Physicochem. Probl. Miner. Process., 60(4), 2024, 191720

http://www.journalssystem.com/ppmp

Physicochemical Problems of Mineral Processing

ISSN 1643-1049

Effect of surfactant and PAM on the settlement of kaolinite particles and its mechanism analysis

Jinxia Zhang [1,3], Mengfei Zhang [1], Fusheng Niu [1,3], Ziye Wang [2], Zehong Cheng [1], Qiuyue Wang [1]

[1] College of Mining Engineering, North China University of Science and Technology, Tangshan 063210, China

[2] GRINM Resources and Environment Tech. Co., Ltd, Beijing 100006, China

[3] Hebei province Key Laboratory of Mining Development and Security Technology, Tangshan 063210, China

Corresponding authors: niufusheng@ncst.edu.cn (Fusheng Niu), wangziye@grinm.com (Ziye Wang)

Abstract: High concentrations of fine-grained clay minerals in tailings water are highly detrimental to environmental protection and water recycling. Using kaolinite as the study subject, this research investigates the effects of various cationic surfactants (DDA, DTAB, TTAB, CTAB) and flocculants (APAM, NPAM, CPAM) on the sedimentation of kaolinite particles. The study explores the impact of single agents, combined agents, and the sequence of their addition on kaolinite particle sedimentation. The results indicate that when using individual agents at low concentrations, CTAB outperforms TTAB, DTAB, and DDA, while APAM is more effective than NPAM and CPAM. The optimal performance is achieved with a CTAB concentration of 2×10^{-4} mol/L and an APAM dosage of 20 mg/L. When combining agents, the best results are observed when CTAB is added before APAM. By fixing the APAM dosage at 20 mg/L and varying the CTAB concentration, the highest sedimentation rate and lowest turbidity are obtained at a CTAB concentration of 1.5×10^{-4} mol/L. Mechanistic insights were obtained through aggregate imaging, area measurement, zeta potential testing, and contact angle testing. Cationic surfactants alter the surface properties of particles, reducing surface electronegativity and increasing hydrophobicity, which diminishes inter-particle repulsion and promotes aggregation, thereby reducing turbidity. Flocculants form larger flocs through adsorption and bridging, accelerating the sedimentation process. When flocculants and cationic surfactants are used together, the resulting flocs are more stable and larger, with an average floc area reaching 5017.6079 μm^2, indicating a significant reduction in fine particles within the solution.

Keywords: clay minerals, kaolinite, cationic surfactants, flocculant, mechanistic insights

1. Introduction

Mineral resources are a crucial foundation for national economic development, impacting various industries such as energy, construction, and manufacturing (Xu, 2024). In recent years, the mechanization of mining and increased extraction efficiency has significantly raised the content of fine clay minerals in tailings water. Proper treatment of tailings water not only enables water recycling but also helps reduce environmental pollution (Li, 2015; Liu et al., 2021). Kaolinite, one of the clay mineral components in tailings water, is characterized by its fine particle size, propensity to form mud, and surfaces that typically carry negative charges and hydrophilic groups. These properties result in electrostatic repulsion and strong hydrophilicity, making particle aggregation and sedimentation difficult (Chen et al., 2016; Kang et al., 2019; Yu et al., 2023). According to Stokes' law, all other conditions are equal, and the sedimentation rate of particles is proportional to their radius. Hence, the sedimentation rate of fine particles is relatively low, leading to a stable dispersed state and slow sedimentation under natural conditions (Wang et al., 2008; Luo, 2021).

Traditional technologies primarily employ coagulation sedimentation (inorganic coagulants combined with polymer flocculants) to treat tailings water and address the poor sedimentation of fine

