Physicochem. Probl. Miner. Process., 62(3), 2026, 225029

http://www.journalssystem.com/ppmp

Physicochemical Problems of Mineral Processing

ISSN 1643-1049

Flotation collectors of kaolinite: A review from fundamental mechanisms to emerging trends

Liting Xu, Jun Chen, Huanhuan Shang, Yali Cheng

Department of Materials Science and Engineering, Anhui University of Science and Technology, Huainan 232001, China

Corresponding author: jchen412@126.com (Jun Chen), chengyali1943@163.com (Yali Cheng)

Abstract: Kaolinite is widely used in papermaking, ceramics and other industries, but its high-value applications are limited by gangue minerals and lattice impurities (e.g., Fe, Ti). Flotation, a key purification technique, is hindered by conventional collectors' poor selectivity and weak affinity. This review classifies collectors into anionic, cationic, mixed and novel types, analyzes key influencing factors (mineral interfacial properties, reagent structure, solution chemistry, process parameters) and elucidates their interaction mechanisms with kaolinite. Current research focuses on conventional kaolinite, while coal-measure kaolinite – abundant but with complex processing challenges – lacks attention. Its inefficient beneficiation stems from insufficient understanding of lattice impurity genetic characteristics, leading to non-targeted collector design. Future studies should prioritize coal-measure kaolinite, decode its lattice impurities, and use machine learning to screen targeted chelating collectors. Establishing a genetic coupling model will guide efficient flotation separation, improving kaolinite purity for high-end applications.

Keywords: collector, kaolinite, impurity separation, lattice defects, targeted collector strategy

1. Introduction

Kaolinite exhibits elevated whiteness, superior plasticity, exceptional refractoriness, and favorable chemical stability, leading to its extensive utilization in industrial sectors including papermaking, ceramics, coatings, and refractory materials (Murray, 1961; Velho and Gomes, 1991). Globally, proven reserves of kaolin are approximately 32 billion tons, with China's identified resources amounting to 3.496 billion tons, ranking among the top in the world (Wu et al., 2021). Kaolinite constitutes the primary mineral phase, and its content and purity directly determine the product grade and application suitability (Dill, 2016).

Kaolinite is a typical 1:1 layered silicate clay mineral. Its fundamental structural unit consists of a silica tetrahedral sheet linked to an alumina octahedral sheet through shared oxygen atoms (Teixeira et al., 2017). This crystalline configuration confers distinct interfacial characteristics: polar hydroxyl groups exposed at sheet edges contribute to high reactivity and plasticity, while the basal planes exhibit chemical inertness due to interlayer charge balance, resulting in stable phase transformation behavior during thermal treatment (Zhang et al., 2015; Zhai et al., 2016). However, natural kaolinite seldom occurs in a pure state and is commonly intergrown with gangue minerals such as quartz and alunite. More notably, impurity ions such as titanium (Ti^{4+}) and iron (Fe^{2+}/Fe^{3+}) can undergo isomorphous substitution for Al^{3+} or Si^{4+} within the crystal lattice, forming stable lattice defects (Liu et al., 2022; Fan et al., 2025). Such defects cannot be effectively eliminated by conventional physical beneficiation techniques. They significantly diminish the whiteness and chemical purity of kaolinite products and adversely affect key functional properties, including electrical insulation and thermal stability (Huang et al., 2023). Consequently, the deep removal of lattice impurities, particularly those incorporated via isomorphous substitution, represents a central challenge in achieving high-value utilization of kaolinite resources.

Flotation serves as a key method for the efficient separation and purification of fine-grained minerals (Chen et al., 2020). The underlying principle is the selective adsorption of collectors onto target mineral surfaces, which generates differences in surface hydrophobicity to enable separation. However,

DOI: 10.37190/ppmp/225029

kaolinite flotation encounters considerable challenges owing to its inherently strong hydrophilicity, its plate-like particle morphology that favors aggregation, and the formation of stable hydration layers by surface polar hydroxyl groups, which collectively inhibit collector adsorption (Fu et al., 2024). This challenge is further exacerbated in coal-measure kaolinite, where organic matter coats the surface and masks active sites, greatly increasing separation difficulty (Fan and Wang, 2012). Consequently, developing novel flotation reagents with high selectivity and strong adsorption affinity has become an essential pathway to overcome these technical barriers.

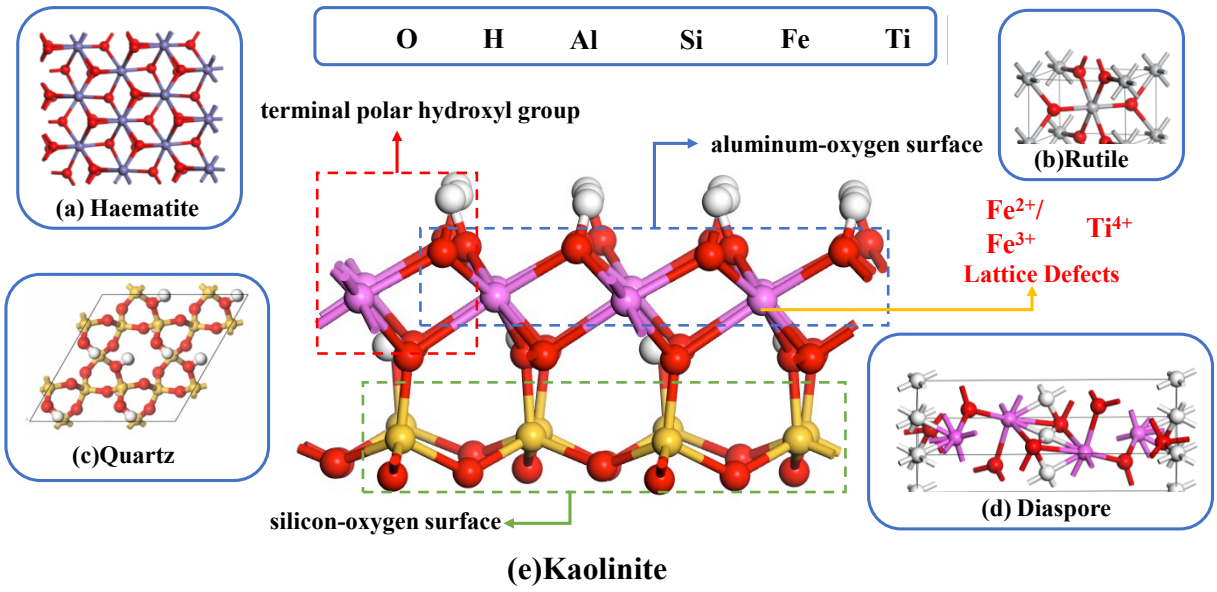


Fig. 1. The crystal lattice model of kaolinite and associated minerals (Teixeira et al., 2017; Liu et al., 2022; Fan et al., 2025)

This review systematically summarizes the research progress on flotation collectors for kaolinite, focusing on anionic, cationic, mixed, and novel collectors to analyze the structure-activity relationship between their molecular structures and flotation performance. Key influencing factors are examined from the perspective of mineral interface properties, reagent structure, solution chemistry, and process parameters, while elucidating both individual and synergistic interaction mechanisms on mineral surfaces. However, current studies predominantly rely on idealized or conventional kaolinite models, with insufficient attention paid to coal-measure kaolinite, which features abundant reserves and complex occurrence states of lattice impurities. Building on a systematic overview of general issues, this review specifically highlights the critical influence of impurities on the aforementioned structure-activity relationships and interaction mechanism. By clarifying existing research gaps, it aims to provide a theoretical basis and technical pathway for future breakthroughs in the fundamental theory of impurity genetic characteristics and surface interfacial reactions in coal-measure kaolinite, as well as for the development of targeted flotation technologies. Kaolinite flotation in this study is defined as an interface-driven separation process for silicate mineral systems, aiming to achieve efficient separation of target kaolinite from associated impurities.

2. Types of collectors for kaolinite flotation

The flotation separation and purification efficiency of kaolinite is fundamentally governed by the capacity of collectors to modulate the surface hydrophobicity of the mineral. However, the distinctive crystal structure and surface properties of kaolinite often render traditional single-component collectors inadequate in simultaneously achieving high selectivity and strong collecting power. Consequently, collector development has increasingly shifted from single-component systems toward multi-component synergistic blends and rationally designed molecular architectures, aiming to overcome the limitations of conventional reagents in selectivity, collecting efficacy, and adaptability to slurry

conditions. Based on their mechanism of action and molecular characteristics, collectors for kaolinite can be broadly categorized into anionic, cationic, blended, and novel types.

2.1. Anionic collectors

Anionic collectors, upon dissociation in aqueous solution, feature negatively charged polar groups. They primarily adsorb onto metal cation sites on the mineral surface via mechanisms such as electrostatic interaction, hydrogen bonding, or chemical coordination, thereby rendering the surface hydrophobic. These reagents function as conventional core collectors in reverse flotation systems designed to separate kaolinite from aluminum-bearing gangue minerals like diaspore and pyrophyllite. Based on molecular structure, they are typically classified into categories such as fatty acids, oxime acids, and hydroxy sulfonates (Peng et al., 2014). Their action mechanism is illustrated in Fig. 2.

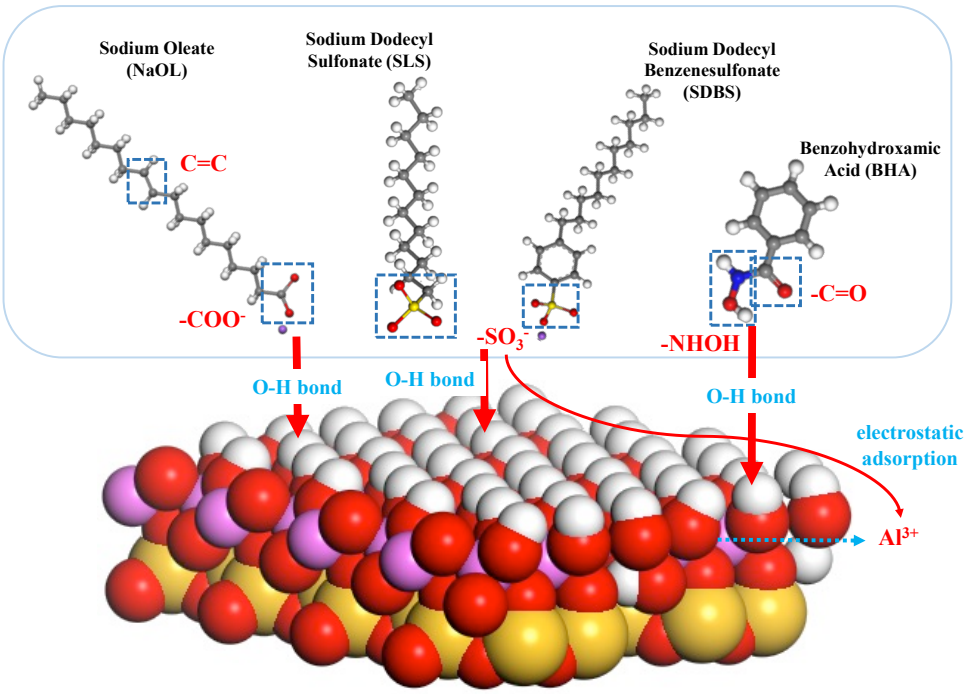


Fig. 2. Schematic diagram of the interaction between anionic collectors and kaolinite (Zhang et al., 2001; Torn et al., 2013; Ding et al., 2019)

2.1.1 Fatty acid collectors

Represented by sodium oleate (NaOL), their action mechanisms exhibit significant differences. On the diaspore surface, carboxylate groups form stable chemisorption with fully exposed Al^{3+} sites. In contrast, on the kaolinite surface, due to the negative charge of the siloxane face causing electrostatic repulsion and the dense hydroxyl groups on the aluminol face limiting Al^{3+} accessibility, NaOL primarily undergoes weak electrostatic or hydrogen-bond adsorption. This fundamental difference in adsorption mode and strength forms the basis for the selective separation by NaOL (Zhang et al., 2001; Xu et al., 2016). Further studies reveal that Fe^{2+} impurities in the kaolinite lattice can enhance chemical complexation with NaOL, improving its floatability (Liu et al., 2024). This observation opens new prospects for utilizing iron-bearing kaolinite resources.

2.1.2 Oxamic acid and hydroxy sulfonate collectors

Representative compounds include benzohydroxamic acid (BHA) and sodium dodecylbenzene-sulfonate (SDBS). Among them, BHA demonstrates excellent selectivity in the reverse flotation separation of kaolinite from diaspore. A comparative study demonstrated that although NaOL shows stronger collecting capability toward diaspore, its selectivity remains poor. The recovery of kaolinite rises markedly with increasing reagent dosage, largely due to enhanced mechanical entrainment (Ding

et al., 2019). In contrast, BHA shows relatively weaker collecting ability but superior selectivity, maintaining kaolinite recovery below 8% with minimal sensitivity to dosage variation. This indicates that the interaction between BHA molecules and the active sites on the diaspore surface is more specific, highlighting its potential for applications requiring high-precision separation. SDBS, as a hydroxy sulfonate collector, adsorbs primarily via electrostatic interaction, which is strongly influenced by the surface charge properties of kaolinite and slurry pH (Torn et al., 2013). Since the siloxane face of kaolinite is typically negatively charged, electrostatic repulsion occurs with the anionic sulfonate groups of dissociated SDBS. This results in low adsorption density on kaolinite surfaces when SDBS is used alone, leading to limited hydrophobicity enhancement and inefficient collection. Therefore, SDBS is commonly employed in combination with other reagents in practical applications.

