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The role of typical metal ions Ca^{2+} and Mg^{2+} in mineral flotation: A review

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Abstract: Unavoidable ions in flotation pulp play a critical role in modulating the selective activation or depression of target minerals. This review systematically examines the behavior of Ca^{2+} and Mg^{2+} in mineral flotation. Their primary sources in the pulp are first outlined. Fundamental mechanisms governing their interactions with mineral surfaces are then discussed to establish a theoretical basis for interpreting their flotation behaviors. The activating, depressing, and dispersing effects of these ions on various mineral surfaces are provided, highlighting their multifaceted functions. In addition, strategies to mitigate the adverse impacts of Ca^{2+} and Mg^{2+} are evaluated. This review is intended to guide the optimization of flotation processes, improve the separation efficiency, and provide theoretical and practical insights for mineral processing.

Keywords: metal ions, flotation, activation, depression, particle interaction

1. Introduction

As a key technology in the modern mineral processing industry, froth flotation is highly dependent on the physicochemical properties of mineral surfaces and the aqueous chemistry of the pulp environment (Li and Gao, 2018; Bai et al., 2023). Within complex mineral pulp systems, the presence of metal ions critically influences the flotation efficiency through their adsorption and interfacial transformations (Gao et al., 2021a; Sun et al., 2021a; Yu et al., 2024). In recent years, the increasing ore complexity and widespread recycling of process water have led to the accumulation of these ions, adversely affecting the recovery of target minerals. Understanding the multiphase interfacial interactions among metal ions, minerals, flotation reagents, and air bubbles has therefore become essential in flotation chemistry research.

Metal ions in flotation pulps, originating primarily from mineral dissolution, recirculation of process water, and reagent addition (Lai et al., 2020; Kuang et al., 2021; Rankin et al., 2025), critically influence flotation efficiency through interfacial processes. These ions modify critical mineral surface properties through adsorption, complexation, and precipitation, collectively forming a synergistic "ions-minerals-reagents" system. Among them, Ca^{2+} and Mg^{2+} deserve particular attention due to their distinctive aqueous chemistry. For example, these ions can form hydrophilic hydroxy complexes or precipitate films on mineral surfaces such as pyrite and galena, thereby depressing these sulfide minerals (Bulut and Yenial, 2016; Ruan et al., 2018). Conversely, they could also activate silicate minerals like quartz and feldspar under specific pH conditions by generating surface active sites (Huang et al., 2021). Moreover, Ca^{2+} and Mg^{2+} adsorption would modulate particle dispersion and aggregation by altering the electrical double-layer, directly impacting pulp rheology and flotation selectivity. Despite significant advances in understanding the role of metal ions in mineral flotation, research on Ca^{2+} and Mg^{2+} has largely been confined to single-mineral systems.

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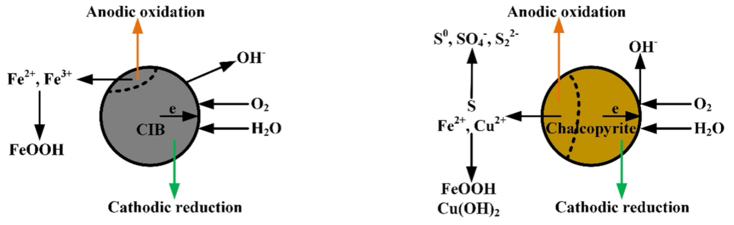
This review bridges the gap by systematically elucidating the sources, interfacial mechanisms, and multi-dimensional roles (depression, activation, and dispersion) of these ions. By integrating multi-scale analysis with targeted regulation strategies, this work provides critical theoretical insights to optimize flotation performance and improve complex ore separation. The findings advance the development of green and sustainable mineral processing technologies.

2. Sources of metal ions

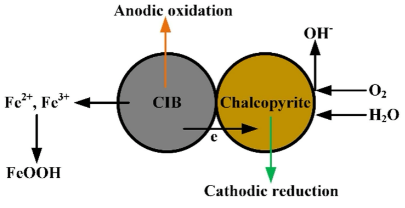
Metal ions in flotation pulp originate from multiple sources, including process water, mechanical crushing and grinding, mineral dissolution, and reagent addition. These ions subsequently modify mineral surface properties through physicochemical adsorption and surface precipitation. Additionally, these ions modulate the reagent adsorption by forming complexes or enhancing surface reactivity, thereby activating or depressing the floatability of target minerals.

2.1. Dissolution of grinding media

During the grinding process, iron ions (Fe^{2+} and Fe^{3+}) are released into the pulp through mechanical friction and chemical corrosion between grinding media and mineral particles. The electrochemical potential difference between steel media and sulfide minerals (such as chalcopyrite and pyrite) generates local galvanic couples. This phenomenon intensifies electrochemical corrosion and promotes metal ion release. These dissolved ions markedly influence mineral surface reactivity and alter redox potential and solution chemistry of the pulp environment. Furthermore, sulfur species on sulfide mineral surfaces are oxidized through galvanic interactions, diminishing their natural hydrophobicity. Concurrently, through the adsorption or precipitation of Fe^{2+} and FeOOH species generated by electrochemical corrosion, the surface charge properties are modified, thereby influencing the subsequent interfacial interactions. These processes collectively depress the flotation selectivity of sulfide minerals through surface passivation, increased reagent consumption, and electrical double-layer compression (Fig. 1) (Mu et al., 2020; Zhang et al., 2020; Zhu et al., 2023). By comparing steel and ceramic grinding media, Zhao et al. (Zhao et al., 2022) demonstrated that the galvanic interaction between iron-based media and chalcopyrite would intensify the surface oxidation of chalcopyrite, promoting the adsorption of FeOOH and copper-cyanide complexes compared to ceramic grinding, as confirmed by XPS and ToF-SIMS. These surface modifications would reduce hydrophobicity and diminish collector adsorption, thereby significantly depressing chalcopyrite floatability when ground in steel mills. In contrast, Cao et al. (Cao et al., 2021) reported that cassiterite ground with stainless steel showed improved flotation performance compared to ground with ceramic media due to the adsorption of dissolved iron species, which shifted zeta potential positively and enhanced the adsorption of salicylhydroxamic acid through the increased active sites and reduced electrostatic repulsion.



(a) Local cell reaction within CIB medium itself **(b) Local cell reaction within chalcopyrite itself**



(c) Galvanic couple action between CIB medium and chalcopyrite

Fig. 1. Local cell (a, b) and galvanic couple (c) interactions between chalcopyrite and grinding media (Zhang et al., 2020)

2.2. Metal ions from mineral dissolution or oxidation

The oxidation and dissolution of mineral surfaces could release metal ions into pulps, thereby significantly influencing separation efficiency (Cao et al., 2018; Irannajad et al., 2019; Wang et al., 2020a; Wang et al., 2020b; Xu et al., 2022).

Feng et al. (Feng et al., 2023) reported that lead ions released from the grinding and separation of zinc minerals could activate smithsonite by bonding with the oxygen sites, enhancing xanthate adsorption and improving flotation recovery (Fig. 2). During the reverse flotation process of phosphorite, dissolution of Ca^{2+} and Mg^{2+} would increase the hydrophobicity of flotation concentrate, while the hydrolysate of Fe^{3+} and Al^{3+} would adsorb on mineral surfaces, blocking the oleate adsorption sites and reducing the hydrophobicity of flotation concentrate (Fig.3) (Cheng et al., 2024). Copper sulfide minerals usually undergo surface oxidation when their surfaces are exposed to air or liquid media during storage, grinding and flotation, resulting in the release of ions and self-activation phenomena. Deng et al. (Deng et al., 2014) observed that the dissolution of chalcopyrite itself and the rupture of secondary fluid inclusions would significantly increase the concentration of Cu^{2+}, enhancing the surface reactivity through interactions with sulfur atoms. These phenomena would be conducive to increasing the flotation rate under certain conditions. Similarly, Zhu et al. (Zhu et al., 2019) combined DFT and experiments to demonstrate that Fe and Ca ions, which exist in the lithium feldspar lattice in the form of isomorphous substitution, were released into the pulp through lattice fracture during grinding and participate in interfacial reactions mediated by solution chemistry and surface processes. Moreover, Moimane et al. (Moimane et al., 2020) reported that the floatability of both chalcopyrite and chalcocite would be severely depressed with the increased oxidation by H_2O_2, with recoveries declining from 89.3% to 5.95% and from 97.5% to 1.80%, respectively, and that chalcocite exhibits greater oxidation sensitivity than chalcopyrite.