DOI: 10.37190/ppmp/191720

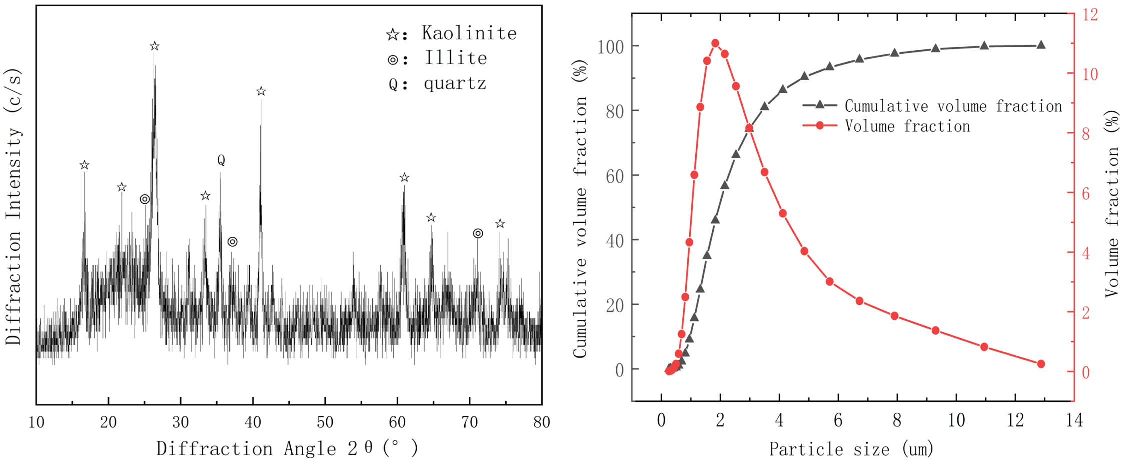
clay minerals. However, these methods often fail to achieve optimal results due to neglecting the surface properties of clay minerals such as kaolinite (Alam et al., 2010; Zhang, 2018). The addition of surfactants to tailings water to render fine mineral particles hydrophobic, thereby promoting their aggregation and sedimentation, holds significant importance. Chen et al. (2017) studied the hydrophobic aggregation and sedimentation of fine coal and kaolinite particles using quaternary ammonium salt agents, demonstrating a significant effect on the hydrophobic sedimentation of highly colloidal coal slime water. Lingyun et al. (2018) investigated the aggregation behavior of kaolinite particles in the presence of different surfactants, finding that cationic surfactants yielded better aggregation results than anionic and nonionic surfactants. Aref (2022) investigated the colloidal behavior of kaolinite particles in water after adding non-anionic polyacrylamide (PAM). It was found that the introduction of PAM led to the formation of bridges between particles, thereby increasing their settling rate to the bottom of the container. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) results revealed that, in the absence of PAM, the floc structure of the sediment was loose and irregularly distributed. In contrast, the presence of PAM significantly compacted the sediment structure. Huang (2023) found that STAC facilitated obtaining a smaller compression layer thickness and lower supernatant turbidity by enhancing the hydrophobicity of kaolinite surfaces, inhibiting hydration, and promoting hydrophobic aggregation of kaolinite particles. Peng et al. (2024) demonstrated that surfactants can assess kaolinite-surfactant slurries' flocculation and settling behavior. These surfactants can accelerate the settling rate within a specific range, which may be attributed to the enhanced interaction between surfactants and kaolinite. However, excessive addition of surfactants can retard the settling rate, potentially due to the colloidal characteristics of the surfactant-water system. Hu et al. (2020) experimentally found that surfactants primarily promote the aggregation of kaolinite particles by adsorbing onto their surfaces and generating hydrophobic forces. Compared to anionic surfactants, cationic surfactants exhibit superior flocculation effects, as they can be used over a broader pH range, and their adsorption reduces the electrostatic repulsion between kaolinite particles. Yang et al. (2022) revealed that dodecylamine (DDA) alone as a flocculant was insufficient for hydrophobic aggregation of fine kaolinite particles to form larger, stronger flocs. However, using octanoic acid (OA) as a co-flocculant enhanced the DDA-induced aggregation of fine kaolinite particles. Yang (2022) found that, compared to single agents, the combination of $CaCl_2$ and PAM was more conducive to montmorillonite sedimentation, while $CaCl_2$ and CTAB were more favorable for montmorillonite filtration and dehydration. The combined use of $CaCl_2$, PAM, and a small amount of CTAB resulted in faster sedimentation and filtration rates. Zhang et al. (2008) investigated the hydrophobic aggregation of ultrafine kaolinite in cationic surfactant suspensions through sedimentation tests, zeta potential measurements, and SEM observations. The results indicated that the zeta potential of kaolinite increased with the concentration of cationic surfactants. At low concentrations, the aggregation was small and loose, while at high concentrations, it was large and compact. At pH 7, the alkyl quaternary ammonium salt CTAB exhibited the best hydrophobic aggregation among the three cationic surfactants tested (i.e., dodecyl ammonium acetate, alkyl quaternary ammonium salt 1227, and CTAB).

Therefore, selecting appropriate surfactants for treating kaolinite suspensions is crucial for the sedimentation of tailings water. This study focuses on kaolinite, using DDA, DTAB, TTAB, and CTAB as cationic surfactants and PAM as a flocculant. The effects of single agents, combination agents, and their sequential additions on sedimentation were investigated through sedimentation experiments. The mechanisms were analyzed using cluster imaging, area measurement, zeta-potential testing, and contact angle testing.

2. Experimental materials and methods

2.1. Experimental materials

The kaolinite used in the experiment was sourced from Shanghai Macklin Biochemical Co., Ltd. Fig. 1(a) shows the kaolinite sample's X-ray diffraction (XRD) analysis. Table 1. presents the results of the X-ray fluorescence (XRF) analysis, indicating that the sample contains 46.58% SiO_2 and 39.25% Al_2O_3, with the remaining components including Fe_2O_3, K_2O, P_2O_5, etc. The main mineral component of the sample is kaolinite, and its theoretical purity meets the requirements for the sedimentation test. Fig. 1(b) shows the particle size distribution of the kaolinite sample used in the experiment. The particle size ranges from 0.26 to 12.88 μm, with 99.36% of the particles being smaller than 10 μm. The average particle size is 1.94 μm, classifying the sample as fine particles.



(a) (b)

Fig. 1. XRD of Kaolinite Sample (a), Particle Size Distribution of Kaolinite Sample (b)

Table 1. Major Chemical Components of Pure Kaolinite (%)

Al_2O_3	CaO	Fe_2O_3	K_2O	MgO	P_2O_5	SiO_2	SO_3	TiO_2	LOI
39.25	0.22	0.71	0.35	0.18	0.43	46.58	0.17	0.22	11.89

2.2. Experimental reagents and equipment

The reagents used in the experiment are as follows: cationic surfactants include dodecylamine (DDA), dodecyltrimethylammonium bromide (DTAB), tetradecyltrimethylammonium bromide (TTAB), and hexadecyltrimethylammonium bromide (CTAB), all of which are of analytical grade and sourced from Shanghai Macklin Biochemical Co., Ltd. The flocculants used are cationic polyacrylamide (CPAM), nonionic polyacrylamide (NPAM), and anionic polyacrylamide (APAM), all of which are of 12 million molecular weight analytical grade and sourced from Tianjin Zhiyuan Chemical Reagent Co., Ltd. Deionized water was used throughout the experiments.