Although anionic collectors play a crucial role in the reverse flotation removal of aluminum-bearing gangue minerals, they inherently face the challenge of balancing collecting capacity and selectivity when used alone. Fatty acid-based collectors offer strong collecting capacity but weak selectivity, whereas hydroxamic acid-based ones provide high selectivity but limited collecting strength. To address these limitations, anionic collectors are frequently utilized in practical kaolinite flotation processes as key components in blended collector systems with optimized overall performance. However, whether used singly or in blends, the design of anionic collectors has predominantly targeted surface-exposed Al^{3+} sites. For lattice defects such as Fe^{2+}/Fe^{3+} present via isomorphous substitution in kaolinite, the development of functional groups with stronger chelating ability and higher selectivity remains an under-explored area in current reagent research.

2.2. Cationic collector

Cationic collectors play a key role in the direct flotation of kaolinite and its separation from oxides such as hematite. They function by forming positively charged polar groups through protonation or dissociation in solution, which adsorb strongly via electrostatic attraction onto the negatively charged sites of the kaolinite siloxane face. This adsorption may be accompanied by hydrogen bonding or weak coordination, effectively neutralizing surface charge and inducing the formation of a hydrophobic layer, thereby enabling selective flotation (Yu et al., 2011). Depending on the chemical environment of the nitrogen atom in the polar group, cationic collectors are mainly classified into amines, quaternary ammonium salts, and ether amines.

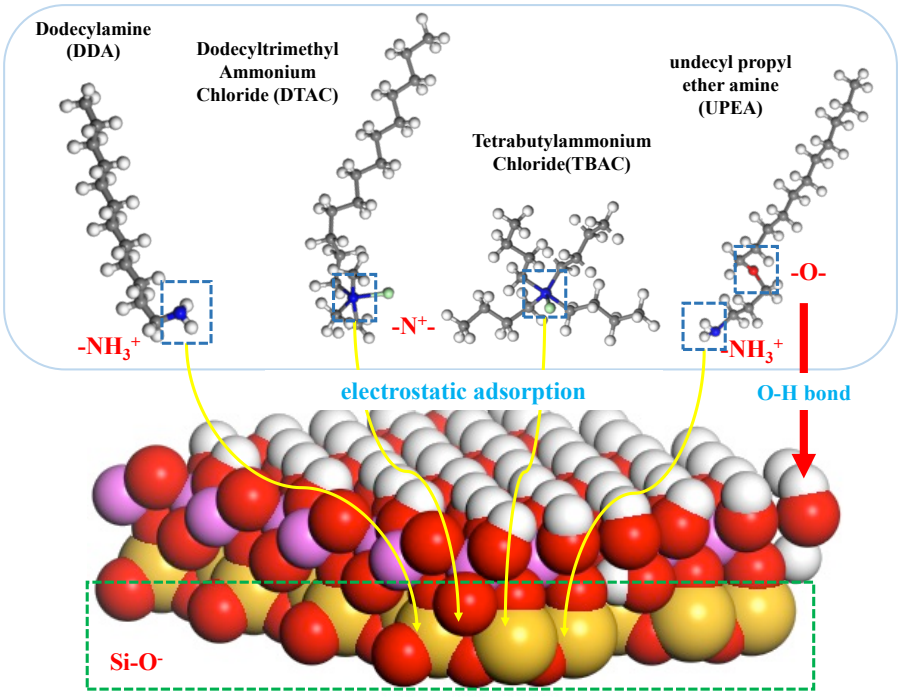


Fig. 3. Schematic diagram of the interaction between cationic collectors and kaolinite (Rodrigues et al., 2013; Yue et al., 2014; Liu et al., 2019)

2.2.1. Amine collectors

Dodecylamine (DDA) is the most widely used amine collector. Theoretical and experimental studies (Liu et al., 2019) have shown that its polar head group adsorbs onto the kaolinite surface primarily through electrostatic attraction and hydrogen bonding under acidic to neutral conditions, with significantly stronger interaction intensity compared to the anionic collector sodium oleate. To overcome the limited collecting capacity of single amine-type collectors, the introduction of dodecyltrimethoxysilane (DTMS) can synergistically enhance the electrostatic adsorption and hydrogen bonding of DDA (Sun et al., 2010). The silanol groups generated by the hydrolysis of DTMS can form a dense hydrogen-bonded network among the hydroxyl groups on the kaolinite surface, thereby reshaping the interfacial microenvironment. This significantly enhance the adsorption density and strength of DDA, ultimately improving flotation recovery and the selectivity of separation from aluminum-bearing minerals. This demonstrates that fine-tuning mineral surface properties through auxiliary reagents is an important approach to enhancing the performance of traditional amine collectors. Furthermore, the macroscopic adsorption behavior and micro-interface changes between such amine collectors and pure kaolinite further corroborate the core mechanism dominated by "electrostatic attraction +hydrogen bonding," providing practical guidance for optimizing reagent dosage, pH, and other operational conditions (Lainé et al., 2024).

2.2.2. Quaternary ammonium salt collectors

Quaternary ammonium salt collectors possess a permanent positive charge, making their performance independent of solution pH and ensuring high adsorption stability. Their action mechanism involves a combination of electrostatic adsorption and synergistic weak hydrogen bonding (Liu et al., 2001). Comparative studies reveal significant performance differences among quaternary ammonium salts with varying structures. For example, dodecyl trimethylammonium chloride (DTAC) and tetrabutylammonium chloride (TBAC) exhibit distinct behaviors (Yue et al., 2014). Although DTAC shows higher adsorption capacity, TBAC demonstrates stronger actual collecting capacity and better flotation performance due to its lower adsorption energy and larger molecule-surface contact area.

In practical separation applications, dodecyl trimethylammonium bromide (DTAB) exhibits excellent selectivity for kaolinite across a broad pH range of 4-10, enabling efficient separation from hematite without the need for depressants. In contrast, traditional ether amines require high alkalinity and depressant assistance under similar conditions (Rodrigues et al., 2013). With their structural stability and wide pH adaptability, quaternary ammonium salts demonstrate unique advantages in direct flotation desilication and separation within complex systems.

2.2.3. Ether amine collectors

Regarding ether amine collectors, during the flotation separation of hematite and kaolinite (Wang et al., 2013), it was observed that mixed ether amine collectors exhibit strong selectivity toward hematite at pH=9, while the recovery of kaolinite remains as low as 2.25%. Efficient separation is achieved without the need for additional depressants. Compared to other collectors, ether amine-based reagents demonstrate superior selectivity, which can be attributed to the naturally low charge density and layered structure of the kaolinite surface. These characteristics restrict the adsorption of ether amine molecules, resulting in the natural depression of kaolinite in this system.

Although single cationic collectors demonstrate favorable selectivity, their collecting capacity is relatively weak. In certain systems, they require highly alkaline conditions in combination with costly multivalent metal cations, and also impose stringent requirements on flotation pulp temperature (Liu et al., 2025). Owing to these limitations, combined collectors or novel types of collectors, which offer advantages such as enhanced synergistic adsorption and broader applicability, are gradually replacing traditional single collectors.

2.3. Blended collector

Blended collectors refer to the combined use of two or more collectors in specific proportions, leveraging synergistic interactions between reagent molecules to overcome the limitations of single collectors in

terms of selectivity or collecting capacity. The core mechanism lies in the complementary adsorption sites, cooperative interfacial modulation, or competitive adsorption suppression among different reagent molecules, enabling more precise hydrophobic modification of target mineral and gangue surfaces. This synergistic effect is not merely an additive sum of the individual components (Padasala et al., 2016).

2.3.1. Anionic blended collectors

Anionic blended collectors consist of two or more anionic collectors combined in formulation, with a typical example being the mixture of NaOL/BHA. Their synergy primarily stems from competitive adsorption and enhanced selectivity. BHA exhibits higher selective affinity for Al^{3+} sites on the diaspore surface, allowing it to preferentially adsorb and occupy key active sites. This preferential adsorption not only directly enhances the hydrophobicity of the target mineral but also suppresses the non-specific adsorption of NaOL which has stronger collecting capacity but poorer selectivity on the kaolinite surface through steric hindrance or electrostatic repulsion. Consequently, the overall selectivity of the system is significantly improved (Sun et al., 2022). Studies show that the NaOL/BHA blend can increase the separation selectivity coefficient between kaolinite and diaspore from 1.2 with NaOL alone to 2.8 (Lan et al., 2025). Although NaOL exhibits weak adsorption affinity for pure kaolinite, its presence modulates the pulp microenvironment and generates steric hindrance and electrostatic repulsion. These effects inhibit the unselective adsorption of excess NaOL on kaolinite and drive BHA to selectively occupy Al^{3+} active sites on diaspore. More BHA molecules anchor on target impurity minerals, forming a denser hydrophobic film and ultimately raising the overall collecting power of the mixed system.

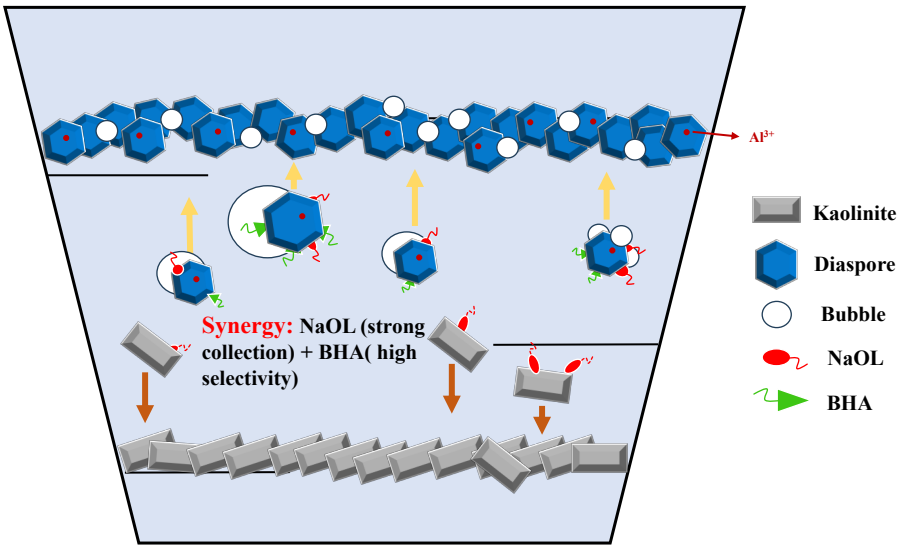


Fig. 4. Schematic diagram of the synergistic mechanism of NaOL/BHA blended collectors in the flotation separation of diaspore from kaolinite (Sun et al., 2022; Lan et al., 2025)

2.3.2 Anionic/cationic blended collectors

Anionic/cationic blended collectors are formulated by combining anionic and cationic collectors, with a common example being the mixture of NaOL/CTAB. The core of their synergistic effect lies in the cooperative regulation of interfacial properties. Collectors with opposite charges may form neutral ion pairs or composite micelles at the mineral/solution interface through electrostatic attraction. Such molecular complexes can create a hydrophobic layer on the mineral surface with higher adsorption energy and denser packing, effectively neutralizing surface charge and disrupting the hydration film, thereby significantly enhancing the adhesion strength and probability between fine particles and air bubbles (Gao et al., 2022). For instance, using a mixed system of NaOL and the cationic collector SCG can lead to a notable improvement in alumina recovery (Wu et al., 2025).

Blended collectors offer an effective approach to addressing the challenge of balancing selectivity and collecting capacity in kaolinite flotation through strategic formulation (Xu et al., 2017). Anionic

blends primarily optimize selectivity via competitive adsorption mechanisms, while anionic/cationic combinations enhance collecting capacity through interfacial assembly mechanisms. However, the effective application of both types relies heavily on precise control of the pulp chemical environment, and their complex interaction mechanisms also present greater challenges for the rational design of reagents and the stable operation of the process.

2.4. New-type collectors

To overcome the limitations of traditional amine collectors in terms of selectivity, pH adaptability, and compatibility with complex mineral interfaces, the development of novel collectors through rational molecular design has emerged as a leading direction in kaolinite flotation. Unlike blended collectors that rely on physical mixing, novel collectors are engineered by introducing specific functional groups or designing particular spatial configurations within a single molecule, fundamentally enhancing their interaction with active sites on the kaolinite surface. These are primarily categorized into three types: Gemini-type, hydroxamate-type, and polyamine-type collectors.

2.4.1. Gemini-type collectors

Gemini collectors are formed by covalently linking two conventional single-chain surfactant molecules near their hydrophilic head groups via a spacer group, forming a dimeric structure with two hydrophilic heads and two hydrophobic tails (Chang et al. 2009). The superior performance of novel Gemini collectors stems from their unique twin architecture. The two cationic head groups enable simultaneous dual-site electrostatic adsorption to multiple negatively charged sites on the kaolinite surface, markedly improving both adsorption strength and stability. At the same time, the paired hydrophobic tails interact through enhanced van der Waals forces, resulting in a denser and more stable hydrophobic layer on the mineral surface. For example, butanediyl-1,4-bis (dimethyldodecylammonium bromide) (BBDB) exhibits a critical micelle concentration significantly lower than that of traditional DDA, indicating a stronger driving force for interfacial adsorption. As a result, BBDB can markedly enhance kaolinite recovery even under low-temperature conditions (Zhang et al., 2021). Studies also show that Gemini collectors with different spacer groups, such as BDDA and EDDA, differ in their collecting capacity toward kaolinite, demonstrating the fine-tuning effect of molecular architecture on performance (Huang et al., 2013).

