- 75+37µm	
		% Solids	5 M. F	
		This research examined pectin as an environmentally friendly depressant for molybdenite in the flotation separation process of chalcopyrite and molybdenite.		
Zhong et al. [78] 	Behavior and Depression Mechanism of Tragacanth Gum on Chalcopyrite during Cu-Mo Flotation Separation.	Collector	PBX	Chalcopyrite recovery decreases with increasing gum dosage. Without gum, 79% is recovered, compared to 85% molybdenite. At dosages of 40, 80, and 100 ppm, chalcopyrite recoveries are 41%, 35%, and 21%, respectively. Molybdenite flotation (85%) remains unchanged with the presence of TG. Tests were conducted at pH 8, and molybdenite recovery decreases sharply at pH 9 in the presence of gum.
		Depressant	TG	
		Regulator	NaOH HCl	
		Particle size	-150+37µm	
		% Solids	5 M. F	
		In the present study, Tragacanth Gum (TG) was employed as a new alternative to inorganic depressants for the flotation of chalcopyrite and molybdenite.		

Gutiérrez et al. [79] 	Evaluation of the Use of Lignosulfonates for the Flotation Separation of Chalcopyrite and Molybdenite.	Collector	PAX	Experimental data indicate that molybdenite recovery is reduced by KLS, and the depressant effect of these reagents increases with pH. At pH 6, molybdenite recovery is 80%, while at pH 9, it drops to 68% with a KLS and CLS dosage of 50ppm. At a 200p.p.m. dosage of both depressants at pH 6, recovery is 45%, and at pH 9, it reaches 30%, making KLS a viable alternative to inorganic depressants.
		Depressant	KLS CLS	
		Regulator	CaO	
		Particle size	-150+37 μ m	
		% Solids	0.66 M. F	
		The aim of this analysis is to investigate the use of low molecular weight lignosulfonates (CLS and KLS) as molybdenite depressants in the Cu-Mo system.		
Wang et al. [80] 	Flotation Separation of Molybdenite from Chalcopyrite Using Rhodanine-3-Acetic Acid as a Novel and Effective Depressant.	Collector	Kerosene	In the absence of 3-Rd, chalcopyrite shows recoveries up to 95%, which slightly decrease as pH increases. However, with the addition of 3-Rd at pH 8, chalcopyrite recovery drastically drops to 21%, while molybdenite exhibits minimal variation with or without 3-Rd (81% and 79%, respectively) at the same pH. Chalcopyrite recovery also varies with 3-Rd dosage: at 10^{-3} mol/L, it is 42%, and at 6×10^{-3} mol/L, it is 19%. Molybdenite shows recoveries of 80% at any 3-Rd concentration.
		Depressant	3-Rd	
		Regulator	NaOH HCl	
		Particle size	- 74+38 μ m	
		% Solids	5.71 M. F	
		The objective of this work is to analyze the use of rhodanine-3-acetic acid (3-Rd) as a depressant for chalcopyrite in the molybdenite and chalcopyrite porphyry system.		
Yan et al. [81] 	Selective Flotation of Cu-Mo Sulfides Using Dithiothreitol as an Eco-Friendly Depressant.	Collector	SIBX Kerosene	Molybdenite maintains high recoveries of around 95% at elevated DDT concentrations without a collector, ranging from 5×10^{-4} mol/L to 2×10^{-3} mol/L at a constant pH of 9. In contrast, chalcopyrite exhibits low recoveries with SIBX and DDT, 75% at 5×10^{-4} mol/L, and without a collector, it drops to 40%. As DDT concentration increases, chalcopyrite recovery declines, reaching 5% at 1×10^{-3} mol/L without SIBX, and with the collector, it reaches 21%.
		Depressant	DDT	
		Regulator	NaOH HCl	
		Particle size	- 75+38 μ m	
		% Solids	2.85 M. F	
		The research covers the study of Dithiothreitol (DDT) as a selective organic depressant for chalcopyrite in the separation of molybdenite.		