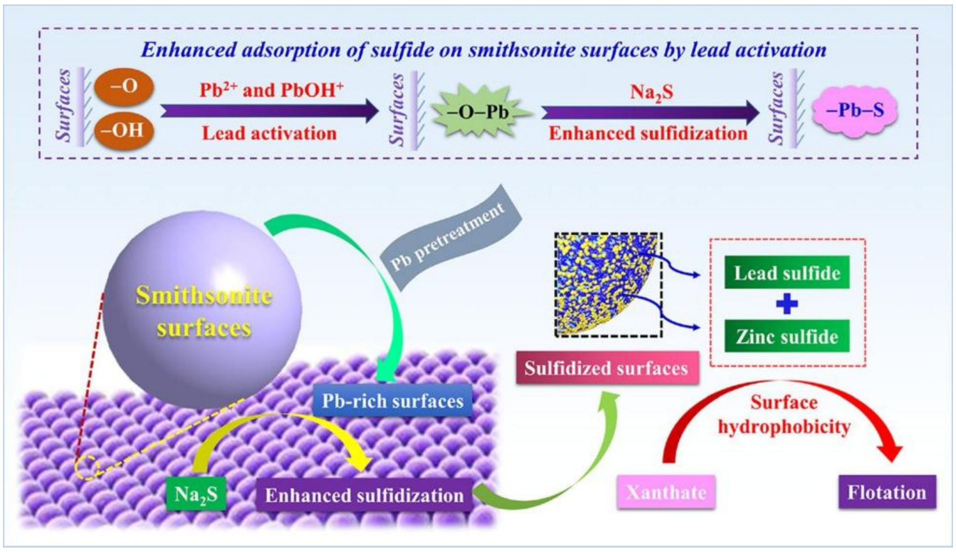


Fig. 2. Lead-activated promotion of sulfide and xanthate adsorption on smithsonite surface (Feng et al., 2023).

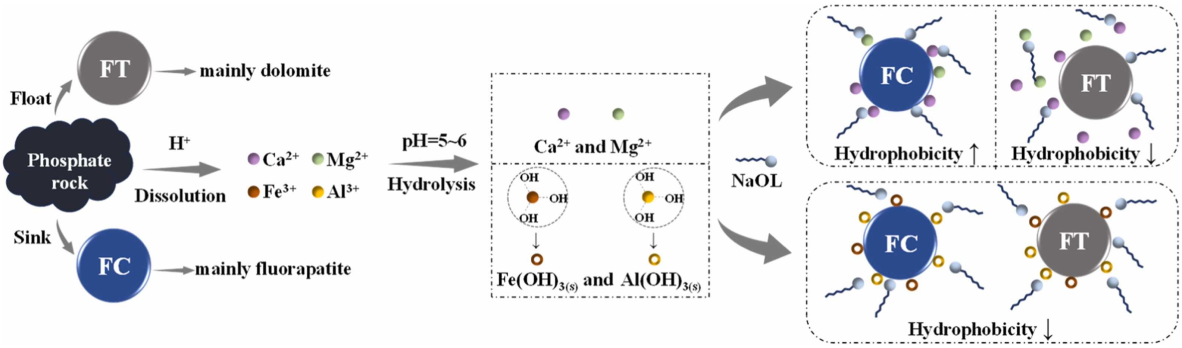


Fig. 3. The role of metal ions in modifying mineral surfaces wettability (Cheng et al., 2024)

2.3. Contribution of process water

Dissolved metal ions in process water represent a significant external source influencing flotation systems. Metal ions such as Ca^{2+}, Mg^{2+}, Na^+, and K^+, commonly found in industrial and recirculated water, could modulate the pulp chemistry by adjusting pH or interacting with flotation reagents (Corin et al., 2024; Duan et al., 2024; Hwang et al., 2024; Zhou et al., 2024; Rankin et al., 2025). Studies indicate that Ca^{2+}, Mg^{2+} and SO_4^{2-} in recycled water markedly affect the flotation selectivity of sulfide minerals through surface charge modification. Specifically, adsorption of Ca^{2+}, Mg^{2+} could reduce the surface electronegativity of galena and sphalerite, thereby enhancing their floatability. In contrast, SO_4^{2-} in solution would adsorb on galena and pyrite through competitive adsorption, increasing the surface negativity (Bulut and Yenial, 2016). The increasing adoption of seawater and intensified water recycling in flotation have made ionic accumulation a critical issue (Jeldres et al., 2016; Peng et al., 2020; Acuña et al., 2024; Ramirez-Madrid et al., 2024; Song et al., 2024a; Wang and Peng, 2014). Song et al. (Song et al., 2022; Song et al., 2024b) demonstrated that seawater could achieve higher separation efficiency between galena and pyrite compared to deionized water. This enhancement was attributed to the synergistic effects of Ca^{2+} and Mg^{2+}, which function through surface hydroxylation and compression of the electrical double layer.

2.4. Metal ions from flotation reagents

Flotation reagents frequently consist of inorganic metal salts that dissociate upon addition into the pulp, releasing the corresponding metal and inorganic ions to modify mineral surface properties or interact with other reagents (Tian et al., 2019a; Tian et al., 2019b). As a widely used pH regulator, lime could significantly alter the aqueous chemistry of flotation pulp system (McCormick et al., 2002; Sun et al., 2023). While it effectively adjusts the optimal alkalinity, Ca^{2+} is inevitably introduced into the pulp and accumulates through water recycling. This accumulation would facilitate unintended surface precipitation and hydroxide complexation, adversely affecting the selective separation of the target minerals (Zanin et al., 2019). In sulfide ore flotation, metal ions could act as activators by reconstituting surface chemistry. For instance, Cu^{2+} could enhance the collector adsorption on pyrite surface, thereby improving its floatability (Pecina et al., 2006). In contrast, the precipitates formed from Cu^{2+} and Fe^{3+} on molybdenite surfaces significantly depress its flotation (Yang et al., 2019). During the separation of fluorite from quartz, combined depressants comprising sodium silicate and metal ions, such as Fe^{3+}, Cu^{2+} or Al^{3+}, could hinder the quartz activation by Ca^{2+}, subsequently reducing the collector adsorption and preventing quartz from entering into the fluorite concentrate (He et al., 2022).

The sources of metal ions in flotation systems are diverse. Externally, they are mainly introduced through process water and the addition of flotation reagents. Internally, they are sourced from the surface oxidation and dissolution of minerals. A thorough investigation of these metal ions and their interfacial behaviors is essential. It will mitigate the adverse effects of unavoidable ions, improve flotation selectivity, and provide a scientific foundation for the optimizing flotation parameters.

3. Mechanisms of metal ions in mineral flotation

As critical interface-active components, metal ions critically influence the mineral floatability through multiple mechanisms in flotation systems. This section elaborates on their specific functions from three principal aspects.