2.4.2. Hydroxamate-type collectors

Hydroxamate-type collectors are characterized by the hydroxamic acid functional group, which exhibits strong chelating ability toward various metal ions and was initially widely applied in rare-earth mineral flotation (Yang et al., 1992). Their core mechanism lies in the formation of stable five-membered chelates between the hydroxamate group and metal ions such as Fe^{3+} or Al^{3+} located at lattice defects or exposed on the kaolinite surface. This chemisorption is highly specific and strong, thereby conferring exceptional selectivity. Through molecular design, for example, introducing carboxyl groups into the hydroxamate structure, the hydrophobic balance and coordination ability toward different metal ions can be finely tuned, enabling efficient separation of hydrated iron oxides from kaolinite (Jiang et al., 2010). Bis-hydroxamate collectors with two chelating groups exhibit enhanced coordination capacity and spatial adaptability, making them suitable for separating complex intergrown systems (Huang et al., 2022). Studies have shown that the hydroxamic acid collector TPA can significantly alter the surface properties of kaolinite and improve flotation recovery even at low dosages (Ouyang et al., 2024).

2.4.3. Polyamine-type collectors

Polyamine-type collectors incorporate two or more amino groups ($–NH_2$) into the molecular backbone, allowing them to adapt to different solution environments by modulating the protonation degree of the amine groups. The key to their performance lies in the stepwise protonation of multiple amine groups, enabling a single collector molecule to carry multiple positive charges under varying pH conditions. For instance, the novel cationic collector DN_{12} contains two amine functional groups and can form a dicationic structure within the pH range of 5-8 (Cao et al., 2001). This multi-anchor electrostatic

adsorption model provides much stronger binding to negatively charged sites on the kaolinite surface compared to traditional mono-amines such as DDA, which carries only a single positive charge. Consequently, polyamine collectors achieve stable and efficient collection over a broader pH window, with recovery exceeding 80%, while also exhibiting significantly enhanced selectivity against other aluminosilicate minerals.

Novel collectors, through innovations in functional groups and molecular structure design, have overcome the performance limitations of traditional reagents by enhancing electrostatic adsorption, promoting specific chelation, and strengthening multi-site electrostatic interactions (Chang et al., 2023). However, the increased molecular complexity also brings challenges such as higher synthesis costs and a greater reliance on pre-rational design to establish clear structure-activity relationships. Future development must be closely aligned with the surface genetic characteristics of kaolinite to enable more targeted molecular design. To intuitively compare the adaptability, advantages and limitations of various collector systems used for impurity-bearing kaolinite flotation, we summarize their core performance indicators in Table 1.

Table 1. Performance comparison of different collectors for impurity-bearing kaolinite flotation

Collector Category	Typical Agents	Core Advantages	Main Drawbacks
Conventional Anionic Collectors	NaOL, BHA, SDBS	Low cost, easy access; hydroxamic acid has outstanding metal chelating selectivity	Poor selectivity of fatty acids; sensitive to pulp metal ions, narrow effective pH
Conventional Cationic Collectors	DDA, DTAB, ether amine	Quaternary ammonium salts are pH-insensitive with wide adaptability, fast adsorption speed	Non-selective electrostatic adsorption easily acts on gangue minerals
Blended Combined Collectors	NaOL/BHA, NaOL/CTAB	Complement the strengths of single reagents, balance collecting capacity and selectivity	Synergy relies strictly on reagent ratio and pH control; formula optimization is complicated
New-type collectors	Gemini (BBDB), Hydroxamate (TPA), Polyamine (DN_{12})	Targeted adsorption toward lattice defects, stable adsorption, excellent selectivity	Complex synthesis procedures, high manufacturing cost

Based on the above comparison, conventional anionic and cationic collectors possess prominent economic advantages for industrial application, yet they cannot balance collecting capacity and selectivity when applied to kaolinite containing abundant lattice impurities. Blended collectors achieve performance promotion via molecular synergistic effects based on commercially available conventional reagents. In contrast, new-type collectors realize prominent advantages in targeted binding toward lattice defects through rational molecular design, whereas their high synthesis cost restricts widespread industrial popularization. Future research can focus on low-cost molecular modification of novel collectors and optimization of compound formulas, to better match the surface characteristics of lattice impurity defects in coal-measure kaolinite.

In summary, flotation collectors for kaolinite have evolved from traditional single ionic types to blended and novel collectors that enhance performance through synergistic formulation and rational molecular design. While various collectors impart hydrophobicity to the kaolinite surface through distinct mechanisms, their efficacy has largely been evaluated based on idealized surface models of kaolinite. In practice, however, when dealing with kaolinite rich in lattice impurities such as Fe, Ti, and Mg, these impurities fundamentally alter the mineral's surface-active sites, charge distribution, and hydration layer structure. Consequently, they introduce complex influences on the adsorption behavior of all the collector types discussed above, necessitating a deeper examination of the key factors that govern collector performance.

3. Factors influencing the effectiveness of kaolinite flotation collectors

As a typical layered clay mineral, kaolinite exhibits a distinctive crystal structure characterized by substantial differences in atomic arrangement and charge distribution across various crystallographic planes. This structural anisotropy leads to inherent surface heterogeneity, manifesting in variations of physical properties such as surface roughness and specific surface area. More critically, it governs the adsorption kinetics and thermodynamics of collectors at the mineral-solution interface, which ultimately dictates the efficiency of kaolinite flotation separation (Gao et al., 2024).

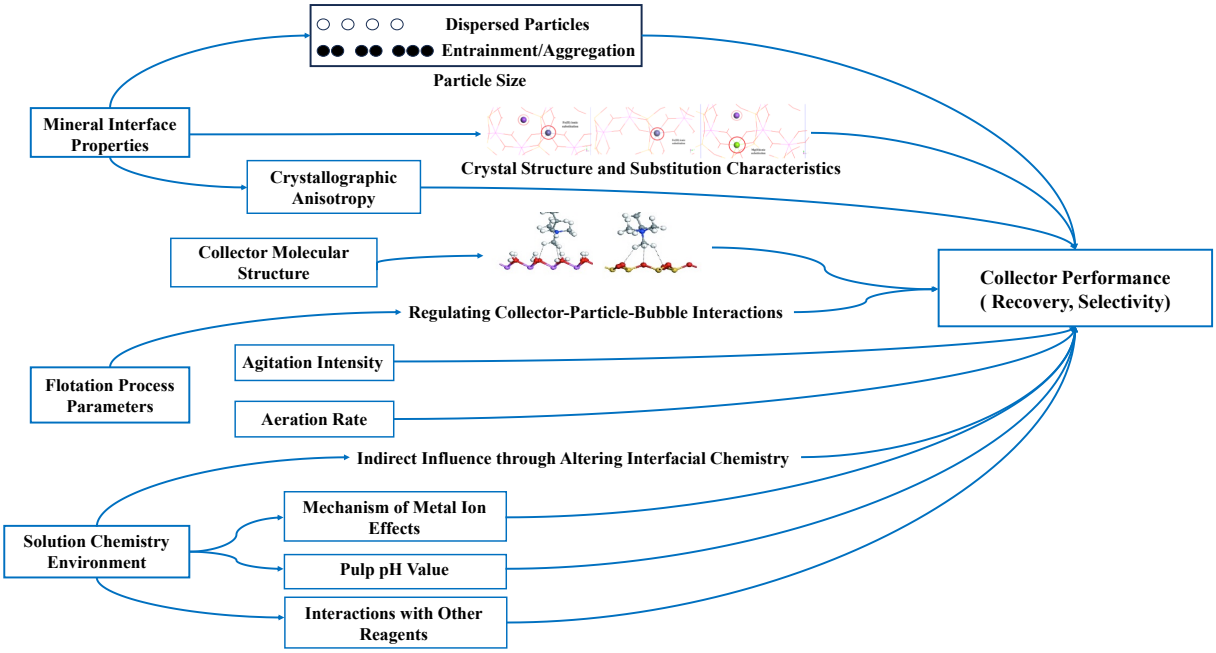


Fig. 5. Schematic diagram of factors influencing the collector performance in kaolinite flotation

3.1. Mineral interfacial properties

The interfacial properties of minerals constitute a fundamental determinant of flotation collector efficacy. Key characteristics such as particle size, crystal structure, lattice substitution features, surface energy state, and crystallographic anisotropy (Liu et al., 2022; Zhang et al., 2022)—govern flotation performance by regulating the adsorption behavior and interfacial interaction mechanisms of collectors at the mineral-solution interface.

3.1.1. Mineral particle size

Changes in mineral particle size systematically alter surface energy and adsorption behavior (Abaka-Wood et al., 2024). In flotation separation tests of diaspore and kaolinite using NaOL as collector, the floatability of diaspore was observed to decrease with finer particle sizes (Guo et al., 2003). Conversely, when DDA was employed, diaspore floatability increased under similar conditions. Therefore, to achieve effective separation between diaspore and kaolinite—whether by direct flotation with sodium oleate or reverse flotation with DDA—a relatively coarse feed particle size is recommended.

Studies on the flotation separation of kaolinite with different particle sizes using quaternary ammonium salts have shown that finer particles, characterized by a higher density of edge sites, exhibit diminished reagent adsorption and consequently poorer flotation performance (Jiang et al., 2013). Research on the fundamental properties of kaolinite and quartz, combining XRF analysis, molecular dynamics simulations, and flotation tests, further indicates that separation efficiency for mixed fine particles is relatively low below a size of 0.030 mm, whereas effective separation is achieved above this threshold, with the 0.125~0.075 mm fraction demonstrating optimal results (Zhou et al., 2022). Additionally, fine kaolinite particles are susceptible to mechanical entrainment during flotation (Zhang et al., 2019). While collector adsorption can reduce interfacial tension between particles and bubbles,

thereby increasing entrainment excessively fine particles may cause particle aggregation, which limits the accessibility of effective adsorption sites. Therefore, collector dosage requires careful optimization based on the specific particle size distribution.

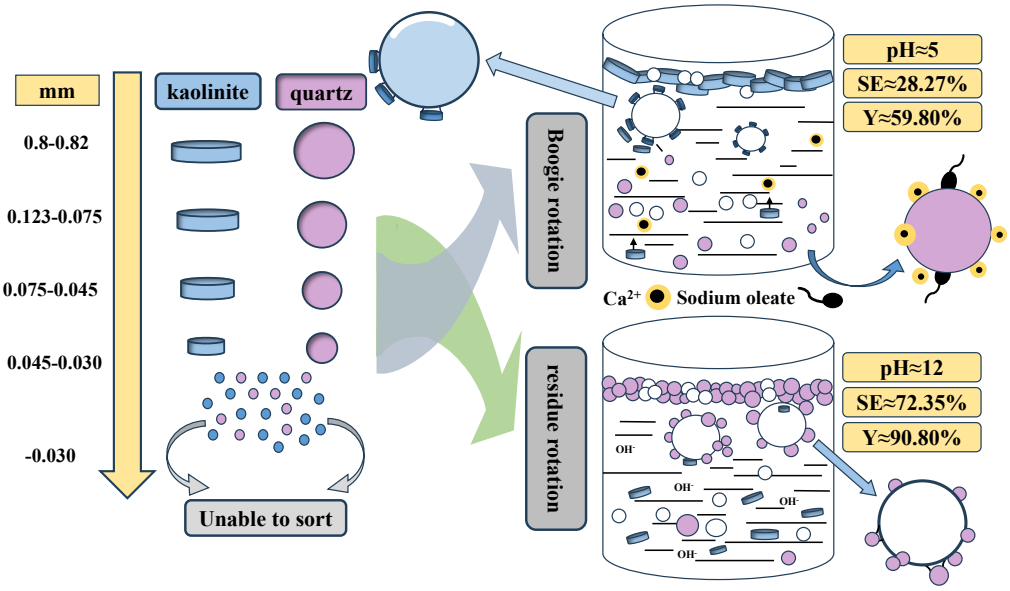


Fig. 6. The influence of particle size on the flotation separation of kaolinite and quartz (Zhou et al., 2022)

3.1.2. Crystal structure and substitution characteristics

Natural kaolinite commonly exhibits lattice defects, with those in coal-measure kaolinite being particularly pronounced due to the complex mineralization environment, such as magmatic activities. One of the key defect types is the substitution by lower-valence cations (Silva et al., 2017), specifically manifested as the selective replacement of Al^{3+} in the octahedral layer by metal ions such as Ti^{4+}, Fe^{2+}/Fe^{3+}, and Mg^{2+}. Such defects play a critical role in modulating the effectiveness of flotation collectors. These defects are key factors regulating flotation collector performance. They alter the electron cloud distribution, atomic coordination environment, and charge balance state on the kaolinite surface. Consequently, they significantly modulate the surface hydration layer, affecting collector adsorption strength, selectivity, and the overall flotation performance of kaolinite. In addition to octahedral Al^{3+} substitution, Al^{3+} isomorphic substitution for tetrahedral Si^{4+} is the most stable tetrahedral defect form in natural kaolinite (Hong et al., 2007), and the theoretical Fe^{3+}–Si^{4+} substitution is also discussed in this work, with all tetrahedral substitution characteristics summarized in Table 2.