The instruments used in the experiments are as follows: a dual digital display thermostatic magnetic stirrer (HJ-6B) from Jintan Jingda Instrument Manufacturing Co., Ltd.; a laser particle size analyzer (Mastersizer 2000) from Malvern Instruments Ltd., UK; an X-ray diffractometer (D/MAX2500PC) from Rigaku Corporation; a precision electronic balance (CP214) from Sartorius Instrument Systems Co., Ltd., Beijing; a Zeta potential analyzer (Zetasizer Nano ZS90) from Malvern Instruments Ltd., UK; a tablet press (FW-4 type) from Tianjin Tianguang Optical Instrument Co., Ltd.; a contact angle meter (CA100D) from Shanghai Yinuo Precision Instruments Co., Ltd.; a turbidity meter (SGZ-400A) from Shanghai Yuefeng Instrument and Meter Co., Ltd.; and a 300x industrial CCD camera microscope (HY-300X) from Shenzhen Guardian Technology Co., Ltd.

2.3. Experimental methods

2.3.1. Sedimentation experiment

Solutions of varying concentrations of polyacrylamide, DDA, DTAB, TTAB, and CTAB were prepared using deionized water. For each experiment, 3.00 g of kaolinite sample was weighed and placed in a graduated cylinder containing a specified amount of deionized water to prepare a slurry with a concentration of 30 g/L. Sedimentation experiments were conducted in 100 cm^3 graduated cylinders under neutral pH conditions. A vertical stirrer was used to disperse the slurry at 400 r/min for 10 minutes. Subsequently, different amounts of the agents were added, and the graduated cylinder was inverted ten times at a controlled speed to prevent foaming of the cationic surfactant solution. The suspension was then quickly transferred to a settling column, and the descent of the straightforward interface was recorded at different settling times to calculate the sedimentation rate.

2.3.2. Main sedimentation indexes

The sedimentation performance was evaluated based on the sedimentation rate (cm/min), supernatant turbidity (NTU), and the thickness of the compressive layer (cm). For cationic surfactants, the sedimentation rate was assessed after 3 minutes, while for polyacrylamide (PAM) and their combinations, the sedimentation rate was measured after 10 seconds. The height of the sedimentation liquid surface represented the thickness of the compressive layer, and the sedimentation rate was calculated using Equation (1). After 10 minutes of sedimentation, 20 cm^3 of supernatant was collected at the 80 cm^3 mark and measured for turbidity using a turbidity meter (Model: SGZ-400A). Each test was conducted in triplicate, and the average value was used as the final data. A comprehensive evaluation index was established based on the average values (Bian, 2017), as shown in Equation (2), to facilitate the comparison of overall sedimentation performance. Faster sedimentation rates, excellent compression ratios, and lower turbidity indicate better sedimentation performance.

$$\mathrm{V} = \frac{\mathrm{S}}{\mathrm{T}} \tag{1}$$

V is the sedimentation rate, cm/min; S is the height of the clarification layer, cm; and T is the sedimentation time, min.

$$\mathrm{C} = \frac{\mathrm{V}\times(1\text{-}\mathrm{H}/\mathrm{H_0})\times 100\%)}{\mathrm{N}} \times 100\% \tag{2}$$

In the formula, C is the comprehensive indicator; N is supernatant turbidity, NTU; V is sedimentation rate, cm/min; H is the compressed layer thickness; H_0 is the initial height.

2.3.3. Floc image analysis and area measurement

Using an industrial CCD camera microscope at 300x magnification (model: HY-300X), we assessed the aggregation of particles before and after treatment with additives. High-purity kaolinite particles were carefully extracted from the solution and uniformly placed onto glass slides. The camera lens was adjusted to an appropriate position for capturing images, which were subsequently analyzed using Image-Pro Plus 6.0 software for area measurements. Initial spatial calibration of the images was performed, followed by automated counting and measurement of the aggregates. The data were then exported for further analysis.

2.3.4. Zeta potential analysis

The Zeta potential of kaolinite particles under various conditions was determined using a Zetasizer Mano zs90 instrument. Three grams of kaolinite samples were uniformly dispersed in deionized water, followed by adding different cationic surfactants. After sufficient reaction time, 1 cm^3 of the suspension was used for measurements, with three consecutive readings taken to obtain an average value.