3.1. Direct interaction between metal ions and minerals

Metal ions interact with mineral surfaces primarily through two mechanisms. First, metal ions could adsorb onto mineral surfaces through electrostatic attraction, modifying the mineral surface charge properties. For example, Ca^{2+} adsorbs onto hydroxylated scheelite surfaces through electrostatic attraction (Dong et al., 2019; Zhang et al., 2019), forming a competitive adsorption layer, leading to the inhibition of subsequent adsorption of dodecylamine. Similarly, whereas electrostatic repulsion hinders carboxymethyl cellulose (CMC) adsorption on chlorite, Ca^{2+} and Cu^{2+} in solution could enhance the adsorption of CMC through distinct pathways. At pH 9, Ca^{2+} could facilitate CMC adsorption on chlorite by reducing the electrostatic repulsion through charge neutralization between Ca^{2+} and CMC, increasing CMC adsorption capacity. In contrast, Cu^{2+} could adsorb directly onto chlorite surface, providing new binding sites for CMC and lowering zeta potentials of both CMC and chlorite surfaces, thereby facilitating CMC adsorption capacity (Feng et al., 2013).

Second, metal ions can also adsorb onto mineral surfaces through ion exchange or lattice substitution. As illustrated in Fig. 4, Cu^{2+} could replace Zn^{2+} on sphalerite surface through redox reactions, forming copper sulfide species that enhance collector adsorption. This process would increase the hydrophobicity of sphalerite surface, thereby enhancing its flotation efficiency (Gerson et al., 1999; Pattrick et al., 1999; Ejtemaei and Nguyen, 2017). Similarly, Pb^{2+} is widely recognized as an activator in the flotation of scheelite and calcite (Wei et al., 2018; Wang et al., 2019; Yao et al., 2022). According to Yu et al., Pb^{2+} would substitute Ca^{2+} in the scheelite lattice through isomorphous replacement, which is mainly caused by their similar ionic radius (Yu et al., 2015). The thermodynamic analysis shows that the solubility product of $PbWO_4$ (pKsp=10.08) is significantly lower than that of $CaWO_4$ (pKsp=9.3), indicating a stronger tendency for $PbWO_4$ precipitate formation. Consequently, Pb^{2+} could stabilize on the mineral surfaces through substitution of Ca^{2+} in both scheelite and calcite.

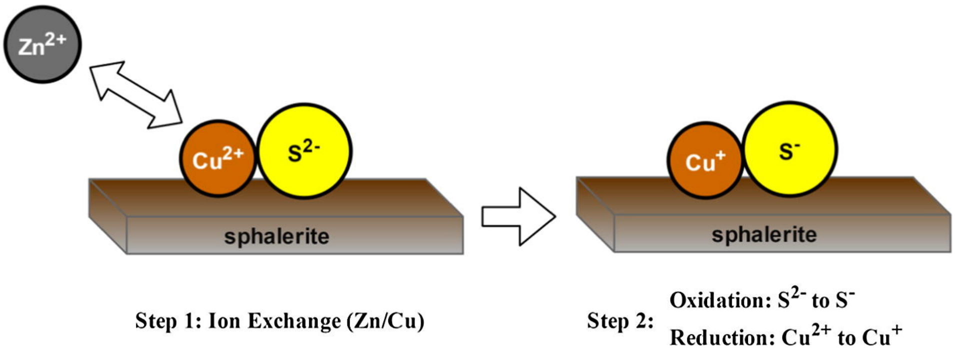


Fig. 4. Cu^{2+} adsorption process on the sphalerite surface (Ejtemaei and Nguyen, 2017)

3.2. Hydrolysis and complexation of metal ions

Two primary hypotheses have been proposed to explain the role of metal ions in mineral flotation. The first involves the formation of metal-hydroxy complexes through coordination with OH^- in pulp (Wu et al., 2022). These complexes can undergo dehydroxylation condensation reactions with oxygen-containing minerals, creating specific adsorption sites that interact with flotation reagents, as illustrated in Fig. 5 (Gao et al., 2017). This interfacial regulation mechanism was initially established by Fuerstenau et al. in studies of the quartz flotation system, highlighting the crucial role of metal ions in mediating the reagent-mineral interactions (Fuerstenau et al., 1965; Fuerstenau and Cummins, 1967). Individual metal ions (in the order of $Ba^{2+}>Fe^{3+}>Ca^{2+}$) significantly enhanced OHA adsorption and flotation recovery of bastnäsite by forming N-M(OH) coordination bonds between the hydrolysis products of the metal ions and the nitrogen atom in OHA, while mixed ions inhibited OHA adsorption due to competitive effects. DFT calculations revealed a reduced adsorption energy and a dual-site adsorption model involving both Ce-O and M-O bonds. This study clarifies these opposing mechanisms and elucidates the role of metal ions as an "adsorption bridge" at the atomic orbital and chemical bond levels (Liu et al., 2024). Similarly, Luo et al. (Luo and Chen, 2022) demonstrated that dihydroxy complexes could adsorb more readily and stably onto quartz surface compared to monohydroxy complexes.

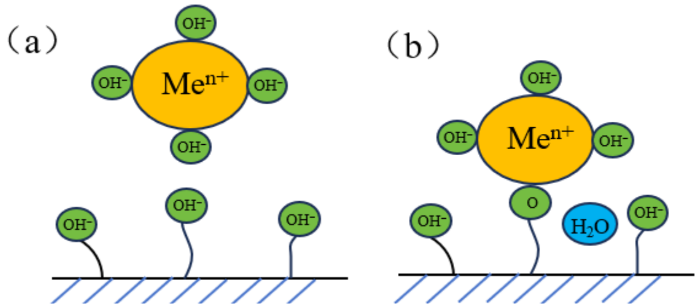


Fig. 5. Formation of metal ion-hydroxy complex on mineral surface (Gao et al., 2017)

The second mechanism entails the adsorption of metal ions through surface precipitation, which alters the efficacy of reagents on flotation (Fig. 6) (Paiva et al., 2011; Gao et al., 2017; Suyantara et al., 2018). Species distribution diagrams indicate that most metal ions hydrolyze into precipitates under alkaline conditions (Hoseinian et al., 2023; Liu et al., 2023). During sphalerite flotation, Cu^{2+} could be used as an activator through the formation of Cu_xS surface products. However, under alkaline conditions, it would be hydrolyzed into $Cu(OH)_2$ precipitate, which would chemisorb onto sphalerite surface and reduce its floatability (Zhao et al., 2021). The dominant species of metal ions existing in solution are critically influenced by pH. For example, Pb^{2+} and $PbOH^+$ dominate in weakly acidic environments, whereas $Pb(OH)_2$ precipitates prevail under alkaline conditions (Yu et al., 2023; Miao et al., 2024). Thus, pulp pH is a critical factor in determining the dominant species and their subsequent effects on flotation.

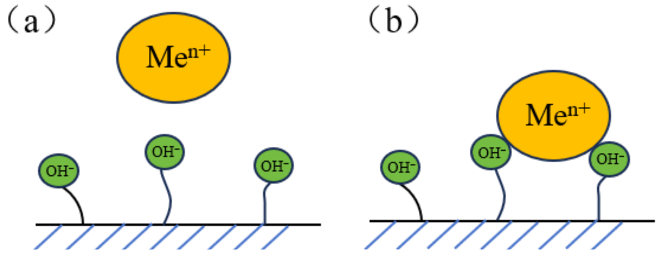


Fig. 6. Formation of metal hydroxide precipitate on mineral surface (Gao et al., 2017)

In mineral flotation systems, the speciation of metal hydroxy complexes depends critically on solution pH. Under acidic conditions, metal ions would form positively charged hydroxy complexes through hydroxide coordination, which would adsorb onto mineral surfaces through chemisorption. As the pH value increases to neutral range, the enhanced hydroxylation would promote polycondensation, leading to the formation of colloidal hydroxide precipitate. Under strongly alkaline conditions, the excessive OH^- would further transform these hydrolyzed products into negatively charged hydroxy complexes. As illustrated by the composition diagram of Al^{3+} in Fig. 7 (Zhang et al., 2023), $Al(OH)^{2+}$ and $Al(OH)_2^+$ dominate at pH 1-4. Above pH 4, the concentration of $Al(OH)_2^+$, $Al(OH)^{2+}$ and Al^{3+} in solution would decrease sharply, while $Al(OH)_3$ precipitate emerges and rapidly becomes the predominant species. With further increase in alkalinity, $Al(OH)_4^-$ becomes the dominant soluble species.