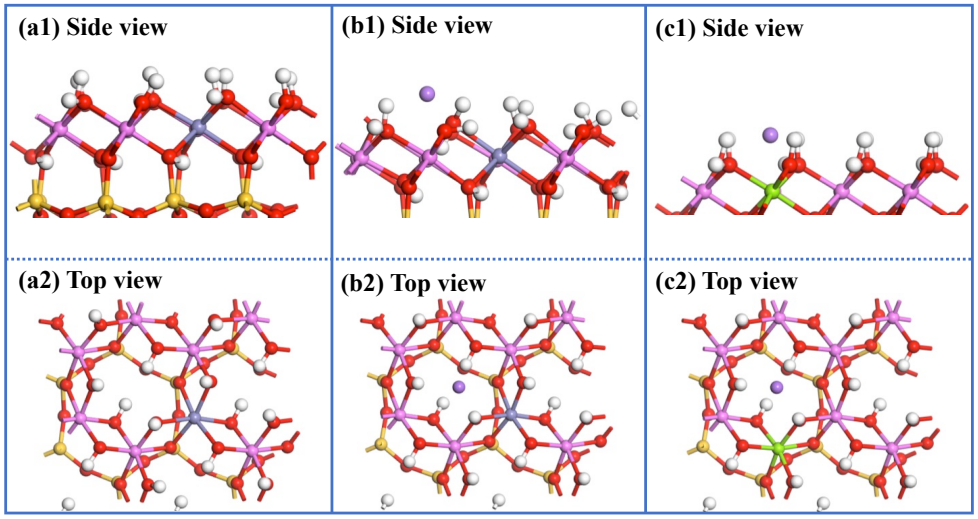


Fig. 7. Doping models of different ions on kaolinite surfaces((a): Fe^{3+}-Al; (b): Fe^{2+}-Al; (c): Mg^{2+}-Al;) (Chen et al., 2023; Chen et al., 2024; Chen et al., 2025)

3.1.2.1. Fe substitution characteristics

When present as lattice defects, both Fe^{2+} and Fe^{3+} ions induce the reconstruction of the surface hydration layer, yet their mechanisms of action differ significantly. Fe^{2+} substitution for Al^{3+} in the octahedral layer introduces additional free electrons into the crystal lattice. On one hand, this increases surface hydrophilicity, directly hindering the coordinative adsorption of anionic collectors. On the other hand, although it can promote the electrostatic adsorption of cationic collectors through surface charge redistribution, interference from competitive counterion adsorption also arises (Chen et al., 2023). Density functional theory further confirms that Fe^{2+} reduces the adsorption energy of the cationic collector DDA on the kaolinite surface, weakening the stable bonding between the collector and the surface (Ling et al., 2023). Fe^{3+} shares the same valence as Al^{3+}, but due to differences in ion electronegativity, substitution leads to a reduction in the band gap of kaolinite from 3.6 eV to 2.8 eV and an increase of 0.02 e in the charge density of surface oxygen atoms (Chen et al., 2025). While this change can enhance the adsorption capacity of anionic collectors, it also triggers non-specific adsorption due to localized lattice distortion, thereby reducing the selectivity of collectors for kaolinite. Simultaneously, Fe(III) can significantly improve the adsorption stability of cationic collectors by strengthening the bonding interaction between the collector and oxygen atoms (Chen et al., 2024).

3.1.2.2. Mg substitution characteristics

The core mechanism of Mg^{2+} substitution for Al^{3+} lies in altering the electron cloud distribution and interatomic interactions on the kaolinite surface. This structural modification directly influences surface charge characteristics (Chen et al., 2025). which in turn governs the adsorption configuration and energy of water molecules, thereby dynamically modulating surface hydration activity (Sun et al., 2022). Its effect exhibits a pronounced dose dependency: moderate Mg^{2+}substitution optimizes surface charge distribution, enhances hydrogen-bonding strength with water molecules, reduces electrostatic repulsion toward anionic collectors, and provides more active sites for collector adsorption. excessive substitution, however, leads to a sharp increase in surface negative charge density due to lattice charge imbalance, creating a strong electrostatic repulsive field that ultimately inhibits effective binding between collectors and the surface (Chen et al., 2024).

3.1.2.3. Ti substitution characteristics

In kaolinite, titanium primarily exists in two forms: first, as isomorphous substitution for Al^{3+} in the octahedral sheet, forming stable lattice defects; second, in minor amounts as nano-inclusions of titanium oxides such as anatase or rutile embedded within the kaolinite crystal (Shoval et al., 2008). Both forms alter the local lattice vibration modes and influence the electron cloud distribution on the mineral surface. Due to the similar ionic radii of Ti^{4+} and Al^{3+}, substitution induces negligible lattice distortion but reduces the band gap of kaolinite and increases its surface positive charge density. This promotes non-specific adsorption of anionic collectors, thereby reducing separation selectivity. Particularly in coal-measure kaolinite, the presence of Ti^{4+} significantly strengthens hydrogen-bonding interactions between the mineral surface and water molecules, forming a more stable hydration film. This film occupies active surface sites, thereby impeding effective contact between collector molecules and the mineral surface, which is one of the core reasons why titanium impurities in coal-measure kaolinite are difficult to remove and why flotation performance tends to fluctuate (Bao et al., 2025).

As shown in Table 2, two categories of isomorphic substitution in kaolinite are summarized, including octahedral Al^{3+} substituted by Fe^{2+}, Fe^{3+}, Mg^{2+}, Ti^{4+}, and tetrahedral Si^{4+} substitution modes. Distinct discrepancies in band structure, surface hydrophilicity, surface charge distribution, and interaction behavior with anionic/cationic collectors can be observed between different substitution types. Notably, the Mg^{2+}-Al substitution exhibits a prominent dose-dependent effect, which is highly consistent with the structure-activity relationship described earlier.

In summary, the isomorphic substitutions in both octahedral and tetrahedral sheets not only directly alter the band structure and surface hydrophilicity of kaolinite but also fundamentally reshape its surface charge balance. However, the actual surface charge behavior (e.g., zeta potential) is not fixed; it is strongly dependent on the modulation of edge-site protonation/deprotonation processes by slurry

pH. Therefore, building upon the understanding of lattice defects, it is necessary to further examine the influence of pH on surface charge properties and collector adsorption behavior, which will be addressed in the following section.

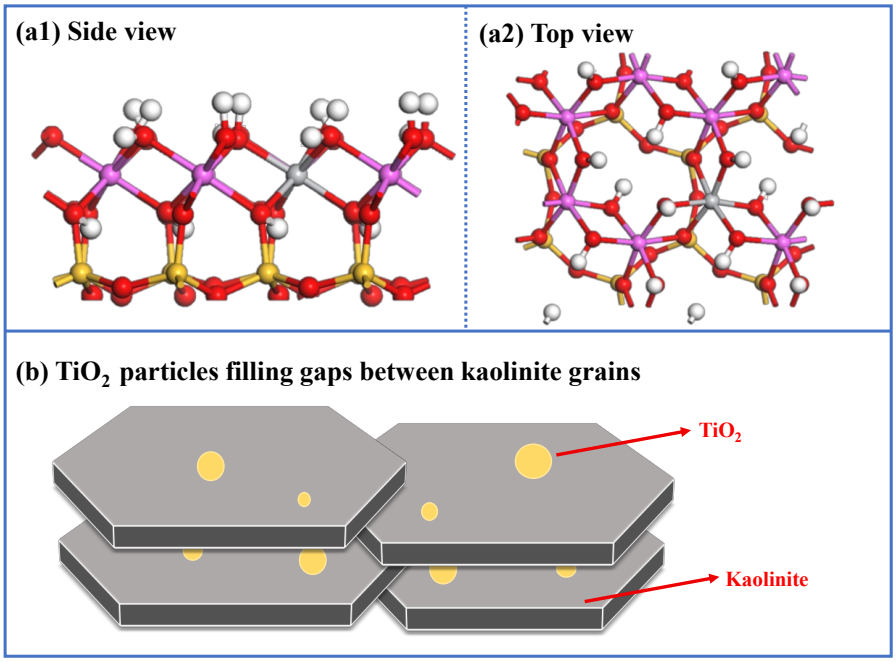


Fig. 8. Schematic of the two occurrence forms of Ti in kaolinite((a) Ti^{4+}-Al; (b) titanium oxide nano-inclusions embedded in the interlayers of kaolinite) (Shoval et al., 2008; Bao et al., 2025)

Table 2. Comparison of different metal ion substitutions in kaolinite

Substitution Type	Band Gap Change	Surface Hydrophilicity	Surface Charge Distribution	Effect on Anionic Collectors	Effect on Cationic Collectors
Fe^{2+}-Al	Not quantitatively specified	Significantly enhanced	Slight negative shift	Hinders coordinative adsorption	Promotes electrostatic adsorption; Counterion interference; Adsorption energy decreased
Fe^{3+}-Al	Significantly narrowed	Enhanced	Significant positive shift	Adsorption capacity increased, selectivity decreased	Enhanced bonding stability; Adsorption energy increased
Mg^{2+}-Al	Not quantitatively specified	Appropriately enhanced; Excessive substitution leads to charge-enhanced hydrophilicity	Appropriately optimized distribution; Excessive negative charge density	Appropriately promotes adsorption; Excessive substitution inhibits adsorption	Appropriately promotes adsorption; Excessive substitution inhibits due to charge repulsion
Ti^{4+}-Al	Narrowed	Significantly enhanced	Significant positive shift	Non-specific adsorption enhanced, selectivity decreased	Active sites occupied by hydration film, binding weakened
Al^{3+}-Si	Slightly narrowed	Weakly enhanced	Permanent negative charge obviously increases	Strengthened non-specific adsorption	Weakened electrostatic attraction
Fe^{3+}-Si	Moderately narrowed	Slightly enhanced	Local negative charge accumulation	Local negative charge accumulation	Local adsorption stability fluctuation

3.1.3 Crystal anisotropy

The crystallographic anisotropy of kaolinite, arising from distinct atomic arrangements, charge distributions, and hydroxyl group densities across its various crystal planes within the 1:1 layered structure, leads to significant differences in collector adsorption strength, interaction mechanism, and flotation response on different surfaces. This anisotropy constitutes a key structural factor governing the flotation selectivity of kaolinite. The predominantly exposed surfaces include the (001) basal plane (siloxane tetrahedral sheet), the (110) edge surface (at the tetrahedral–octahedral junction), and the $(00\bar{1})$ basal plane (alumina octahedral sheet). Using DFT simulations combined with experimental validation, studies have characterized the surface properties and collector interactions of these three planes under defined conditions (pH=7, T=25°C, collector concentration=1×10^{-4} mol/L) for both cationic and anionic collectors, as summarized in Table 3 (Jiang et al., 2014; Guo et al., 2017).

Table 3. Adsorption capacity of DDA and NaOL, and flotation recovery of different kaolinite surfaces

Crystal face	Surface hydroxyl density(nm^2)	Surface charge(mV)	DDA adsorption(mg/g)	Oleic acid adsorption (mg/g)	Dominant adsorption mechanism	Flotation recovery (%)
(001)	2.8	-38	1.12	0.78	Electrostatic interaction	85.2%
(110)	4.5	-12	0.68	0.95	Hydrogen bonding	62.5%
$(00\bar{1})$	3.2	-25	0.85	0.82	Electrostatic+ weak coordination	73.1%

As shown in Table 3, the (001) basal plane exhibits stable negative charge due to the substitution of Si^{4+} by Al^{3+} in the lattice, along with low hydroxyl density. Its adsorption of cationic collectors is dominated by electrostatic interaction, resulting in significantly higher adsorption capacity and flotation recovery compared to other crystal surfaces. The (110) edge surface exposes numerous Al-OH groups, and its edge charge fluctuates considerably with pH. Anionic collector adsorption here is governed primarily by hydrogen bonding and weak coordination, leading to a higher adsorption amount of oleate than on the basal plane. The $(00\bar{1})$ basal plane possesses both a limited number of Si-O^- sites and Al-OH groups, exhibiting moderate adsorption strength for both types of collectors without significant selectivity. Simulation studies further confirm (Xu et al., 2014) that the adsorption energy of oleate on the (001) basal plane is higher than that on the (110) edge surface, which is attributed to the formation of strong coordination bonds with surface Si-O and hydroxyl groups on the basal plane, compared to the weak hydrogen bonding dominant on the edge surface. This difference contributes to improved separation efficiency. However, at elevated collector concentrations, non-selective adsorption on the edge surface can reduce bubble adhesion selectivity. Therefore, crystallographic anisotropy is a key consideration in designing highly selective collectors for kaolinite.

Various mineral properties of kaolinite influence the adsorption sites, adsorption energy, and adsorption state of collectors through different mechanisms, thereby governing separation efficiency.

3.2. Structural properties of the reagents

The molecular structure and intrinsic properties of collectors are fundamental in determining the flotation performance of kaolinite. The type of hydrophilic group, hydrophobic chain structure, charge distribution, and functional group activity collectively regulate the interaction strength, selectivity, and interfacial hydrophobicity with the kaolinite surface, thereby directly determining flotation recovery and separation efficiency.

From the perspective of hydrophilic groups, the positively charged sites of cationic collectors can undergo strong electrostatic attraction with the negatively charged surfaces of kaolinite (Li et al., 2004), while anionic collectors achieve adsorption through the formation of chemical bonds or complexes with metal ions on the kaolinite surface. However, such chemisorption is highly influenced by solution pH and the pulp environment. Increasing the carbon chain length significantly enhances the

hydrophobicity of collectors. Long hydrocarbon chains also exert a prominent effect on the water solubility of collectors: longer carbon chains raise the proportion of nonpolar hydrophobic alkyl groups, which reduces water solubility remarkably, while excessively short hydrocarbon chains bring excessive water solubility and fail to build stable surface hydrophobic films. A moderate chain length facilitates the formation of a hydrophobic layer on the kaolinite surface, thereby improving flotation performance; chains that are too short provide insufficient hydrophobicity, whereas excessively long chains may hinder adsorption due to steric hindrance. Studies on the adsorption of various amines/ammonium salts on kaolinite have shown that0(Chen et al., 2017) structural factors such as the number and position of amino functional groups and the length of the hydrocarbon chain significantly affect collecting performance. At the molecular level, dodecyl quaternary ammonium salts can form multilayered adsorption on the kaolinite surface due to van der Waals interactions of their hydrophobic chains (Abaka-Wood et al., 2024). Compared to octyl derivatives (C8), these compounds exhibit significantly higher adsorption energy and correspondingly improved flotation recovery. In contrast, sodium oleate preferentially undergoes coordinative adsorption on the (001) basal plane of kaolinite at low concentrations, but exhibits non-selective adsorption on the edge surfaces at high concentrations, leading to a notable reduction in separation selectivity.