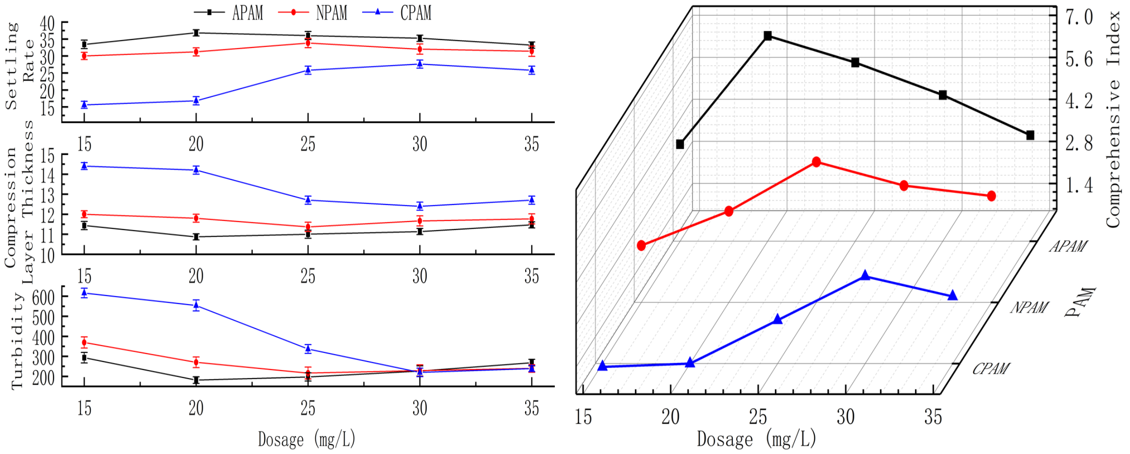
2.3.5. Contact angle measurement

The contact angle measurement of kaolinite samples before and after reagent treatment was conducted using a contact angle goniometer (model: CA100D). Initially, 0.5g of the sample was ground into a fine powder to ensure uniform particle size. The powder was then compressed into an approximately 2mm thick thin sheet using a tablet press (model: FW-4A). The prepared sheet was gently placed on the sample stage and adjusted to a horizontal position for measurement. The contact angle was measured three times consecutively, and the average value was recorded.

3. Results and analysis

3.1. Effects of flocculants on the settling of kaolinite particles

Different flocculants exhibit varying settling effects on kaolin under different dosages, as shown in Fig. 2(a), with comprehensive evaluation indicators depicted in Fig. 2(b). From Fig. 2(a), it is evident that as the dosage of flocculant increases, the settling rate initially increases and then decreases, while the compression layer's thickness and the supernatant's turbidity first decrease and then increase. The effectiveness of APAM is superior to that of NAPM and CPAM, achieving lower supernatant turbidity, compression layer thickness, and a faster settling rate even at lower dosages. According to Fig. 2(b), the optimal comprehensive indicators are observed at APAM dosages of 20 mg/L, NPAM dosages of 25 mg/L, and CPAM dosages of 30 mg/L. When used alone, flocculants result in higher turbidity but faster-settling rates. PAM primarily enhances kaolin settling by bridging and adsorbing kaolin particles, forming flocs that facilitate larger particle sizes that are conducive to settling. Based on experimental results, APAM at a dosage of 20 mg/L exhibits the highest settling rate of 36.7 cm/min and the lowest supernatant turbidity of 181.1 NTU; thus, this concentration was chosen for subsequent experiments.



(a) (b)

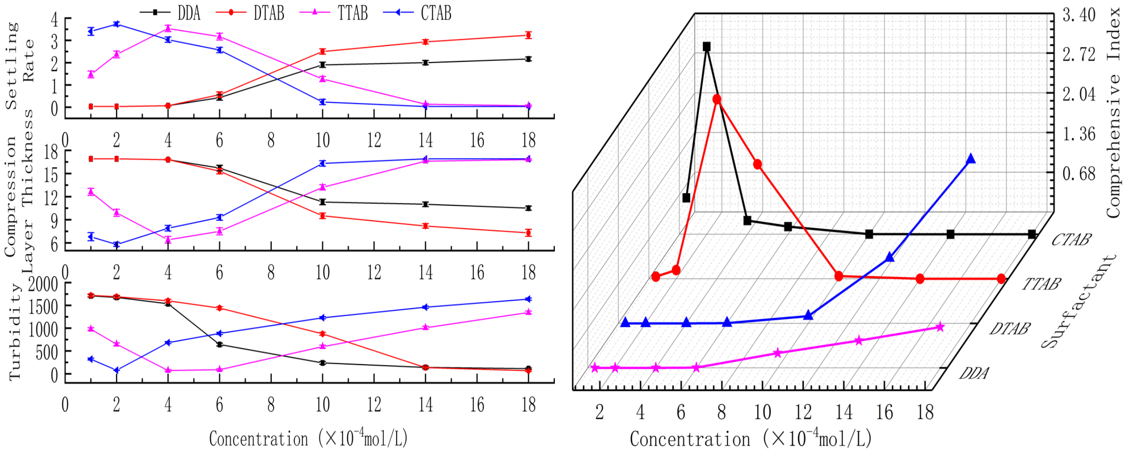
Fig. 2. Settling performance of kaolinite with different PAMs (a), Comprehensive evaluation index for kaolinite settling with different PAMs (b)

3.2. Effects of cationic surfactants on the sedimentation of kaolinite particles

Investigating the impact of different cationic surfactants on kaolin settling, given the typically hydrophilic and negatively charged surface groups on kaolin particles, cationic surfactants can alter the mineral surface charge and hydrophobicity (Min et al., 2020). The experiment selected the cationic surfactants DDA, DTAB, TTAB, and CTAB. The settling effects under different cationic surfactant types and concentrations are shown in Fig. 3(a), with comprehensive evaluation indicators in Fig. 3(b). From Fig. 3(a), it is observed that within the range of cationic surfactant concentrations tested, TTAB and CTAB exhibit initially enhanced settling effects, followed by a decline as concentration increases. DDA and DTAB show initial enhancement followed by stabilization with increasing concentration. Under identical conditions, DTAB demonstrates superior settling rates compared to DDA, whereas DDA shows lower supernatant turbidity than DTAB. Fig. 3(b) indicates that CTAB performs optimally at lower concentrations compared to TTAB, DTAB, and DDA, achieving the best comprehensive indicators at a solution concentration of 2×10^{-4} mol/L with a settling rate of 3.7 cm/min and turbidity of 76.5 NTU. Cationic surfactants generally result in lower turbidity but slower settling rates when used alone.