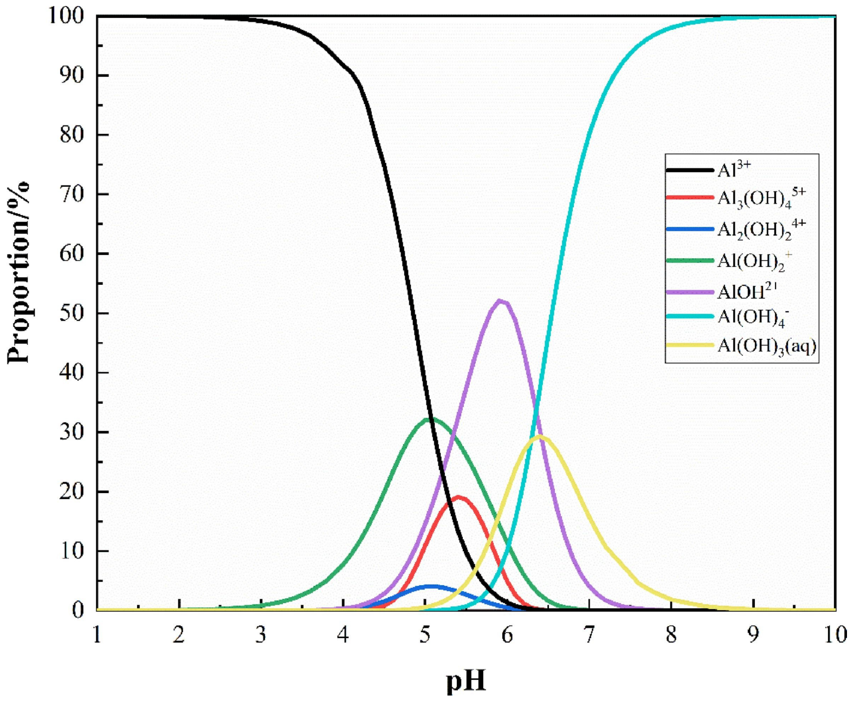


Fig. 7. Composition diagram of aluminum ion in solution (Zhang et al., 2023)

3.3. Interaction between metal ions and flotation reagents

Metal ions in pulp could interact directly with the flotation reagents. This interaction modifies reagent properties or forms metal-reagent complexes, significantly influencing flotation performance (Chen, 2021; Wei et al., 2021; Dong et al., 2023; Zhao et al., 2024). For example, the addition of Fe^{2+} could enhance the depressive effect of sodium silicate. When applied in an optimal ratio, the combination of Fe^{2+} and sodium silicate would exhibit stronger selective adsorption and depression compared to silicate alone (Deng et al., 2018). Ultrasonic pretreatment could promote the oxidation of Fe^{2+} to Fe^{3+} on ilmenite and olivine surfaces, while exhibiting minimal impact on titanaugite. This selective oxidation facilitates the preferential adsorption of sodium oleate (NaOL) onto $Fe(OH)_3$ species formed on ilmenite surface. Concurrently, ultrasonic pretreatment would release a large amount of Ca^{2+} and Mg^{2+} from the surfaces of titanaugite and olivine into the pulp, reducing the surface active sites and diminishing oleate adsorption. These changes collectively improve the separation of ilmenite from titanaugite and olivine (Fang et al., 2020). Studies indicate that Fe^{3+} inhibits the sulfuration flotation of smithsonite by forming weak and unstable Fe-S bonds, accompanied by a surface hydration film that hinders HS^- adsorption on the mineral surface. These combined effects reduce the active sites available for collector attachment on smithsonite surface (Luo et al., 2022). In systems activated with copper sulfate, $Cu(OH)_2$ adsorbed on mineral surfaces could react with xanthate to form an unstable complex that readily decomposes, thereby reducing the mineral surface hydrophobicity (Leppinen, 1990). Conversely, in spodumene flotation, the presence of Ca^{2+} could promote the formation of colloidal oleate complexes that strongly adsorb onto the spodumene surface, enhancing its surface hydrophobicity (Gao et al., 2021b). Pb^{2+} could react with benzohydroxamic acid (BHA) to form a complex of $Pb^{2+}/Pb(OH)^+$-BHA (Fig. 8), which exhibits enhanced collecting capacity compared to the sequential addition of Pb^{2+} and BHA (Tian et al., 2017; Tian et al., 2018).

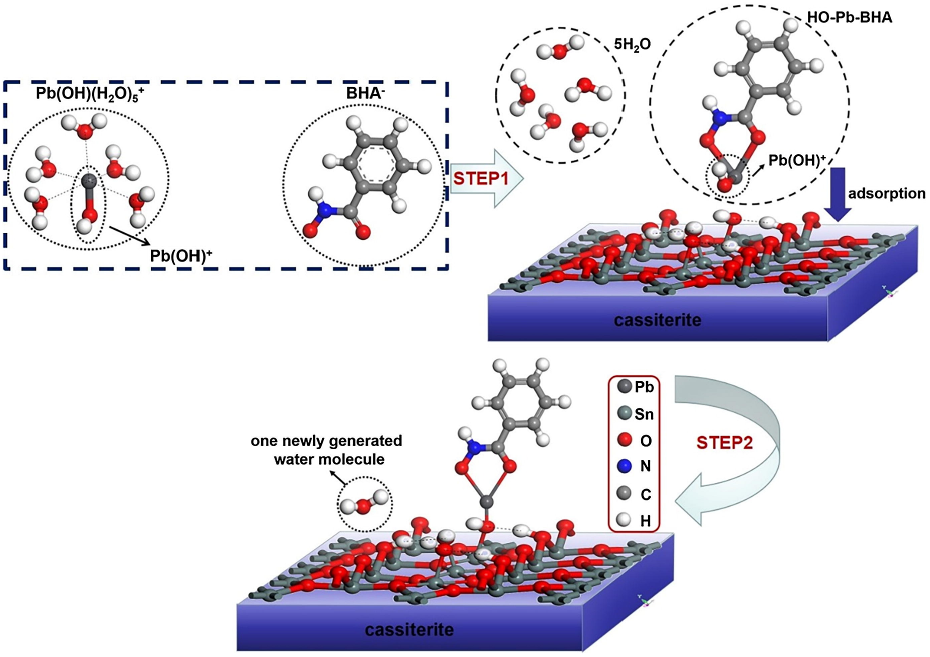


Fig. 8. Proposed adsorption mechanism of HO-Pb-BHA on cassiterite at pH 8-9 (Tian et al., 2018)

Metal ions could significantly influence mineral flotation through multiple mechanisms, including electrostatic interactions with the mineral surfaces, ion exchange, hydroxy complex formation, and hydroxide precipitation. Additionally, the reactions between metal ions and flotation reagents also critically influence flotation performance.