The hydrophilic head group of a collector dictates the adsorption mechanism, while the hydrophobicity and adsorption strength are governed by the length and configuration of the hydrophobic chain. Adsorption selectivity, in turn, can be finely adjusted through the number, type, and spatial arrangement of functional groups.

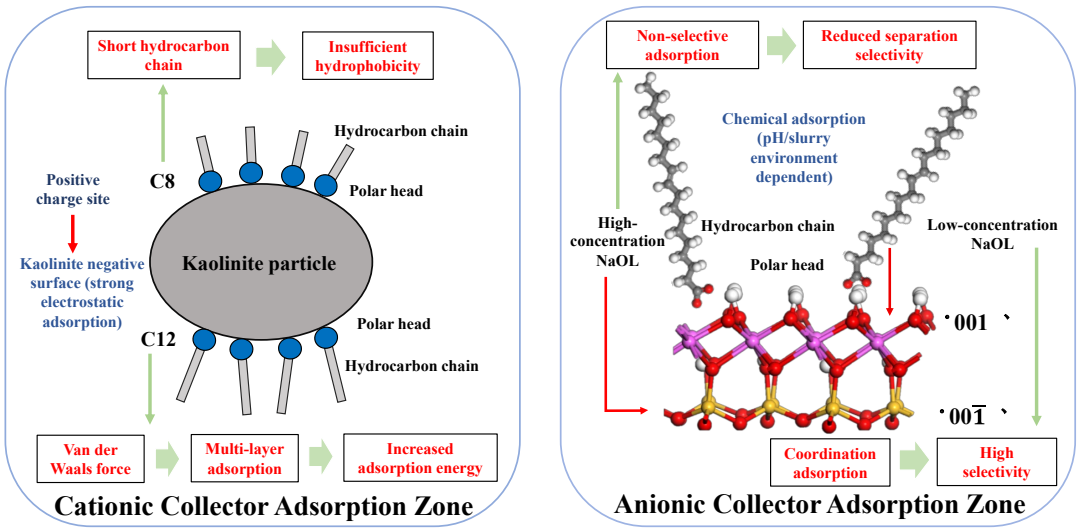


Fig. 9. Schematic of Cationic and Anionic Collector Structures on Adsorption and Flotation Behavior of Kaolinite (Li et al., 2004; Abaka-Wood et al., 2024)

3.3. Solution chemistry environment

The solution chemistry environment regulates the adsorption behavior of collectors and the hydrophobicity of mineral surfaces through multiple mechanisms involving its complex composition and properties (Xu et al., 2025). Key influencing factors include ion species and valence states, solution pH, and interactions with other reagents.

3.3.1. Mechanism of metal ion influence

In the flotation system of diaspore and kaolinite, Ca^{2+} and Mg^{2+} can modulate the adsorption of NaOL by altering the interfacial electrostatic environment (Zhang et al., 2001). However, these ions can also reduce the absolute surface potential of both diaspore and kaolinite and alter the electrostatic environment of the mineral surfaces, leading to a significant improvement in the separation efficiency of kaolinite. Further research has revealed that (Fang et al., 2019). the core mechanism by which Ca^{2+} and Mg^{2+} enhance kaolinite flotation lies in their modulation of hydrogen bonding and dipole–dipole

interactions between the kaolinite surface and sodium oleate, which changes the adsorption behavior of the collector and consequently affects the floatability of kaolinite. In this process, the regulation of mineral surface hydration properties by hydrated cations is a critical step (Min et al., 2024). In the case of multivalent cations, Fe^{3+} has a relatively minor effect on the floatability of kaolinite, while Al^{3+} forms $Al(OH)_3$ precipitates in the pH range of 4-8. These precipitates adsorb onto the kaolinite surface, blocking active sites and significantly inhibiting its flotation performance (Zhou et al., 2009).

3.3.2 Pulp pH value

The solution pH plays a critical role in regulating the hydrophobicity and separation efficiency of kaolinite, as it governs the mineral's surface charge, the dissociation state of the collector, and the resulting adsorption mechanisms. Owing to distinct chemical properties, different classes of collectors exhibit specific pH-dependent performance, which fundamentally relies on the match between the collector's dissociation form and the surface characteristics of the mineral (Shang et al., 2025).

For anionic collectors, the degree of dissociation increases significantly under alkaline conditions, leading to more molecules converting into negatively charged active ions. When the mineral surface carries a positive charge, this promotes electrostatic attraction between the collector and the surface, thereby improving flotation performance (Lu et al., 2020). Conversely, under strongly acidic conditions, anionic collectors predominantly exist in molecular form. Although these molecules exhibit strong hydrophobicity, their electrostatic interaction with the mineral surface is substantially weakened, resulting in a notable reduction in adsorption efficiency.

Cationic collectors are more suitable under acidic or neutral conditions. In such environments, amine-based collectors readily undergo protonation to form positively charged cations, which electrostatically adsorb onto negatively charged mineral surfaces. Taking DDA as an example, in flotation tests conducted on kaolinite, quartz, and montmorillonite (Wang et al., 2024) showed that under unadjusted pH conditions, kaolinite and quartz exhibited favorable floatability even at low collector concentrations, whereas montmorillonite required higher reagent dosages to achieve similar flotation performance. When the reagent dosage was fixed, the most significant changes in surface potential before and after adsorption for all three minerals occurred at pH values of 4, 6, and 8, consistent with the flotation results, confirming the effectiveness of this pH range.

3.3.3 Interactions with other reagents

In practical flotation systems, besides collectors, auxiliary reagents such as coagulants, flocculants and frothers are often employed to optimize the separation environment or enhance subsequent solid–liquid separation. The introduction of these reagents alters the interfacial chemical environment of the pulp, leading to synergistic or competitive interactions with the collector, which ultimately affects the separation outcome (Fan et al., 2023).

3.3.3.1. Influence of flocculants

Polyacrylamide (PAM) flocculants are widely used for the settling of fine-particle mineral suspensions. The polar groups on their molecular chains may occupy active sites on the kaolinite surface or hinder collector adsorption through steric hindrance effects (Bao et al., 2021). Studies indicate that cationic polyacrylamide (CPAM) can modulate the flotation response of kaolinite through charge neutralization and bridging adsorption. Its competitive adsorption with collectors at the interface further regulates the flotation separation process (Li et al., 2016). In contrast, anionic polyacrylamide (APAM) coats the kaolinite surface via chemisorption, enhancing surface hydrophilicity and thereby significantly depressing its floatability. Meanwhile, APAM adsorbs only weakly onto coal particles, which helps optimize the selective adsorption of collectors between coal and kaolinite, improving separation efficiency (Besra et al., 2003).

3.3.3.2. Influence of other modifiers

In addition to flocculants, certain inorganic or organic modifiers can specifically alter the interfacial properties of kaolinite. For instance, sodium fluosilicate (Na_2SiF_6) can modify the floatability of kaolinite

through selective dissolution or surface modification, thereby playing a regulatory role in the flotation separation of coal and kaolinite, as reported in literature (Xia et al., 2021). Likewise, in bauxite flotation systems, specific modifiers such as certain composite reagents containing polyacrylamide have been shown to influence the separation efficiency of cationic collectors by modifying the surface properties of diaspore and kaolinite (Yin et al., 2025).

In summary, a flotation system is a complex multi-reagent environment. Metal ions primarily influence collector adsorption through charge regulation, while pH plays a decisive role in determining the dissociation and adsorption patterns. Other reagents such as coagulants, flocculants, and modifiers profoundly affect the efficiency of collectors and the final separation selectivity via direct interfacial competition, site masking, or indirect alteration of the chemical environment.

3.4. Flotation process parameters

Flotation process parameters significantly influence the adsorption efficiency and selectivity of collectors by operating through two key mechanisms: interfacial energy input and bubble behavior modulation.

Firstly, through regulated energy input, high-speed stirring at ≥1500 r/min induce lattice distortion in kaolinite, markedly increasing surface hydroxylation and active sites. When combined with grinding processes that control the median particle size to 20-30 μm—thereby reducing fine particle aggregation—these measures work synergistically to enhance the adsorption energy and efficiency of quaternary ammonium collectors (Yang et al., 2023; Xu et al., 2015).

Secondly, via bubble behavior regulation, strengthening the interaction between the hydrophobic chains of collectors and bubbles can significantly raise the adhesion probability. When sodium oleate is employed as the collector, nanobubbles promote the formation of a hydrophobic adsorption layer on the kaolinite surface, increasing the contact angle and consequently improving separation efficiency (Rosa and Rubio, 2018). Moreover, nanobubbles can reduce collector consumption and enhance selective adhesion efficiency by forming a gas film layer on particle surfaces.

In summary, the performance of flotation collectors for kaolinite is comprehensively regulated by interfacial properties of the mineral, molecular structure of the reagents, solution chemistry environment, and flotation process parameters. The synergy or antagonism among these factors directly affects collector efficiency and selectivity. The essence of these influences lies in the interactions between collectors and the kaolinite surface, underscoring the necessity of investigating the adsorption mechanisms of collectors on kaolinite.

4. Interaction mechanisms of collectors on the kaolinite surface

As reviewed above, the types of collectors and the factors governing their performance have been systematically discussed. Ultimately, the regulation of these macroscopic factors is rooted in the physicochemical essence of the microscopic interaction mechanisms between collector molecules and the kaolinite surface. Accordingly, this section focuses on elucidating both individual and synergistic mechanisms of these interfacial interactions. By revealing the molecular-level basis of flotation separation, this analysis aims to provide a theoretical foundation for the rational design of efficient, tailored collectors.

4.3. Mechanisms dominated by single interactions

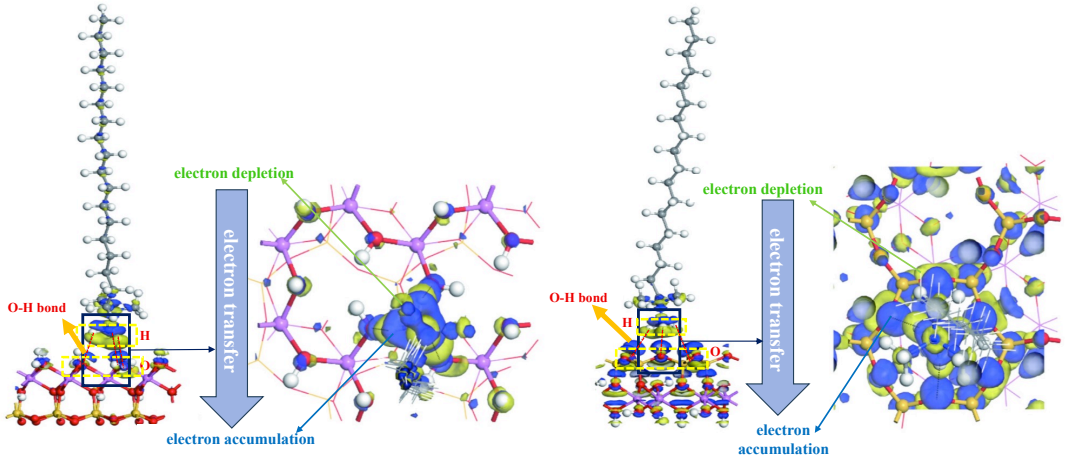
Interactions dominated by a single mechanism refer to adsorption between collectors and the kaolinite surface that is predominantly mediated by one specific type of force, primarily electrostatic attraction and hydrogen bonding, which correspond to the distinct active-site characteristics of different crystal faces, respectively.

4.1.1. Electrostatic attraction

The surface charge of kaolinite exhibits crystal-face specificity, which forms the fundamental basis for electrostatic interactions. The siloxane basal plane carries a permanent negative charge due to the substitution of Si^{4+} by Al^{3+} in the lattice, whereas the charge on the edge faces varies with pH (positive

below pH<6 and negative above pH>6). Cationic collectors, such as CTAB, DTAC, and OTAC, are strongly attracted via electrostatic forces between their quaternary ammonium groups and the negatively charged siloxane oxygen (Si-O$^-$) on the basal plane (Chen et al., 2014), leading to oriented adsorption of the "cationic head–negative site" type. Under acidic conditions, the basal plane maintains a higher and more stable negative charge, resulting in significantly greater adsorption of cationic collectors compared to neutral conditions. This clarifies why the basal plane serves as the primary adsorption site for cationic collectors and how their densely packed adsorption layer substantially enhances the floatability of kaolinite (Balan et al., 2014).

To reveal the mechanism of electrostatic attraction at the atomic scale, researchers selected the OTAC$^+$ as a model and employed DFT to simulate its adsorption behavior on the (001) and (00$\bar{1}$) surfaces of kaolinite (Chen et al., 2021). As shown in Fig. 9, adsorption energy decomposition and charge density analysis confirm that the interaction between OTAC$^+$ and the kaolinite surface is dominated by electrostatic attraction, further validating the predominance of electrostatic forces between cationic collectors and the basal plane of kaolinite.