3.3. Effects of flocculant and surfactant addition sequence on the settling of kaolinite particles

Based on the settling effects of different flocculants and cationic surfactants on kaolin, experiments selected the combination of APAM and CTAB to investigate the influence of dosing sequence on settling. APAM was used at a dosage of 20 mg/L and CTAB solution at a concentration of 2×10^{-4} mol/L. Results are shown in Fig. 4. From Fig. 4, it is observed that adding CTAB first, followed by APAM, achieves a faster settling rate (43.22 cm/min), lower compression layer thickness (9.8 cm), and lower supernatant turbidity (63.6 NTU) compared to simultaneous addition and APAM-first addition. This may be attributed to the cationic surfactant initially altering particle surface properties, reducing hydrophilicity and surface charge, thereby initiating aggregation into smaller flocs that are more easily bridged and adsorbed by high-molecular-weight flocculants, resulting in larger and more stable flocs and superior settling effects. Therefore, subsequent experiments selected the dosing sequence of adding CTAB first, followed by APAM, for further investigation.



(a) (b)

Fig. 3. Settling performance of kaolinite with different cationic surfactants (a), Comprehensive evaluation index for kaolinite settling with different cationic surfactants (b)

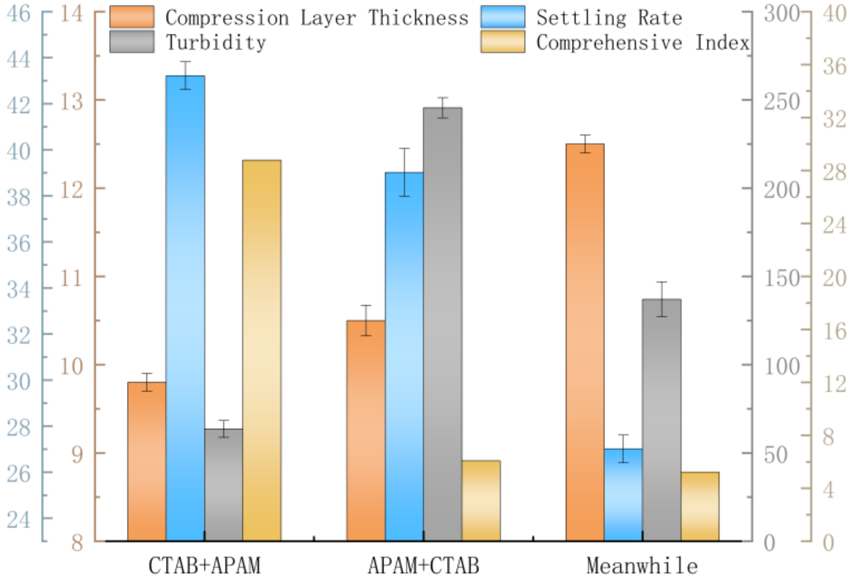


Fig. 4. Impact of addition sequence on kaolinite settling

3.4. Effects of flocculant and surfactant combination on the settling of kaolinite particles

Based on the effects of single-agent and combined-agent dosing sequences on kaolin settling, APAM was selected as the flocculant and CTAB as the cationic surfactant, with the dosing sequence of CTAB followed by APAM. Under an APAM dosage of 20 mg/L, the influence of different CTAB concentrations in solution on kaolin settling effects was investigated, as shown in Fig. 5. From Fig. 5. it is observed that with a constant APAM dosage, increasing CTAB concentration initially enhances settling effects before declining. At a concentration of 1.5×10^{-4} mol/L, the settling rate is 45.02 cm/min, the supernatant turbidity is 52.3 NTU, and the compression layer thickness is 9.5 cm, achieving the highest comprehensive evaluation indicators and optimal settling effects. Compared to CTAB or APAM alone, their combined use may leverage electrostatic neutralization and adsorption bridging effects, reducing particle surface charge and hydrophilicity and increasing floc size, resulting in lower turbidity and faster settling rates.

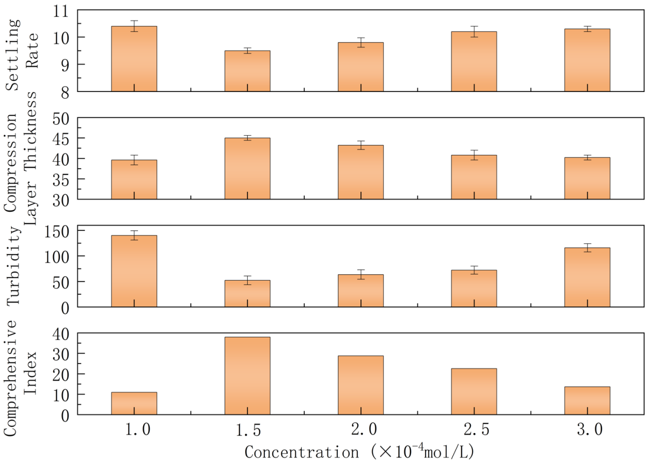
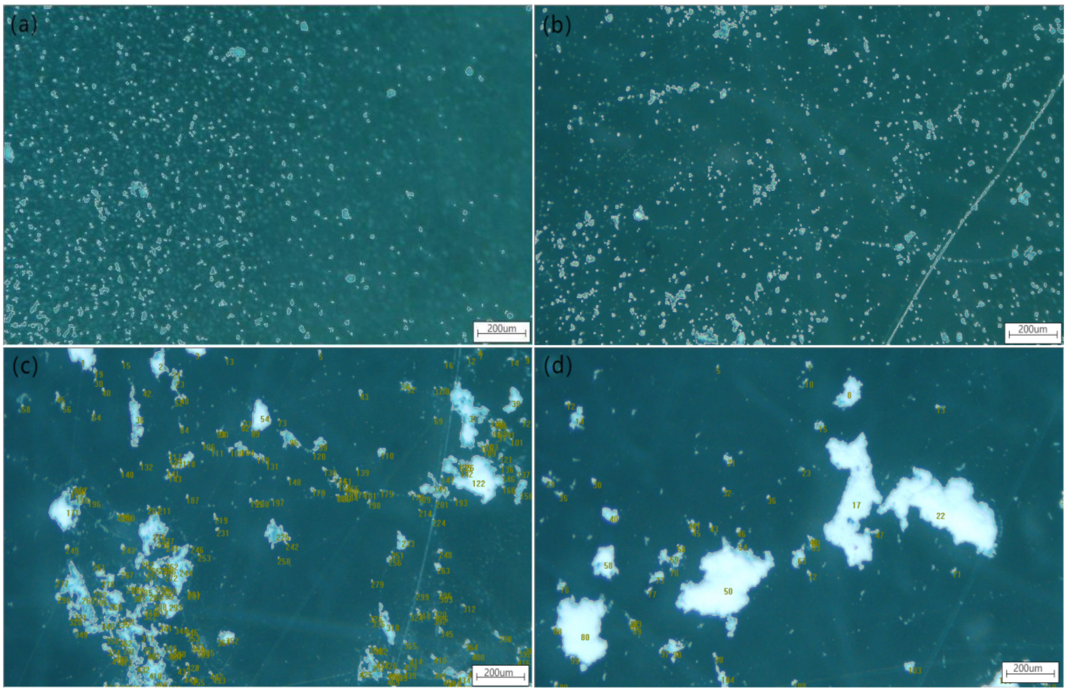