4. Influence of Ca^{2+} and Mg^{2+} in mineral flotation

As the most common divalent metal ions in flotation systems, Ca^{2+} and Mg^{2+} are widely derived from ores, process water and flotation reagents. These ions critically influence flotation performance by modulating mineral surface properties and reagent interactions, thereby affecting both selectivity and separation efficiency. This section examines the roles of Ca^{2+} and Mg^{2+} in mineral flotation, emphasizing their activation, depression and dispersion effects, and discusses strategies to mitigate their adverse impacts.

4.1. Depression of Ca^{2+} and Mg^{2+}

In certain flotation processes, the presence of Ca^{2+} and Mg^{2+} could significantly hinder the selective separation of minerals. This section details the depression mechanisms of Ca^{2+} and Mg^{2+} in flotation.

Solution chemistry analysis indicates that Ca^{2+} and Mg^{2+} predominantly exist as free ions at pH 3-7. Under alkaline conditions at pH 10-11, $Ca(OH)^+$ and $Mg(OH)^+$ become the dominant species (Yao et al., 2024). When Ca^{2+} adsorbs on sillimanite in the presence of dodecylammonium chloride, it could reduce the mineral surface zeta potential, thereby significantly diminishing the electrostatic attraction between dodecylammonium and the mineral. This would result in decreased adsorption of dodecylammonium and weakened surface hydrophobicity (Chen et al., 2017). In wolframite flotation systems, Ca^{2+} and Mg^{2+} could adsorb on wolframite surface through physisorption and increase the zeta potential, thereby interfering with Pb^{2+} activation and inhibiting the consequent adsorption of fatty acid (Shang and Zhou, 2018). Alkaline conditions promote the hydrolysis of Ca^{2+} and Mg^{2+}, leading to hydroxy complexes or colloidal hydroxide precipitates. These species would adsorb onto mineral surfaces, thereby modifying their electrochemical properties and altering the interaction between reagents and minerals (Zhou et al., 2020). Additionally, the adsorption of these hydrolyzed species inhibit subsequent reagent adsorption by forming hydrophilic surface films (Hirajima et al., 2016).

Beyond direct hydrolysis, Ca^{2+} and Mg^{2+} could also interact with other ions derived from minerals to affect mineral flotation behavior. For example, Ca^{2+} could react with MoO_4^{2-} at molybdenite edges to form calcium molybdate precipitates, depressing its floatability (Wan et al., 2017; Sun et al., 2021b). Due to the similarities in ionic size between Ca^{2+}/Na^+ and Ba^{2+}/K^+, divalent cations are able to replace monovalent ions in feldspar lattices through isomorphous replacement. Thus, slight increases in Ca^{2+} concentration would promote its preferential adsorption onto Na-feldspar surface through ion exchange, significantly reducing the surface zeta potential. This would effectively inhibit the adsorption of amine collectors, facilitating the separation between Na-feldspar and K-feldspar (Demir et al., 2003).

Reagent consumption by Ca^{2+} and Mg^{2+} represents another depression mechanism on mineral flotation. Surface chemistry studies indicate that Ca^{2+} adsorption would depress the high-iron sphalerite flotation by competitively occupying surface active sites (Fig. 9), hindering the activation of Cu^{2+} and reducing the xanthate adsorption through electrostatic screening (Zhang et al., 2021). Furthermore, isomorphous substitution of Fe in sphalerite lattice obviously enhances the adsorption of Ca^{2+} through surface charge redistribution, which synergistically reduces the mineral floatability by passivating active sites and compressing the electrical double-layer. In phosphate ore flotation, Ca^{2+} dissolved from phosphorite would react with SO_4^{2-} to form the calcium sulfate precipitates. These precipitates would adsorb onto dolomite surfaces, reducing the available active sites for oleate adsorption and consequently depressing dolomite hydrophobicity in NaOL system (Fig. 10) (Chen et al., 2022). The interaction of Mg^{2+} in phosphate flotation system is regulated by the ion concentration. At low concentrations, it would form $Mg_3(PO_4)_2$ precipitates that activate phosphate surfaces and enhance the collector adsorption. In contrast, above a critical concentration, excessive Mg^{2+} consumes oleate and forms a dense $Mg(OH)_2$ layer that strongly depresses flotation (Li and Zhang, 2013). As a common depressant, CMC would react with metal ions, such as Cu^{2+} and Ca^{2+}, through distinct mechanisms (Burdukova et al., 2008; Feng et al., 2013). Ca^{2+} could neutralize the surface charge on CMC, facilitating its adsorption on chlorite and talc. In contrast, Cu^{2+} would adsorb directly onto chlorite surface, reducing surface charge of both the mineral and CMC, diminishing electrostatic repulsion and enhancing adsorption density.

As shown in Table 1, depression of mineral flotation by Ca^{2+} and Mg^{2+} occurs mainly through multiple mechanisms. First, they could adsorb on mineral surfaces, altering surface charge properties and thereby weakening electrostatic interactions with collectors. Second, Ca^{2+}, Mg^{2+} and their hydroxy complexes compete with target minerals for reagent coordination, effectively consuming flotation reagents. Additionally, under highly alkaline conditions, these ions would form hydrophilic hydroxide precipitates and adsorb on mineral surfaces, enhancing surface hydrophilicity. Concurrently, Ca^{2+} and Mg^{2+} could also compete with activating metal ions and collectors for mineral surface active sites, thereby hindering their adsorption. These synergistic interactions would collectively depress the floatability of the target minerals.

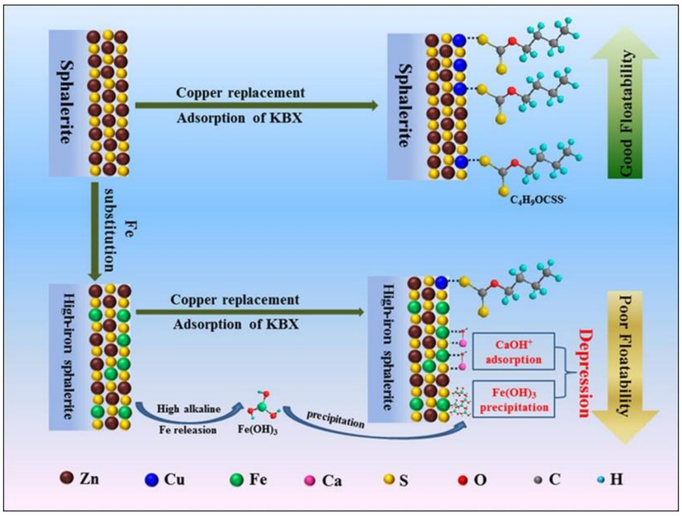


Fig. 9. Schematic of the marmatite depression mechanism (Zhang et al., 2021)

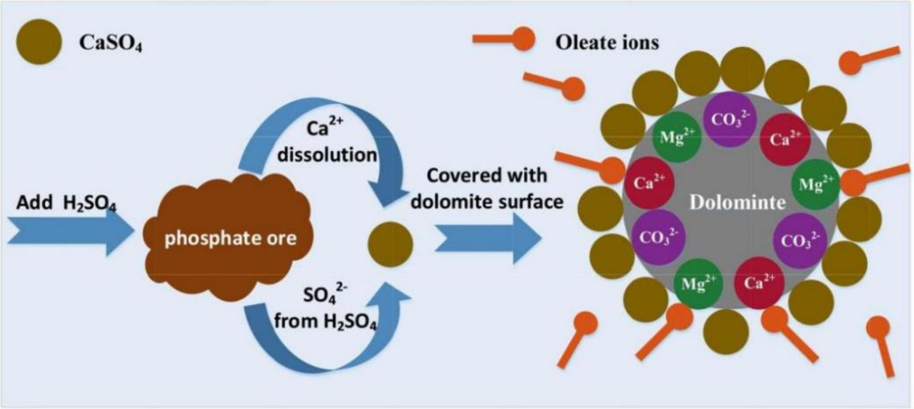


Fig. 10. Depression of dolomite hydrophobicity by Ca^{2+} under NaOL system (Chen et al., 2022)