Yang et al. [82] 	Thiopronin as a New Copper Depressant for the Selective Flotation Separation of Chalcopyrite and Molybdenite.	Collector	SBX Kerosene	Chalcopyrite recovery without thiopronin shows high levels, similar to molybdenite, with 94% and 95%, respectively. The pH range offers a broad working interval, from acidic levels of 4 to alkaline levels of 12. With the addition of 25ppm thiopronin, chalcopyrite recovery decreases with increasing pH; at a pH of 5, it reaches 20%, which is a turning point, as with greater alkalinity, recovery barely reaches 5%, while molybdenite maintains an average recovery of 95%.
		Depressant	Tiopronin Na_2S	
		Regulator	NaOH HCl	
		Particle size	- 75+38 μm	
		% Solids	5 M. F	
		In this study, an environmentally friendly surfactant called thiopronin was tested as a new copper depressant in the separation of copper and molybdenum sulfides.		
Liao et al. [83] 	Flotation Separation of Molybdenite from Chalcopyrite Using Ferrate (VI) as a Selective Depressant in the Absence of a Collector.	Collector	N/A	Molybdenite does not show significant alterations with the use of K_2FeO_4 , unlike chalcopyrite, which exhibits substantial changes. Chalcopyrite depression is related to ferrate ion concentration; without the depressant, it achieves 75% recovery, while molybdenite reaches 85%. At 1×10^{-4} mol/L and 2×10^{-4} mol/L dosages, chalcopyrite recoveries are 60% and 30%, respectively. Molybdenite shows minimal changes in recovery. Another influencing variable is pH: at alkaline levels of 10, chalcopyrite recovery significantly increases to 60%, while at pH 9, it remains at 20% with a 3×10^{-4} mol/L concentration.
		Depressant	K_2FeO_4	
		Regulator	KOH HCl	
		Particle size	-75+45 μm	
		% Solids	5 M. F	
		This work studied the effect of ferrate in the flotation of chalcopyrite and molybdenite in the absence of a collector at pH levels ranging from 4 to 9.		
Lui et al. [84] 	Synthesis of Hydroxylated Xanthate Salt and Its Use as a New Selective Depressant in Copper and Molybdenum Separation.	Collector	N/A	Molybdenum recovery using HXS exhibits a 9.91% improvement in efficiency compared to NaHS_2 . HXS adsorbs onto the chalcopyrite surface, facilitating a selective flotation process. Molybdenite is floated first, followed by the activation of chalcopyrite. Recovery rates reached 88.36% for molybdenum and 99.94% for copper.
		Depressant	HXS	
		Regulator	NaOH	
		Particle size	74 μm	
		% Solids	33	
		The flotation responses of chalcopyrite and molybdenite were investigated when HXS was used as a new depressant through bench-scale flotation tests.		

Conclusion

A vast array of techniques has been developed, refined, and implemented for the selective separation of copper and molybdenum from porphyry minerals, with chalcopyrite and

molybdenite receiving particular attention as the primary sources of these metals [85]. The complexities associated with the flotation process of these sulfide minerals have driven extensive research, leading to the innovation of various depressants aimed

at enhancing the efficiency of separation. China, which holds the world's largest reserves of molybdenum, has emerged as a key player in this research domain. The country's significant interest in the effective separation of molybdenum is not coincidental, given its strategic importance in the steel industry. As a global leader in steel production, China's efforts to optimize molybdenum recovery reflect its broader economic objectives, ensuring a stable and efficient supply chain for this critical metal. The advances in flotation technologies, particularly those that enhance the selective depression of chalcopyrite in the presence of molybdenite, underscore the importance of these metals to China's industrial ambitions.

Copper, on the other hand, is indispensable across a wide range of industries, from electronics to construction, making it a metal of global importance. The demand for copper continues to grow, driven by its critical role in technological advancements and infrastructure development worldwide. As such, the global mining and metallurgical communities have focused heavily on optimizing the extraction and processing of copper, recognizing its vital role in the world economy.

This comprehensive review of the literature highlights the ongoing and intensive research efforts aimed at improving the flotation processes for these two critical metals. The development of innovative depressants has not only enhanced the separation efficiency but also contributed to the sustainability and economic viability of copper and molybdenum production. The global dependence on a continuous and reliable supply of these metals cannot be overstated, as they are integral to various industrial sectors, thereby reinforcing the need for continued research and technological advancements in their extraction and processing.

In conclusion, the ongoing exploration of new depressants and flotation techniques represents a critical frontier in the field of mineral processing. The global importance of copper and molybdenum, coupled with the increasing complexity of ore deposits, necessitates sustained innovation in separation technologies. The findings presented in this review underscore the significance of these developments and their far-reaching implications for the global economy, particularly in countries like China, where the strategic importance of these metals is acutely recognized. The continued refinement of these processes will be essential in meeting the growing demand for copper and molybdenum, ensuring their availability for future generations.

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