Fig. 5. Settling performance of kaolinite with different flocculant-cationic surfactant combinations

4. Mechanism analysis

4.1. Floc image analysis and area measurement

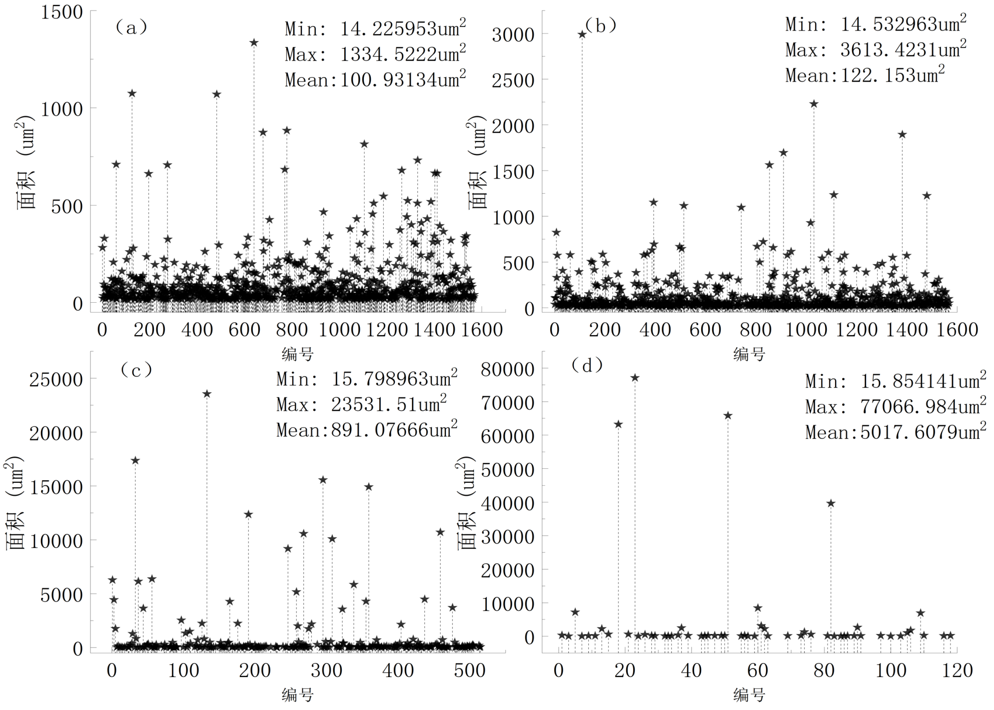
Using a high-resolution CCD camera lens, the morphologies of particle aggregates before and after treatment with additives were observed, with results shown in Fig. 6. Panel (a) depicts the original mineral image; (b) shows aggregates after CTAB addition; (c) after APAM addition; and (d) after CTAB+APAM addition. Fig. 6(a) shows that before adding additives, kaolin particles are small and evenly distributed in the solution, making them difficult to aggregate and settle due to gravity. Fig. 6(b) shows that after CTAB addition, reduced interparticle repulsion leads to the formation of small particle flocs, resulting in slower settling. Fig. 6(c) indicates that after APAM addition, kaolin particle flocs enlarge, but many small particles remain suspended in the solution, leading to higher supernatant turbidity. Fig. 6(d) shows that after CTAB followed by APAM addition, larger and more stable flocs are formed, with fewer dispersed particles in the solution. Image analysis reveals that the combined use of cationic surfactant and flocculant accelerates settling rates and reduces supernatant turbidity.