Table 1. Primary mechanisms in metal ion-induced depression of minerals

Mineral	Ions	Primary Mechanism	References
Molybdenite	Ca^{2+}	Forms calcium molybdate precipitates, covering surface active sites.	Wan et al., 2017
Sphalerite	Ca^{2+}	Competitively occupies surface sites, hindering Cu^{2+} activation and reducing xanthate adsorption.	Zhang et al., 2021
Dolomite	Mg^{2+}	Forms a dense $Mg(OH)_2$ layer at high concentrations, hindering oleate adsorption.	Li and Zhang, 2013
Na-Feldspar	Ca^{2+}	Adsorbs via ion exchange, reduces surface zeta potential, and inhibits amine collector adsorption.	Demir et al., 2003
Wolframite	Ca^{2+}/Mg^{2+}	Physisorption interferes with Pb^{2+} activation and subsequent fatty acid adsorption.	Shang and Zhou, 2018
Sillimanite	Ca^{2+}	Adsorption reduces surface zeta potential, weakening electrostatic attraction to dodecylammonium.	Chen et al., 2017

4.2. Activation of Ca^{2+} and Mg^{2+}

In addition to their depressive roles, Ca^{2+} and Mg^{2+} could also activate the mineral surfaces or enhance reagent performance by modulating the solution chemistry.

For instance, the adsorption of Ca^{2+} and Mg^{2+} generates additional active sites on smithsonite surfaces, intensifying the collector interaction and facilitating the adsorption layer formation, thereby improving the smithsonite recovery (Araújo and Lima, 2017). In lepidolite flotation, the adsorption of Mg^{2+} could enhance NaOL adsorption through combined electrostatic and coordinative mechanisms. The surface charge modulation would increase the density of active sites to enhance collector adsorption, and in parallel, the interaction with Al, F and O sites induces mineral surface hydroxylation and reconstruction. XPS analysis confirms that these processes would effectively lower the energy barrier for NaOL adsorption and promote the hydrophobic film formation (Xu et al., 2024). Owing to its stronger polarization ability, Mg^{2+} forms more stable colloidal Mg-OOCR complexes than Ca^{2+} (Fig. 11). In α-BDDA anion collector system, the presence of Ca^{2+}, Mg^{2+} and Cu^{2+} would selectively activate spodumene during the flotation separation from quartz and feldspar, whereas Fe^{3+} would non-selectively activate all three minerals and hinder the selectivity. Ca^{2+} and Mg^{2+} would adsorb onto spodumene primarily as free ions, while Cu^{2+} would adsorb as the hydrolyzed species $Cu(OH)^+$. Owing to their stronger adsorption affinity, Ca^{2+} and Mg^{2+} exhibit superior adsorption and activation than Cu^{2+}, reaching maximum activation at pH 12.5 and 10.0 respectively (Liu et al., 2015; Xie et al., 2021). Furthermore, in sodium oleate systems, Mg^{2+} exhibits stronger activation of quartz than Ca^{2+} below pH 8, whereas this trend reverses above pH 10 (Nie et al., 2023).

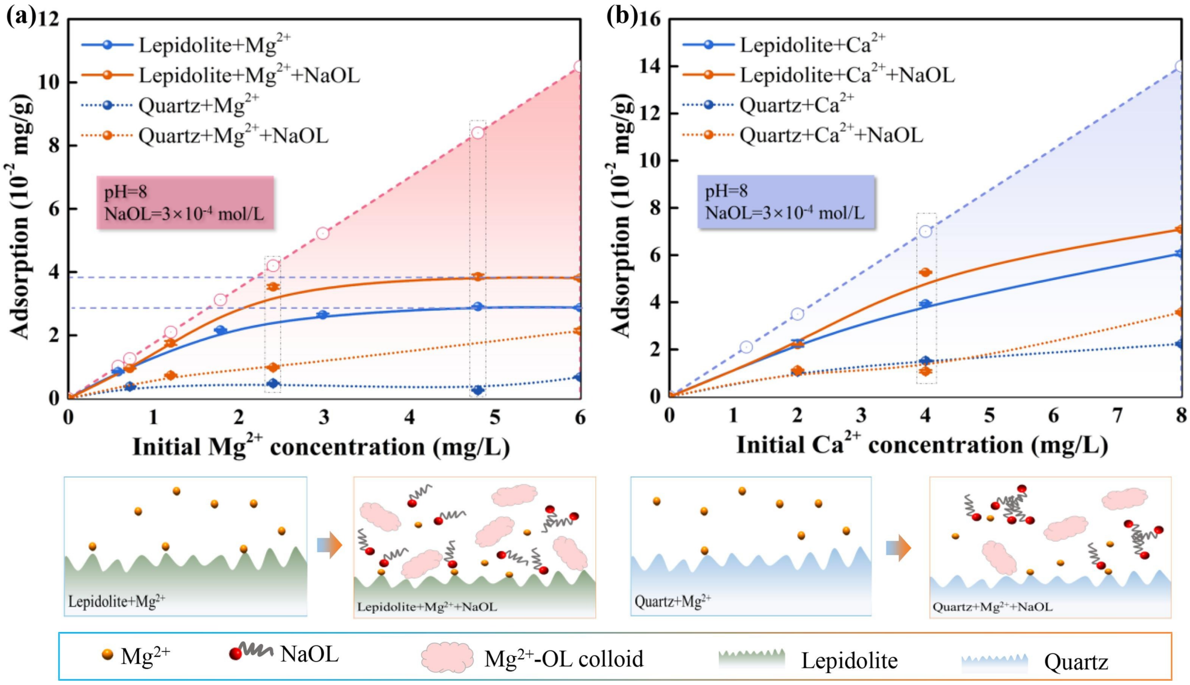


Fig. 11. Influence of NaOL on the adsorption of Mg^{2+} and Ca^{2+} on lepidolite and quartz (Xu et al., 2024)

Ca^{2+} could not adsorb significantly onto cassiterite or quartz surfaces and hardly affect their floatability under acidic conditions. However, at pH 9.1, excessive Ca^{2+} is extensively hydrolyzed, forming $Ca(OH)^+$ and initiating $Ca(OH)_2$ precipitate. These hydrolysis products would react with oxygen sites on quartz surface and markedly enhance its floatability (Feng et al., 2018). Both Ca^{2+} and Mg^{2+} could form hydroxo complexes such as $[M(OH)]^+$, which adsorb onto quartz surface through chemisorption (Tang et al., 2024a). This process induces a positive shift in surface potential and creates active sites on the mineral surface, promoting the oriented adsorption of HAY collectors through the synergistic effect of the electrostatic-hydrogen bond interactions. Consequently, quartz hydrophobicity and flotation efficiency are improved (Zhou et al., 2014). Besides, the role of Ca^{2+} hydrolysis products in quartz flotation varies with pH. At a Ca^{2+} concentration of 0.5×10^{-3} mol/L, $Ca(OH)^+$ serves as the primary activating species across pH 4-12, whereas $Ca(OH)_2$ precipitate dominates above pH 13, depressing quartz flotation (Shi et al., 2001; Cong et al., 2018; Liu et al., 2020). Through adsorption energy calculations and structure parameter analysis, Wang et al. identified the hollow site of Si centers and the top site of O atoms as the primary adsorption sites on quartz (101) surface. As illustrated in Fig. 12, Ca^{2+} in aqueous solution primarily forms hydrated complexes like $[Ca(H_2O)_4]^{2+}$ and $[Ca(OH)(H_2O)_3]^+$, wherein Ca^{2+} and surface O atoms accept electrons from O atoms in water ligands (Wang et al., 2018).