(a) (001) plane (b) (00$\bar{1}$) plane

Fig. 10. Charge density and electrostatic interaction mechanism of OTAC$^+$ adsorption on different basal planes of kaolinite (Chen et al., 2021)

4.1.2. Hydrogen bonding

Collectors containing polar groups such as amino (-NH$_2$), hydroxyl (-OH), and ether (-O-) groups including cationic amine collectors and nonionic fatty alcohol collectors—can form hydrogen bonds with Si-OH and Al-OH groups on the kaolinite surface. Since the kaolinite surface is typically covered by a hydration layer, differences in hydrogen bonding with water molecules on different surfaces indirectly influence collector adsorption behavior. Hydroxyl groups (-OH) on the Al-OH face can act as hydrogen bond donors or acceptors to bind with water molecules, whereas the Si-O face exhibits weak hydrogen bonding with water due to its scarcity of hydroxyl groups (Chen et al., 2019). This distinction implies that the hydration layer on the Al-OH face is more stable, requiring collectors to compete with water molecules to form hydrogen bonds with surface hydroxyls. In contrast, the weaker hydration on the Si-O face results in less interference from water molecules during hydrogen bonding between collectors and the surface. Notably, when lattice defects such as Fe^{3+} are present in kaolinite, the hydroxyl activity on the Al-OH face is enhanced, increasing the hydrogen bond energy with amine collectors from -2.5 eV to -3.2 eV (Ling et al., 2023). Therefore, Fe^{3+} doping strengthens hydrogen bonding, which is a key reason for the more stable adsorption of cationic collectors on Fe^{3+}-substituted kaolinite surfaces.

DFT studies on the adsorption of chitosan onto the kaolinite surface have revealed that the amino and hydroxyl groups of chitosan preferentially form hydrogen bonds with the hydroxyl groups on the Al-OH face of kaolinite (Ge et al., 2023). This observation is consistent with the higher reactivity of hydroxyl groups on the Al-OH face and their ability to stabilize adsorption through a hydrogen-

bonding network. These findings further confirm that hydrogen bonding between the polar groups of collectors and the kaolinite surface exhibits distinct surface selectivity.

4.4. Mechanisms of composite interaction coupling

While single-interaction mechanisms dominate under specific conditions, most practical flotation systems involve a combination of multiple forces, leading to more complex adsorption behaviors. The interaction between reagents and the kaolinite surface is rarely dominated by a single mechanism, but typically involves the coupling of multiple forces, including hydrogen bonding, electrostatic attraction, van der Waals interactions, and chemisorption. The synergy or antagonism among these interactions directly determines the surface hydrophobicity and separation efficiency of the mineral.

4.2.1 Composite interactions of cationic collectors

The combined action of cationic collectors is centered on the synergy of electrostatic attraction - hydrogen bonding - van der Waals forces. The quaternary ammonium head group undergoes strong electrostatic adsorption with the Si-O$^-$ sites, forming the foundation of adsorption (Chen et al., 2014) Simultaneously, the nitrogen atom in the head group and polar groups in the molecular backbone can form hydrogen bonds with Al-OH groups on different crystal faces, enhancing the specificity and stability of adsorption (Jiang et al., 2014). Meanwhile, hydrophobic alkyl chains aggregate through van der Waals interactions, forming a dense and stable hydrophobic film on the mineral surface, which significantly increases surface hydrophobicity and flotation recovery (Sun et al., 2010). Under acidic conditions, amine collectors are protonated to -NH_3^+, further strengthening electrostatic interactions. Together with hydrogen bonding, this leads to oriented adsorption and stable attachment of the collectors on the mineral surface.

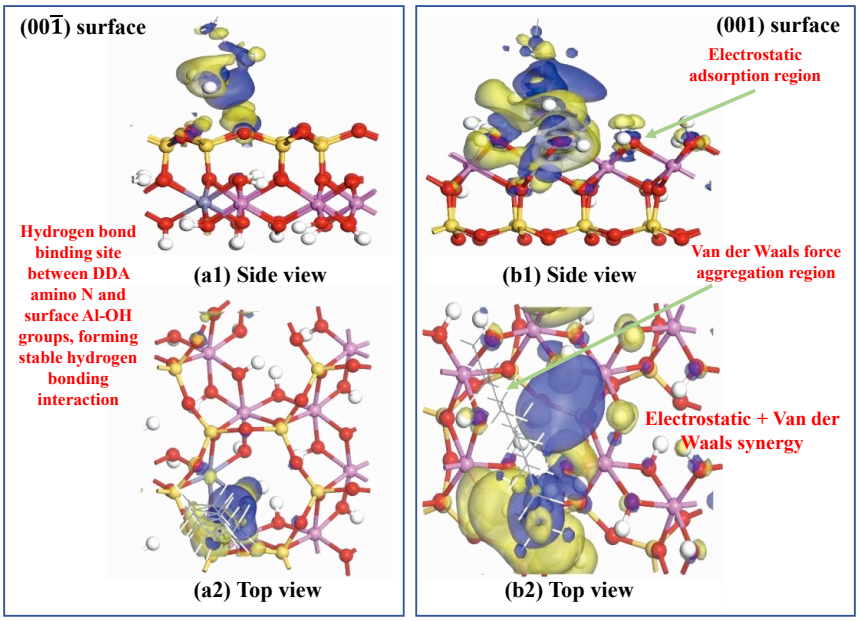


Fig. 11. Adsorption of DDA and DDA$^+$ on (001) and (00$\bar{1}$) facets of Fe^{2+} doped kaolinite((a): DDA adsorbed on the (00$\bar{1}$) surface; (b): DDA$^+$ adsorbed on the (001) surface;) (Ling et al., 2023)

Density functional theory provides a direct visualization of this combined mechanism. As shown in Fig. 11, for DDA$^+$ adsorbed on the (001) surface of Fe^{2+} doped kaolinite, the quaternary ammonium head group displays a strong electrostatic adsorption configuration with the negatively charged surface sites, while the alkyl chains are closely packed with notable van der Waals interactions. On the (00$\bar{1}$) surface, clear hydrogen bonds are formed between the amino group of DDA and the Al-OH groups on the surface (Ling et al., 2023). This study confirms that the adsorption of cationic collectors results from the combined effects of electrostatic attraction, hydrogen bonding, and van der Waals forces, and that the

subtle charge modulation induced by Fe^{2+} doping further influences the synergistic balance among these interactions.

4.2.2 Composite interactions of anionic collectors

The composite interaction of anionic collectors relies on the synergy of chemisorption–electrostatic attraction–hydrogen bonding, but its strength on kaolinite is weaker than on target minerals such as diaspore. Taking NaOL as an example, on the kaolinite surface, electrostatic repulsion arises from the siloxane face, and the dense hydroxyl groups on the aluminol surface limit the accessibility of active Al^{3+} sites, making strong chemisorption similar to that on diaspore—difficult to achieve (Zhang et al., 2001; Xu et al., 2016). Instead, adsorption primarily occurs through weak electrostatic attraction between carboxylate ions and the edge faces of kaolinite, combined with hydrogen bonding with surface Al-OH groups (Liu et al., 2024; Han et al., 2016). This relatively weak electrostatic-hydrogen bonding synergy results in a loose adsorption configuration and low adsorption free energy, which explains the limited collecting capacity and poor selectivity of NaOL toward kaolinite.

However, isomorphous impurities commonly present in the kaolinite lattice, such as Fe^{2+}/Fe^{3+}, can significantly alter the adsorption mode of anionic collectors. DFT calculations reveal that on the kaolinite surface containing Fe^{2+} impurities, oleate ions can form more specific and stronger chemical complexes with Fe^{2+} sites, this results in a more stable and densely packed adsorption configuration, which significantly enhances both adsorption efficiency and the floatability of the kaolinite surface (Liu et al., 2024). This highlights the critical role of lattice defects in shifting the interaction mechanism of anionic collectors from "weak physisorption" toward "strong chemisorption". Further support from EDLVO theory and atomic force microscopy studies confirms, at the force level (Wu et al., 2022), the fundamental differences in the nature and magnitude of interaction forces between kaolinite and diaspore in the NaOL system, underpinning the above mechanistic analysis.

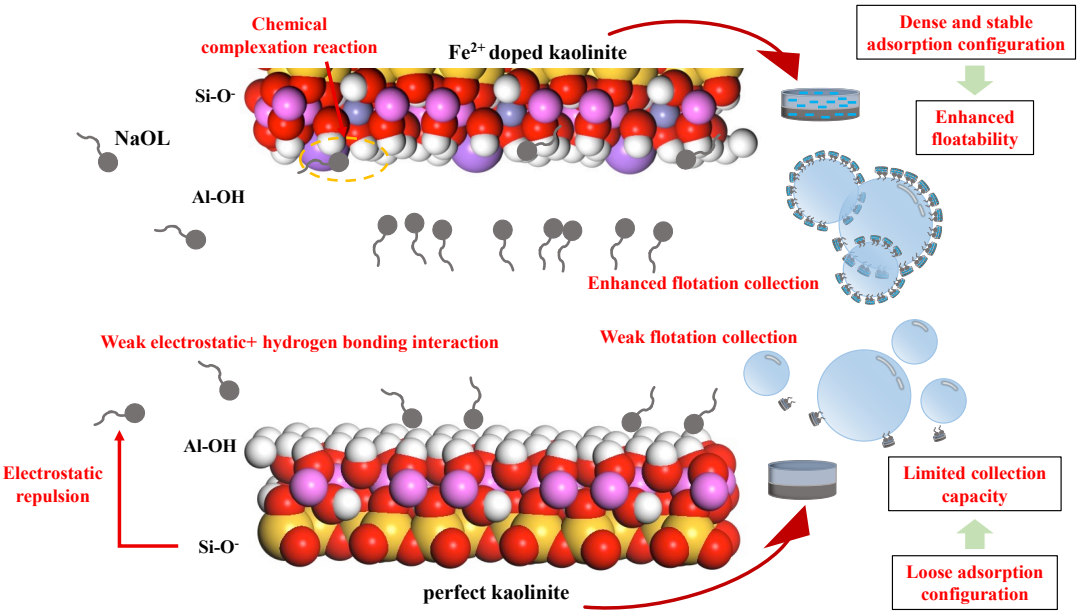


Fig. 12. Mechanistic depiction of sodium oleate adsorption on perfect and Fe-doped kaolinite surface (Zhang et al., 2001; Liu et al., 2024)

4.2.3 Composite effect of novel collectors

To overcome the limitations of traditional reagents, novel collectors are rationally designed to achieve stronger and more selective composite interaction modes.

4.2.3.1. Gemini-type collectors

Gemini surfactants possess a unique structure of dual hydrophilic head groups and dual hydrophobic chains, which creates a synergy of dual-site electrostatic adsorption-hydrogen bonding-enhanced van

der Waals forces. The twin cationic head groups can simultaneously anchor onto two negatively charged sites on the kaolinite surface, achieving multiplied adsorption strength and stability. The spacer group between the heads may further contribute through hydrogen bonding, while the dual hydrophobic chains form a denser hydrophobic layer through stronger inter-chain van der Waals interactions. Studies show that this design lowers their critical micelle concentration and enables excellent flotation performance even under low-temperature conditions (Zhang et al., 2021).

4.2.3.2. Hydroxamate-type collectors

Hydroxamate-type collectors feature a characteristic functional group that forms stable five-membered chelates with metal ions such as Fe^{3+} and Al^{3+} present on the kaolinite surface or at lattice defects. This establishes a composite mechanism of strong chemical chelation complemented by electrostatic/hydrogen-bonding interactions. The high specificity and bonding energy of this coupled interaction provide the basis for selective separation. Molecular design can further introduce additional groups to fine-tune the hydrophilic-hydrophobic balance and coordination selectivity (Jiang et al., 2010). For example, the collector TPA can effectively displace the hydration film through such well-matched interactions, significantly increasing the contact angle of kaolinite (Ouyang et al., 2024).

4.2.3.3. Polyamine-type collectors

Polyamine-type collectors incorporate multiple amine groups, which undergo stepwise protonation to form a polycationic structure within a specific pH range. This enables an enhanced synergy of multi-site electrostatic adsorption and hydrogen bonding. Compared to monoamines, they exhibit stronger binding to the negatively charged surface of kaolinite and more stable interactions, thereby achieving efficient collection across a broader pH range (Cao et al., 2001).

These novel collectors achieve more precise and stable modification of the kaolinite surface at the molecular level by strengthening one key interaction force and enhancing its synergy with other forces. Studies show that in Fe-doped kaolinite-quartz systems, the presence of Fe impurities alters the active sites on the kaolinite surface, intensifying inter-particle electrostatic and hydrogen-bonding interactions, further confirming how the interfacial microenvironment regulates the composite interaction effect.

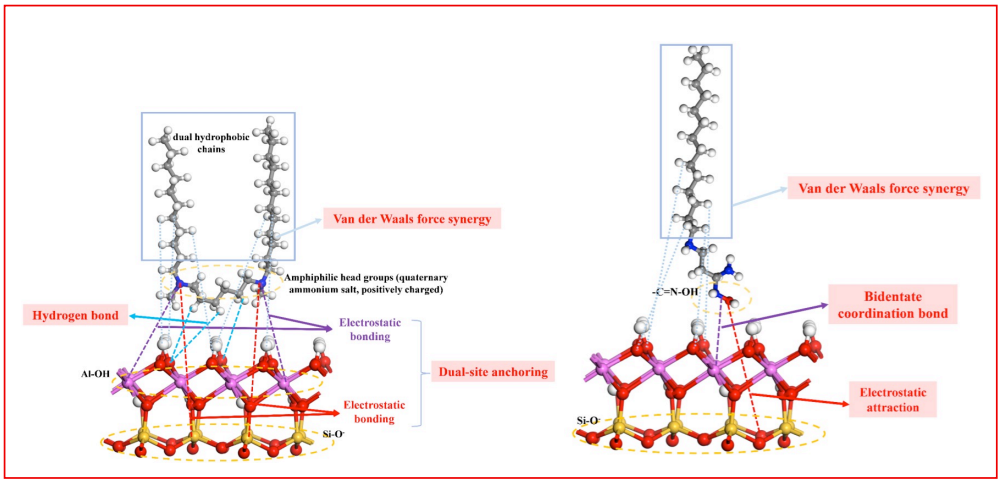


Fig. 13. Schematic of the composite interaction mechanisms of Gemini bis-quaternary ammonium salt and TPA oxime-type novel collectors with kaolinite (Zhang et al., 2021; Huang et al., 2022)

In summary, the interaction mechanisms of collectors on the kaolinite surface have evolved from simple, single interactions to complex couplings of multiple forces. Cationic collectors primarily rely on a stable interplay of electrostatic attraction, hydrogen bonding, and van der Waals forces. Anionic collectors exhibit relatively weaker interactions with ideal kaolinite, primarily following a weak electrostatic–hydrogen bonding pattern. However, lattice impurities can induce enhanced specific chemisorption. Novel collectors, through rational molecular design, strengthen key interactions such as chelation or multi-site electrostatic adsorption while optimizing their synergy with secondary forces.