a: Raw mineral b: CTAB c: APAM d: CTAB+APAM

Fig. 6. Floc images before and after reagent addition

The area of kaolinite particle aggregates under a CCD camera was calculated using Image-Pro Plus 6.0 software. Each number represents a specific floc, with the area of each numbered floc detailed in Fig 7. Figs 7(a), (b), (c), and (d) correspond to the labels in Figs 6(a), (b), (c), and (d), respectively. Due to the high number of small particles in Figs 6(a) and (b), which complicates the observation, no numbering was applied to the flocs in those figs. As shown in Fig 7(a), kaolinite particles in the solution are relatively dispersed, with small areas and an average area of 100.93134 μm². Fig 7(b) demonstrates that kaolinite particles begin to aggregate after adding cationic surfactants, with the maximum floc size reaching 3613.4231 μm² and an average area of 122.153 μm². The overall size is relatively small, and the settling rate is slower. The effect of APAM is shown in Fig 7(c), where the number of flocs significantly decreases, and the flocs formed are larger, with a maximum area of 23531.51 μm². However, the flocs are unstable and prone to dispersion, resulting in smaller particles and higher supernatant turbidity. Under the combined effect of CTAB and APAM, as shown in Fig 7(d), the formed flocs are larger, with maximum areas of 77066.984 μm² and 65811.859 μm², respectively, and an average area of 5017.6079 μm². The settling rate, which is proportional to the radius of the particles, is faster, and the number of fine particles is significantly reduced compared to Figs 7(b) and (c). The amount of suspended particles in the supernatant, which determines the turbidity, is relatively lower.



a: Raw mineral b: CTAB c: APAM d: CTAB+APAM

Fig. 7. Floc areas before and after reagent addition

4.2. Zeta potential analysis

Zeta potential is a critical indicator for evaluating particle surface charge properties, directly affecting particle stability in suspension. A smaller absolute Zeta potential indicates weaker repulsive forces between particles, facilitating particle aggregation and settling. Cationic surfactants, composed of hydrophilic and hydrophobic groups, interact with mineral surfaces, with positively charged hydrophilic groups tending to adsorb negatively charged mineral particles, reducing their surface negative potential through electrostatic adsorption (Guo, 2022). Different cationic surfactant effects on mineral Zeta potential are shown in Fig. 8. Increasing cationic surfactant concentration gradually shifts Zeta potential from negative to positive values, with further increases indicating improved settling effects initially followed by a decline, consistent with experimental results. Without additives, kaolin Zeta potential is -39.8 mV, indicating strong repulsive forces and poor aggregation and settling. When different cationic surfactants are added, Zeta potential generally increases, with CTAB showing the most significant increase. At a concentration of 2×10^{-4} mol/L, CTAB achieves the best performance with an absolute Zeta potential of 3.83 mV, followed by TTAB, DDA, and DTAB with Zeta potential values of 10.8 mV, 30.5 mV, and 28.1 mV, respectively. Notably, TTAB at a concentration of 4×10^{-4} mol/L and DDA and DTAB at 14×10^{-4} mol/L demonstrate optimal performance.

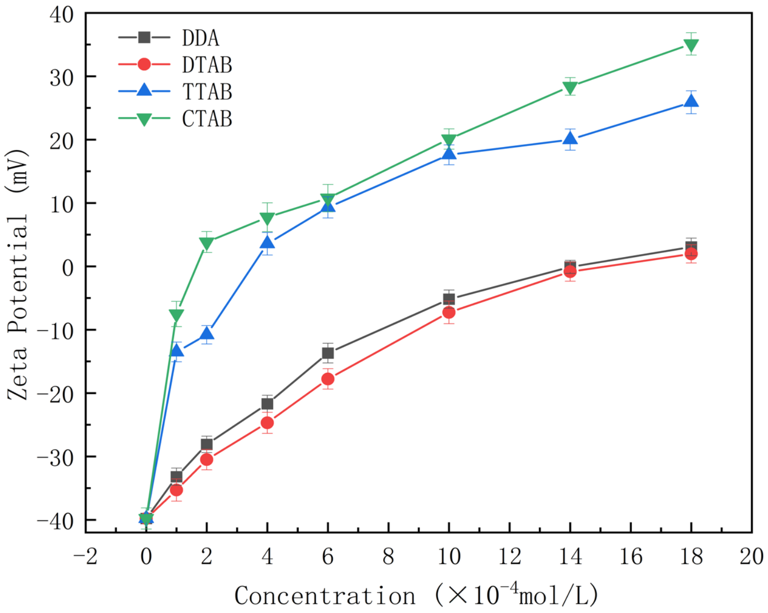


Fig. 8. Zeta potential of minerals before and after cationic surfactant addition

Cationic surfactants can reduce the negative charge of mineral surfaces through electrostatic adsorption. According to the DLVO theory, this leads to the electric double layer (EDL) compression. The thickness of the EDL is influenced by various factors, as described by equation (3) (Sridharan et al., 1982; Liu et al., 2021). From equation (3), it can be seen that as the concentration of electrolytes in water increases, the ionic charge increases, and the dielectric constant decreases, resulting in a smaller EDL thickness. This reduction in EDL thickness facilitates colloid coagulation. Therefore, adding cationic surfactants can neutralize the negative charge on particle surfaces. This leads to EDL compression and particle coagulation, a mechanism known as charge neutralization, a type of EDL compression mechanism.

The EDL structure of kaolinite particles is illustrated in Fig. 9. As shown in Fig. 9, the EDL structure on particle surfaces comprises an adsorption layer and a diffusion layer. When kaolinite particles form a colloidal dispersion system with the solute, the particle surfaces carry a negative charge. The adsorption of counterions on the particle surfaces results in a closely packed layer near the solid particle surface, forming an adsorption layer with a thickness of one or two ionic diameters. Some counterions diffuse into the solution at a certain concentration, forming a diffusion layer. The interface between the adsorption layer and the diffusion layer is called the slipping plane, and the potential difference between the slipping plane and the solution interior is known as the zeta potential (ζ potential). The ζ potential reflects the charged nature of the adsorption layer, with its magnitude indicating the thickness of the diffusion layer. The greater the absolute value of the ζ potential, the more stable the colloidal particles are (Yan, 2023). The results indicate that the presence of cationic surfactants can influence the colloidal stability of kaolinite suspensions and the interactions between particles by altering the surface charge properties, effectively reducing the ζ potential of kaolinite particles.

$$H^{-1} = \sqrt{\frac{\varepsilon KT}{2n_0 z^2 e^2}} \tag{3}$$

In the equation, H^{-1} represents the thickness of the electric double layer (EDL), n_0 denotes the number of electrolyte particles per unit volume, z^2 is the ionic valence, e^2 stands for the elementary charge, ε represents the dielectric constant of water, K is the Boltzmann constant, T is the absolute temperature.