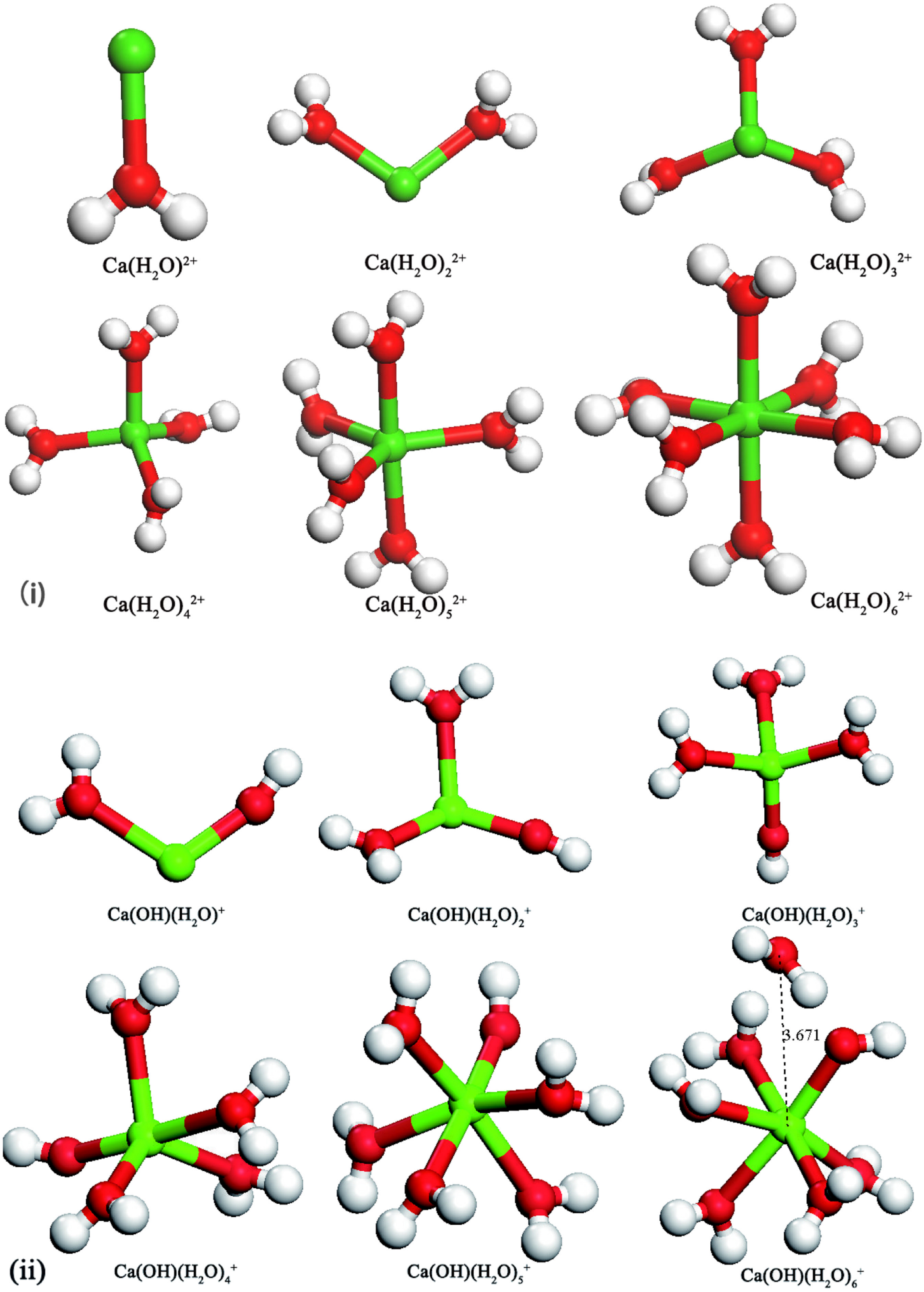


Fig. 12. Equilibrium geometries of hydration structures of Ca^{2+} (i) and $Ca(OH)^+$ (ii). (Ca: green; H: white) (Wang et al., 2018)

As shown in Table 2, Ca^{2+} and Mg^{2+} would form hydroxo complexes such as $[M(OH)]^+$ or hydroxide precipitates through hydrolysis under alkaline conditions, which adsorb onto mineral surfaces through chemisorption. This process significantly increases the density of surface active sites and enhances the binding capacity for anionic collectors like fatty acids. Consequently, these interfacial chemical modifications would promote collector adsorption and enhance surface hydrophobicity, thereby activating the mineral surface.

Table 2. Primary mechanisms in metal ion-induced activation of minerals

Mineral	Ions	Primary Mechanism	References
Quartz	Ca^{2+}/Mg^{2+}	Hydroxy complexes provide active sites, promoting the adsorption of anionic collectors.	Liu et al., 2015; Xie et al., 2021
Cassiterite	Ca^{2+}	Hydrolyzes to $Ca(OH)^+$ under alkaline conditions, enhancing collector adsorption on the quartz surface.	Feng et al., 2018
Smithsonite	Ca^{2+}/Mg^{2+}	Provides additional active sites, intensifying collector interaction and facilitating adsorption layer formation.	Araújo and Lima, 2017
Lepidolite	Mg^{2+}	Modulates surface charge and induces hydroxylation, lowering the energy barrier for NaOL adsorption.	Xu et al., 2024

4.3. Effect of Ca^{2+} and Mg^{2+} on mineral particles dispersion

Ca^{2+} and Mg^{2+} in pulp not only function as activators or depressants in flotation but also modulate the interparticle interactions by altering mineral surface charge properties.

The species, valence, and pH-dependent speciation of metal ions critically control the dispersion and agglomeration of micro-fine wolframite. Divalent and trivalent metal ions significantly promote the agglomeration of micro-fine wolframite particles by destabilizing suspensions, primarily through the adsorption of hydroxide or hydroxy complex species (Kuang et al., 2022). Under weakly alkaline conditions, electrostatic repulsion dominates the interaction between galena and calcite particles due to their negatively charged surfaces, preventing the hetero-aggregation. However, adsorption of the hydrolyzed $Ca(OH)^+$ species onto galena surfaces would neutralize its surface charge and facilitate the hetero-aggregation between particles through the electrostatic interactions (Wang et al., 2024). The dispersion behavior of aluminosilicate minerals is strongly pH-dependent in the presence of Ca^{2+} and Mg^{2+}. Under acidic conditions, these ions exert minimal influence on the dispersion stability, whereas under alkaline conditions, their hydrolyzed species would adsorb and strongly disrupt the dispersion stability, leading to particle agglomeration (Zhou et al., 2011; Ejtemaei et al., 2016; Guo et al., 2023). Similarly, the dispersion behavior of kaolinite is also strongly affected by pH value in the presence of Ca^{2+} and Mn^{2+}. These ions would adsorb specifically onto kaolinite surface, reducing surface negative charge and enhancing the adsorption of polyacrylamide (PAM) flocculant, thereby optimizing the flocculation efficiency (Mpofu et al., 2003).