A deep understanding of these microscopic interaction mechanisms, particularly the modulation by lattice impurities, forms the theoretical cornerstone for developing high-performance targeted flotation reagents and achieving efficient purification of challenging resources such as kaolinite.

5. Conclusions

To address the challenge of deep removal of lattice impurities in kaolinite and achieve high-value utilization of the resource, this review systematically summarizes recent advances in flotation collectors and their interaction mechanisms. The key conclusions are as follows:

1. Collector types – traditional anionic or cationic collectors, relying on single interaction modes, often fail to balance selectivity and collecting ability. Blended collectors effectively overcome the performance boundaries of single reagents through intermolecular synergy. With innovative molecular designs. Novel collectors, designed with tailored molecular architectures, significantly strengthen and specify interactions with target sites, representing the forefront of flotation reagent development.
2. Influencing factors – beyond conventional parameters such as particle size, pH, and ionic strength, lattice defects play a critical role at the microscopic regulatory level. The isomorphous substitution of Al^{3+} by impurities like Fe, Ti, and Mg is not merely an atomic replacement, rather, it systematically reconstructs the hydration layer structure and reactivity of the mineral surface by altering the local electron density, band structure, and charge distribution. This fundamentally changes the adsorption mode, strength, and selectivity of the same collector on kaolinite surfaces with different defect types.
3. Interaction mechanisms – research has evolved from early models of simple electrostatic adsorption or hydrogen bonding to revealing multi-component synergistic mechanisms involving electrostatic forces, hydrogen bonding, van der Waals interactions, and specific chemical bonding. Cationic collectors primarily rely on the synergy of electrostatic attraction and hydrogen bonding on negatively charged basal planes. Anionic collectors interact only weakly with perfect kaolinite, whereas lattice Fe^{2+}/Fe^{3+} impurities can serve as activation anchors, shifting adsorption from weak physisorption to strong chemisorption. Novel collectors are precisely designed to maximize these favorable synergistic effects.

It is necessary to clarify the practical limitation of froth flotation for lattice impurity purification. Flotation realizes separation based on the difference in surface hydrophobicity between mineral particles, which can efficiently remove free iron/titanium oxide impurity minerals symbiotically mixed with kaolinite. However, lattice impurity ions (Fe^{2+}, Fe^{3+}, Ti^{4+}) enter the crystal skeleton via isomorphic substitution and form stable chemical bonds with lattice oxygen atoms. Accordingly, single froth flotation cannot strip these internal lattice impurity ions to accomplish thorough deep removal. To achieve deep purification of lattice isomorphic impurities, flotation can serve as an effective pre-enrichment procedure, while follow-up reductive acid leaching or high-temperature calcination activation combined with acid pickling is required to break lattice bonds and dissolve embedded impurity ions. Despite these advances, most existing studies are based on relatively pure conventional kaolinite, leaving a significant gap in understanding the complex "impurity-rich and organic-rich" system of coal-measure kaolinite. The fundamental challenge in its separation stems from the lack of systematic analysis of the genetic characteristics of lattice impurities and organic matter within it, as well as how they jointly modulate the micro-interface environment, thereby hindering the achievement of stable and efficient separation. The interface regulation logic of collectors in kaolinite flotation can be extended to the separation of other silicate mineral systems, providing a reference for the efficient separation of low-grade mineral resources via flotation.

6. Future perspectives

Based on this analysis, future research could focus on the following directions:

1. Utilize advanced characterization techniques to investigate the atomic-scale structure and origins of lattice impurities and surface organic matter in coal-measure kaolinite, providing a foundation for targeted treatment.

2. Integrate computational approaches—such as density functional theory (DFT), molecular dynamics (MD), and machine learning—to establish a multi-level structure-activity relationship model. This will enable quantitatively evaluate of the complexation energies and interaction mechanisms between functional groups and impurity sites, while facilitating the rapid screening of high-affinity, selective collector molecules from extensive molecular libraries.
3. Foster interdisciplinary collaboration to develop a comprehensive knowledge chain linking mineral genetics to interfacial control, thereby shifting kaolinite flotation from an empirical practice to a predictive, intelligently designed, and precise controlled process.

Acknowledgments

This research was supported by the National Key Research and Development Program of China (No. 2024YFC2910700), the National Natural Science Foundation of China (Nos. 52474282 and 52404273), and Postgraduate Innovation Fund Project of Anhui University of Science and Technology (No, 2025cx2084), are gratefully acknowledged.

References

MURRAY, H., 1961. *Industrial applications of kaolin*. Clays and Clay Minerals 10, 291-298.

VELHO, J., GOMES, C.d.S.F., 1991. *Characterization of Portuguese kaolins for the paper industry: beneficiation through new delamination techniques*. Applied Clay Science 6(2), 155-170.

WU, Y., CHEN, C., YUAN, F., 2021. *Temporal-spatial distribution regularities of kaolin deposits in China*. Acta Geoscientica Sinica 42(5), 628-640. (In Chinese)

DILL, H.G., 2016. *Kaolin: Soil, rock and ore: From the mineral to the magmatic, sedimentary and metamorphic environments.* Earth-Science Reviews 161, 16-129.

TEIXEIRA, C.E., BRANDÃO, P.R.G., NUNES, R.W., 2017. *Methodological reconstruction of dioctahedral 1:1 phyllosilicate polytypes.* Applied Clay Science 146, 201-205.

ZHANG, Y., YANG, F., CHENG, F., 2015. *Study on kaolinite dehydroxylation characteristic and kinetics in coal gangue.* Coal Conversion 38(3), 78-81. (In Chinese)

ZHAI, X., LI, J., XING, J., FANG, Z., MO, J., 2016. *Density functional theory study on the electronic structure of kaolinite.* Journal of Guangxi University of Science and Technology 27(1), 49-53+70. (In Chinese)

LIU, L., LIU, Q., LI, Y., CAO, H., KANG, X., 2022. *Occurrence of iron in the minerals of carboniferous coal gangue of the pingshuo open-pit mine, North China.* Clays and Clay Minerals 70(5), 695-711.

FAN, J., JIANG, Y., LIU, Y., LIU, X., LIU, M., FU, L., MIN, X., HUANG, Z., 2025. *Research progress on impurity occurrence state and purification method of typical kaolin in China*. Metal Mine (2), 95-105. (In Chinese)

HUANG, Y., FU, Q., DONG, J., ZHANG, Y., LI, Y., SUN, H., 2023. *Research progress on the characteristics of iron impurities and iron removal technology in kaolin ore in China.* China Non-metallic Minerals Industry (5), 14-20. (In Chinese)

CHEN, W., FU, J., HAN, H., MU, Y., GAN, J., 2020. *Advance in the separation of ultrafine minerals.* Conservation and Utilization of Mineral Resources 40(4), 134-145. (In Chinese)

FU, B., LIU, H., LI, X., WANG, J., ZAMASH, E., SU, Z., 2024. *Research progress in the flotation separation of kaolinite.* China Mining Magazine 33(S2), 384-389. (In Chinese)

FAN, M., WANG, X., 2012. *The surface properties of kaolinite and flotation characteristics.* Modern Chemical Research 9(3), 52-57. (In Chinese)

PENG, J., ZHONG, H., WANG, S., TANG, Q., 2014. *Research progress on non-sulfide ore collectors.* Modern Chemical Industry 34(1), 39-42. (In Chinese)

ZHANG, G., FENG, Q., LU, Y., OU, Y., 2001. *Mechanism on diaspore and kaolinite collected by sodium oleate.* The Chinese Journal of Nonferrous Metals (2), 298-301. (In Chinese)

XU, L., DONG, F., WU, H., LIU, J., WANG, Z., WANG, J., 2016. *Surface crystal chemistry in selective flotation of diaspore from kaolinite using anionic collector.* Acta Mineralogica Sinica 36(2), 265-270. (In Chinese)

LIU, L., KONG, C., ZHAO, H., LU, F., 2024. *Elucidating the enhancement of kaolinite flotation by iron content through density functional theory: A study on sodium oleate adsorption efficiency.* International Journal of Mining Science and Technology 34(6), 855-866.

DING, M., LU, Y., CHEN, H., XU, L., MENG, W., 2019. *Study on the mechanism of flotation separation of diaspore from kaolinite by the binary mixed collector.* Nonferrous Metals (Mineral Processing Section) (2), 103-107. (In Chinese)

TORN, L.H., DE KEIZER, A., KOOPAL, L.K., LYKLEMA, J., 2003. *Mixed adsorption of poly (vinylpyrrolidone) and sodium dodecylbenzenesulfonate on kaolinite.* Journal of Colloid and Interface Science 260(1), 1-8.

YU, X., ZHONG, H., LIU, G., LIU, G., SU, X., 2011. *A novel cationic organsilicon collector QAS222 for reverse flotation of bauxite.* Journal of Central South University (Science and Technology) 42(7), 1865-1872. (In Chinese)

LIU, L., MIN, F., CHEN, J., LU, F., SHEN, L., 2019. *The adsorption of dodecylamine and oleic acid on kaolinite surfaces: Insights from DFT calculation and experimental investigation.* Applied Surface Science 470, 27-35.

SUN W., CHEN, ZHANG, 2010. *Effects of dodecyl-trimethoxy silane on flotation behavior of aluminum-silicate using dodecylamine as collector.* Journal of China University of Mining & Technology 39(4), 550-556. (In Chinese)

LAINÉ, J., FOUCAUD, Y., HOUNFODJI, J.W., PELÉE, DE, SAINT-MAURICE., BONILLA-PETRICIOLET, A., MENDOZA-CASTILLO, D.I., TURRER, H., BADAWI, M., 2024. *Adsorption of amine surfactants onto kaolinite: A multiscale investigation.* Minerals Engineering 216, 108851.

LIU, X., HU, Y., JIANG, H., CAO, X., QIU, G., 2001. *Crystal structure and surface property of kaolinite in hard kaolins and soft kaolins.* The Chinese Journal of Nonferrous Metals (4), 684-687. (In Chinese)

YUE, T., SUN, W., CHEN, P., 2014. *Mechanism of reverse flotation desilication for bauxite by quaternary ammonium salt collector.* The Chinese Journal of Nonferrous Metals 24(11), 2872-2878. (In Chinese)

RORDRIGUES, O.M.S., PERES, A.E.C., MARTINS, A.H., PEREIRA, C.A., 2013. *Kaolinite and hematite flotation separation using etheramine and ammonium quaternary salts.* Minerals Engineering 40, 12-15.

WANG, X., TANG, Y., CHEN, M., ZHANG, T., 2013. *Research on the flotation performances of hematite and kaolinite.* mining research and development 33(2), 63-67. (In Chinese)

LIU, C., XU, L., DENG, J., WANG, D., XUE, K., TIAN, J., 2025. *An in-depth exploration of the impact of novel collector HPDDA on the low-temperature flotation behavior of bastnaesite and quantum chemical calculation.* Separation and Purification Technology 354, 128544.

PADASALA, S., KANOJE, B., KUPERKAR, K., BAHADUR, P., 2016. *Mixed micellization study of alkyltrimethylammonium and alkyltriphenylphosphonium bromides in aqueous solution.* Journal of Surfactants and Detergents 19, 389-398.

SUN, W., LAN, L., ZENG, H., ZHOU, J., KHOSO, S.A., WANG, L., 2022. *Study on the flotation separation mechanism of diaspore from kaolinite using mixed NaOL/BHA collector.* Minerals Engineering 186, 107719.

LAN, L., SUN, W., YAANG, Y., JIANG, F., LI, W., 2025. *Auxiliary collector optimizing foam characteristics and adsorption behavior towards efficient flotation desilication of bauxite.* Separation and Purification Technology 353, 128322.

WU, C., MA, Y., ZHANG, X., ZHANG, X., JI, P., 2025. *Study on mechanism of flotation separation of diaspore and kaolinite by mixed collector.* Metal Mine (4), 134-140. (In Chinese)

XU, L., TIAN, J., WU, H., YI, F., DONG, F., 2017. *A Review on the synergetic effect of the mixed collectors on mineral surface and its application in flotation.* Conservation and Utilization of Mineral Resources (2), 107-112. (In Chinese)

GAO, Y., FU, X., AN, Z., YUE, T., SUN, W., 2022. *Surface complexation model theory application in NaOL and CTAB collector adsorption differences of diaspore and kaolinite flotation.* Separation and Purification Technology 295, 121288.

CHANG, Q., ZHONG, H., XIA, L., HUANG, Z., 2009. *Study on the reverse flotation with novel Gemini cationic collector for separating kaolinite from diaspore.* Light Metals (11), 7-10. (In Chinese)

ZHANG, S., HUANG, Z., WANG, H., LIU, R., CHEN, C., SHU, Y., HU, Y., GUO, Z., YU, X., HE, G., WENG, F., 2021. *Flotation performance of a novel Gemini collector for kaolinite at low temperature.* International Journal of Mining Science and Technology 31(6), 1145-1152.

HUANG, Z., ZHONG, H., SHUAI, W., XIA, L., LIU, G., 2013. *Comparative studies on flotation of aluminosilicate minerals with Gemini cationic surfactants BDDA and EDDA.* Transactions of Nonferrous Metals Society of China 23(10), 3055-3062.