In acidic media, Ca^{2+} and Mg^{2+} could adsorb onto muscovite surfaces through electrostatic interactions, increasing the surface charge density and enhancing the electrostatic repulsion, thereby improving the dispersion stability. Under alkaline conditions, these ions would form hydroxy complexes that adsorb onto muscovite surface and induce the flocculation through bridging mechanisms (Fig. 13) (Tang et al., 2016). The dissolution of dolomite would release Ca^{2+} and Mg^{2+} into the pulp, where they subsequently adsorb onto dolomite surfaces as hydroxy complexes or hydroxide precipitates. This adsorption would reduce the interaction energy barrier between dolomite particles, promoting aggregation through bridging and destabilizing the dispersion behavior of dolomite. A comparative study (Tang et al., 2024b; Tang and Luo, 2025) revealed that Ca^{2+} and Mg^{2+} distinctly influence starch gelatinization and hematite flocculation. Low concentrations of Mg^{2+} (≤ 4 mmol/L) could enhance flocculation by forming moderate cross-linking bridges with starch carboxyl groups, enlarging flocs and accelerating settling. In contrast, Ca^{2+} consistently inhibited starch gelatinization, increasing turbidity, reducing viscosity, and impairing floc formation and settling. These results highlight the critical role of cation type and concentration in starch-based flocculation performance. Furthermore, Mg^{2+} exhibits a stronger destructive effect on particle dispersion than Ca^{2+} due to the lower solubility product of its hydroxides, leading to a more pronounced aggregation under the equivalent concentration (Fang, 1998; Yuan et al., 2024). Additionally, the adsorption of most ions could also compress the electric double layer, modifying mineral surface potential and further enhancing the mineral particle aggregation. Although Ca^{2+} and Mg^{2+} generally lack mineral-specific selectivity, their effects depend strongly on the ion concentration and solution chemistry (Xu et al., 2017; Guo et al., 2003; Liu et al., 2022).

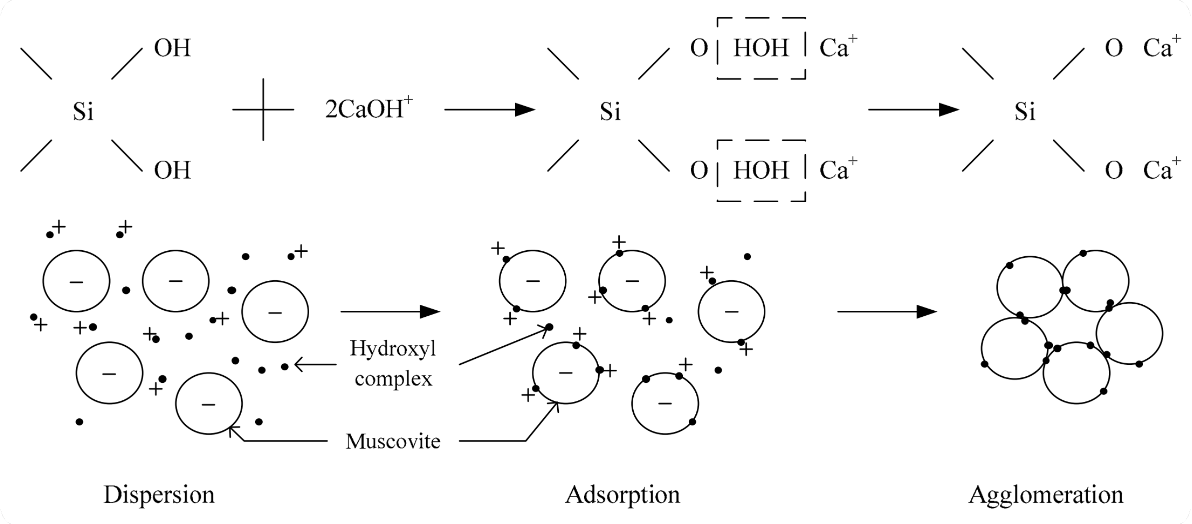


Fig. 13. Bridging effect of hydroxy complex (Tang et al., 2016)

4.4. Elimination of adverse effects in mineral flotation

In mineral flotation, Ca^{2+} and Mg^{2+} exhibit dual interfacial behavior. The adsorption of Ca^{2+} and Mg^{2+} selectively enhances the hydrophobicity of target minerals while depressing gangue minerals, thereby offering valuable applications in mineral flotation. Conversely, non-selective coordination with non-target minerals would lead to ineffective reagent consumption and impaired separation efficiency, necessitating the mitigation of these adverse effects.

The fluoride precipitation method removes Ca^{2+} and Mg^{2+} from pulp by forming low-solubility precipitates such as CaF_2 and MgF_2 (Su et al., 2016; Zhao et al., 2019; Pei et al., 2024). Alternatively, carbonate addition could facilitate the removal of these ions through the precipitation of $CaCO_3$ and $MgCO_3$. During the removal of Ca^{2+} and Mg^{2+} from Mn^{2+} solution, stepwise precipitation of Ca^{2+} and Mg^{2+} could be achieved through crystal phase control using carbonate (Lin et al., 2016). A synergistic CaO-Na_2CO_3 precipitation process enables efficient ion removal in seawater-based systems through the collaborative optimization of pH adjustment and the carbonate dosing (Jeldres et al., 2017). Additionally, the addition of tripolyphosphate could chelate Ca^{2+} to form stable soluble complexes, thereby mitigating its coagulating effect (Sun et al., 2010b). In sulfide ore flotation recirculation water, high concentrations of Ca^{2+} and SO_4^{2-} could be treated by adding CaO and amorphous $Al(OH)_3$ to promote the formation of ettringite precipitation through coordinated regulation (Guerrero-Flores et al., 2022). These approaches transform harmful ions into functional materials, enabling their secondary utilization. Beyond precipitation, chelation and complexation would offer another practical strategy for mitigating the adverse effects through the interaction between specific reagents and metal ions. The addition of sodium hexametaphosphate could react with Ca^{2+} strongly, forming a highly soluble and stable complex species (Bustos-Flores et al., 2021). Similarly, chelating reagents such as BATPA could reduce Ca^{2+} adsorption, thereby alleviating its depressive effect on magnesite flotation (Luo et al., 2017).

Precipitation and complexation are the two primary strategies to mitigate the adverse effects of Ca^{2+} and Mg^{2+}. The precipitation method enables a nearly complete removal by converting the soluble ions into insoluble solid phases. However, careful control is required to prevent the adsorption of precipitates onto mineral surfaces, which could otherwise interfere with flotation performance.

5. Conclusion

A fundamental understanding of Ca^{2+} and Mg^{2+} is crucial for advancing flotation technology, offering both theoretical and practical benefits. Based on a thorough analysis of their primary sources and interfacial interaction mechanisms, this work provides a systematic examination of the roles of Ca^{2+} and Mg^{2+}.

(1) Metal ions influence the flotation performance through multiple mechanisms, including electrostatic adsorption, lattice substitution, formation of hydroxy complexes or hydroxide precipitates, and interactions with flotation reagents.

(2) The interfacial behavior of Ca^{2+} and Mg^{2+} in mineral flotation is governed by both pH and reagent chemistry. Adsorption of these metal ions can obviously modify surface charge properties, leading to particle dispersion or aggregation. Under alkaline conditions, hydroxide precipitates could further promote particle settling through bridging effects.

(3) Chemical precipitation and complexation represent the predominant strategies for mitigating the adverse effects of Ca^{2+} and Mg^{2+}. These methods employ specific reagents to convert ions into insoluble precipitates or stable complexes, reducing their concentration and effectively minimizing interference in flotation.

(4) Based on the established understanding of Ca^{2+} and Mg^{2+} roles in flotation systems, future research should focus on the development of AI-assisted technologies for predicting and regulating ionic behavior, and the design of environmentally reagents with specific affinity for Ca^{2+} and Mg^{2+}. These technological advances will significantly improve separation efficiency for complex refractory ores, supporting the evolution toward environmentally sustainable flotation operations.

Acknowledgments

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