YANG, Z., ZHANG, Q., ZHENG, Z., WANG, G., 1992. *Separation of cerite calcium and rare earths-bearing barium fluorophlogopite.* Nonferrous Metals 44(1), 46-53. (In Chinese)

JIANG, Y., ZHAO, B., ZHOU, X., ZHOU, L., 2010. *Flotation of diaspore and aluminosilicate minerals applying novel carboxyl hydroxamic acids as collector.* Hydrometallurgy 104(1), 112-118.

HUANG, Z., ZHANG, S., WANG, H., LIU, R., CHEN, C., SHU, S., HU, Y., ZENG, Y., YU, X., HE, G., FU, W., BUROV, V.E., POILOV, V.Z., 2022. *Recovery of wolframite from tungsten mine tailings by the combination of shaking*

table and flotation with a novel "crab" structure sebacoyl hydroxamic acid. Journal of Environmental Management 317, 115372.

OUYANG, L., WU, J., HUANG, Z., BURDONOV, A.E., VCHISLO, N.V., WANG, H., HE, G., YU, X., MA, J., LI, W., 2024. *A novel 3-tetradecylamine propyl amidoxime collector for highly efficient flotation of fine kaolinite.* Powder Technology 445, 120125.

CAO, X., HU, Y., JIANG, Y., LI, H., 2001. *Flotation mechanism of aluminum silicate minerals with N-dodecyl-1, 3-diaminopropane.* The Chinese Journal of Nonferrous Metals (4), 693-696. (In Chinese)

CHANG, Z., LI, Y., SHEN, Z., ZHOU, L., WANG, Q., 2023. Advancements in the application and mechanism of fine-grained mineral flotation collectors. Chinese Journal of Engineering 45(11), 1807-1819. (In Chinese)

GAO, Y., FU, X., HAN, H., LI, W., 2023. *Construction and application of mineral flotation adsorption equilibrium model: accurately analyze ions/reagents adsorption behavior on mineral surface.* Strategic Study of Chinese Academy of Engineering 25(6), 248-258.

LIU, M., YU, H., ZHANG, H., WANG, K., TAN, X., LIU, Q., 2022. *Roles of the hydrophobic and hydrophilic groups of collectors in the flotation of different-sized mineral particles.* Colloids and Surfaces A: Physicochemical and Engineering Aspects 637, 128262.

ZHANG, N., PANG, T., HAN, R., CHEN, S., LI, Z., YU, Y., SHI, Z., LIU, L., QU, J., ZHOU, A., 2022. *Interactions between bubble and particles of key minerals of diasporic bauxite through the extended DLVO theory.* International Journal of Mining Science and Technology 32(1), 201-214.

ABAKA-WOOD, G.B., XU, S., AYEDZI, L.D., ADDAI-MENSAH, J., SKINNER, W., 2024. *Flotation recovery of monazite from kaolinite using sodium oleate collector: Understanding mineral–collector interaction.* Minerals Engineering 209, 108605.

GUO, J., LI, M., FANG, Q., HU, Y., 2003. *The influence of particle size on separation of diaspore and kaolinite.* Multipurpose Utilization of Mineral Resources (5), 17-21. (In Chinese)

JIANG, H., LIU, G., HU, Y., XU, L., YU, Y., XIE, Z., CHEN, H., 2013. *Flotation and adsorption of quaternary ammonium salts collectors on kaolinite of different particle size.* International Journal of Mining Science and Technology 23(2), 249-253.

ZHOU, C., LIU, L., CHEN, J., MIN, F., LU, F., 2022. *Study on the influence of particle size on the flotation separation of kaolinite and quartz.* Powder Technology 408, 117747.

ZHANG, K., LIU, J., HOU, D., CAO, Z., 2019. *Kaolinite entrainment behavior during flotation.* Coal Technology 38(8), 139-143. (In Chinese)

SILVA, M.S.E., LAGES, A.S., SANTANA, G.P., 2017. *Physical and chemical study of lattice kaolinites and their interaction with orthophosphate.* Anais da Academia Brasileira de Ciências 89, 1391-1401.

HONG, H., MIN, X., ZHOU, Y., 2007. *Orbital calculations of kaolinite surface: on Substitution of Al3+ for Si4+ in the tetrahedral sites.* Journal of Wuhan University of Technology 22, 661-666.

CHEN, J., LING, Y., MIN, F., CHENG, Y., CHU, X., SHANG, H., 2023. *Mechanism research on surface hydration of Fe(II)-doped kaolinite, insights from molecular dynamics simulations.* Journal of Molecular Liquids 386, 122469.

CHEN, J., SHANG, H., LING, Y., JIA, F., CHENG, Y., MIN, F., 2024. *Influence mechanism of Fe^{3+} doping on the hydrophobic regulation of kaolinite/water interface: Experiments and MD simulations.* International Journal of Mining Science and Technology 34(11), 1575-1586.

LING, Y., CHEN, J., SUN, Y., CHU, X., LU, F., MIN, F., 2023. *DFT calculations on the adsorption of dodecylamine on* surface of Fe2+-doped kaolinite. Journal of China University of Mining & Technology 52(3), 596-606. (In Chinese)

CHEN, J., BAO, L., XIE, A., SHANG, H., CHENG, Y., MIN, F., 2026. *Microscopic mechanism of Fe(II/III) substitution in the lattice on the band gap of coal-series kaolinite.* Journal of China Coal Society 51(3), 2186-2198. (In Chinese)

SUN, Y., CHEN, J., GE, W., LING, Y., CHU, X., MIN, F., 2022. *Insights into the influence mechanism of Mg^{2+} doping on hydration activity of kaolinite surface: A DFT calculation.* Chemical Physics 560, 111576.

CHEN, J., SUN, Y., LING, Y., CHU, X., CHENG, Y., MIN, F., 2024. *Effects of Mg(II) doping amount on the hydration characteristics of kaolinite surface: Molecular dynamics simulations and experiments.* Surfaces and Interfaces 45, 103869.

CHEN, J., ZHOU, C., SUN, Y., YU, G., MIN, F., 2025. *Influence mechanism of lattice Mg(II) impurities on the surface charge characteristics of kaolinite.* Coal Preparation Technology 53(3), 14-23. (In Chinese)

SHOVAL, S., PANCZER, G., BOUDEULLE, M., 2008. *Study of the occurrence of titanium in kaolinites by micro-Raman spectroscopy.* Optical Materials 30(11), 1699-1705.

BAO, L., CHEN, J., MIN, F., SHANG, H., CHENG, Y., XU, L., 2025. *Surface hydration of Ti-bearing gangue minerals in coal kaolinite based on analytical testing and DFT calculations.* Applied Surface Science 2025.164424

JIANG, H., SUN, Z., XU, L., HU, Y., HUANG, K., ZHU, S., 2014. *A comparison study of the flotation and adsorption behaviors of diaspore and kaolinite with quaternary ammonium collectors.* Minerals Engineering 65, 124-129.

GUO L., LI, Z., ZHU, Z., LIU, Y., FAN, M., 2017. *Study and dynamics simulation of cationic collecting performance on kaolinite.* China Mining Magazine 26(5), 112-116+121. (In Chinese)

XU, L., HU, Y., DONG, F., GAO, Z., WU, H., WANG, Z., 2014. *Anisotropic adsorption of oleate on diaspore and kaolinite crystals: Implications for their flotation separation.* Applied Surface Science 321, 331-338.

LI, H., HU, Y., WANG, D., XU, J., 2004. *Mechanism of interaction between cationic surfactant and kaolinite.* Journal of Central South University (Science and Technology) (2), 228-233. (In Chinese)

CHEN, J., MIN, F., LIU, L., LIU, C., LU, F., 2017. *Experimental investigation and DFT calculation of different amine/ammonium salts adsorption on kaolinite.* Applied Surface Science 419, 241-251.

XU, C., HE, D., TANG, Y., YE, L., LI, Z., 2025. *Effect of solution environment on the foam properties of two anionic collectors in magnesite flotation.* Chinese Journal of Engineering 47(1), 25-32. (In Chinese)

ZHANG, G., LU, Y., OU, Y., FENG, Q., 2001. *A new collector RL for flotation of bauxite.* The Chinese Journal of Nonferrous Metals (4), 712-715. (In Chinese)

FANG, C., YU, S., WEI, X., PENG, H., OU, L., ZHANG, G., WANG, J., 2019. *The cation effect on adsorption of surfactant in the froth flotation of low-grade diasporic bauxite.* Minerals Engineering 144, 106051.

MIN, F., SHU, Q., CHEN, J., LIU, C., LING, Y., 2024. *Influence mechanism of hydrated cations on surface hydration of slime mineral particles.* Journal of China Coal Society 49(2), 1111-1122. (In Chinese)

ZHOU, Y., WANG, Y., HU, Y., SUN, D., YU, M., 2009. *Influence of metal ions on floatability of diaspore and kaolinite.* Journal of Central South University (Science and Technology) 40(2), 268-274. (In Chinese)

SHANG, Y., LI, Z., WANG, J., CHANG, J., WANG, H., GUO, B., 2026. *Study on surface hydration characteristics and particle self-aggregation structure of kaolinite.* Clean Coal Technology 32(3), 253-262. (In Chinese)

LU, F., HOU, B., ZHANG, M., 2020. *Study on the flotation characteristics of coal measure minerals in the dodecylamine system.* Journal of Chifeng University (Natural Science Edition) 36(5), 39-41. (In Chinese)

WANG, Y., ZHAO, Q., GUO, Y., HU, S., TIAN, G., ZHANG, M., CAO, X., LIU, H., ZHANG, J., 2024. *Interfacial interactions of nanoscale zero-valent iron particles with clay minerals in the aquatic environments: experimental and theoretical calculation study.* Water Research 264, 122220.

FAN, Y., CHANG, T., ZHANG, J., XU, H., CUI, J., TIAN, H., YIN, Y., 2023. *Research on influence of CPAM ionic degree on settling characteristics of high muddied coal slime water.* Coal Science and Technology 51(3), 251-260. (In Chinese)

BAO, Y., ZHANG, Y., CHEN, J., WANG, Y., 2021. *Study on entrainment recovery characteristics of gangue minerals in flotation process of fine coal.* Multipurpose utilization of mineral resources (6), 20-25. (In Chinese)

LI, L., ZHENG, Y., MA, Y., SONG, Z., ZHAO, Q., 2016. *Research progress in flocculants for treating coal slurry water.* Modern Chemical Industry 36(10), 42-45. (In Chinese)

BESRA, L., SENGUPTA, D.K., ROY, S.K., AY, P., 2003. *Influence of surfactants on flocculation and dewatering of kaolin suspensions by cationic polyacrylamide (PAM-C) flocculant.* Separation and Purification Technology 30(3), 251-264.

XIA, W., LI, Y., WU, F., NIU, C., 2021. *Enhanced flotation selectivity of fine coal from kaolinite by anionic polyacrylamide pre-conditioning.* Journal of Molecular Liquids 334, 116083.

YIN, X., YAO, J., GONG, X., YU, J., YIN, W., WANG, Y., 2025. *Role of cationic polyacrylamide in the flotation separation of diaspore and kaolinite.* Journal of Molecular Liquids, 2025.127911

YANG, S., WU, Y., CHAI, W., CAO, Y., 2023. *Effect of energy input on surface properties and dispersion of diaspore and kaolinite in flotation process.* Chemical Engineering and Processing-Process Intensification 192, 109518.

XU, L., HU, Y., DONG, F., HAO, J., WU, H., WANG, Z., LIU, R., 2015. *Effects of particle size and chain length on flotation of quaternary ammonium salts onto kaolinite.* Mineralogy and Petrology 109, 309-316.

ROSA, A.F., RUBI, J., 2018. *On the role of nanobubbles in particle–bubble adhesion for the flotation of quartz and apatitic minerals.* Minerals Engineering 127, 178-184.

CHEN, P., SUN, W., YUE, T., 2014. *Dynamics simulation of tributyl tetradecyl phosphonium chloride on kaolinite (001) plane.* Journal of China University of Mining & Technology 43(2), 294-299. (In Chinese)

BALAN, E., CALAS, G., BISH, D.L., 2014. *Kaolin-group minerals: From hydrogen-bonded layers to environmental recorders.* Elements 10(3), 183-188.

CHEN, J., LING, Y., SUN, Y., LIU, L., MIN, F., 2021. *Molecular simulation study of quaternary ammonium salts adsorption on kaolinite surfaces.* Journal of China University of Mining & Technology 50(6), 1204-1211. (In Chinese)

CHEN, J., MIN, F., LIU, L., LIU, C., 2019. *Mechanism research on surface hydration of kaolinite, insights from DFT and MD simulations.* Applied Surface Science 476, 6-15.

GE, W., MAO, H., LING, Y., MIN, F., CHEN, J., LIU, L., ZHANG, Y., SONG, S., 2023. *Insight into the adsorption mechanism between chitosan and kaolinite surface by density functional theory calculation.* Chemical Physics 575, 112069.

HAN, Y., LIU, W., ZHOU, J., CHEN, J., 2016. *Interactions between kaolinite Al-OH surface and sodium hexametaphosphate.* Applied Surface Science 387, 759-765.

WU, Y., YANG, S., CHAI, W., CAO, Y., 2022. *Interaction forces between diaspore and kaolinite in NaOL solution probed by EDLVO theory and AFM analysis.* Minerals 12(9), 1123.

SHANG, H., CHEN, J., MIN, F., CHENG, Y., BAO, L., WU, Z., 2026. *Microscopic interaction mechanism between Fe-doped kaolinite and quartz: DFT calculations and experiments.* Fuel 403, 136074.