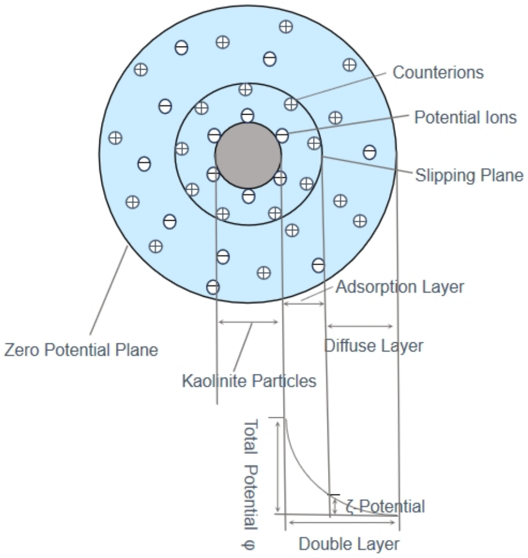


Fig. 9. Double Layer Structure of kaolinite particles

4.3. Wettability analysis

The wettability of particle surfaces can be characterized by contact angle measurements, where a larger contact angle indicates a stronger hydrophobicity of the particle surface. The effects of different cationic surfactants on the contact angles of kaolin particles are illustrated in Fig. 10. From Fig. 10; it is observed that the contact angle of the original mineral is 8.6°, indicating that kaolin exhibits strong hydrophilicity and has difficulty settling in contact with water. All contact angles show an increasing trend upon adding different cationic surfactants, suggesting that the particle surfaces become less prone to contact with water molecules, thereby increasing their hydrophobicity. Other cationic surfactants have varying impacts on the hydrophobicity of kaolin particles, with CTAB showing the most significant effect at the same concentration, followed by TTAB, DDA, and DTAB. At a concentration of 2×10^{-4} mol/L, CTAB achieves a contact angle of 23.5°, which is optimal compared to TTAB, DTAB, and DDA. The measurement of contact angles indicates that CTAB has the greatest impact on the hydrophobicity of kaolin at the same concentration, consistent with the results of settling experiments, where even at lower concentrations, CTAB achieves optimal effects.

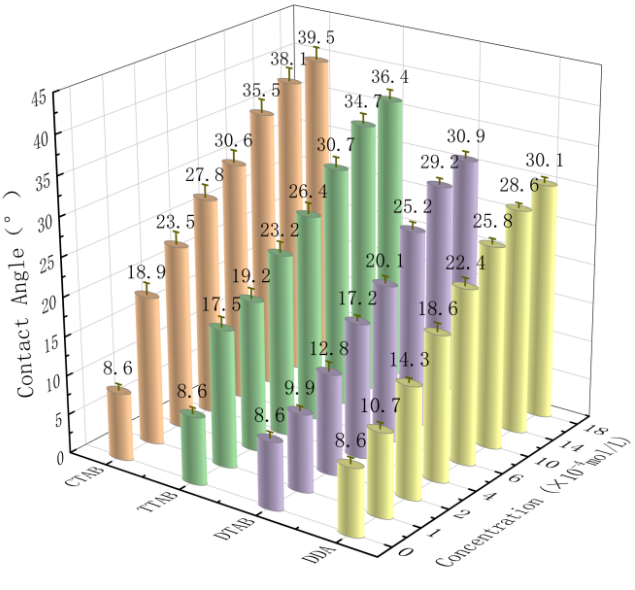


Fig. 10. Contact angles of minerals before and after cationic surfactant addition

4.4. Mechanism of action

Based on the analysis of flocculation images, flocculation area measurements, Zeta potential analysis, and wettability analysis, the mechanism by which the agent induces kaolinite particle sedimentation is illustrated in Fig. 11. As shown in Fig 11, kaolinite particles, due to their strong hydrophilicity, are uniformly distributed in the solution, maintaining colloidal stability under natural conditions. Upon the addition of cationic surfactants, according to the DLVO theory, part of the cationic surfactant neutralizes the surface charge of the particles, reducing the electrostatic repulsion between them. Additionally, it may react with the oxygen-containing functional groups on the kaolinite surface, thereby decreasing hydrophilicity and thinning the hydration film on the particle surface. This leads to hydrophobic flocculation and coagulation sedimentation, though the formed flocs are relatively small (Huang and Cheng, 2023). Therefore, the polymer adsorbs onto the particles when a cationic surfactant is used with a polymer flocculant. The adsorbed polymers then form bridges between each other, creating larger flocs through this bridging action, thereby achieving rapid sedimentation. According to Stokes' law, the sedimentation velocity of colloidal particles in a liquid is related to its influencing factors, as described by equation (4) (Li et al., 2005; Liu et al., 2021). From equation (4), it is evident that, under otherwise identical conditions, the larger the particle size, the faster the sedimentation velocity, making it easier to achieve dewatering and separation. Thus, the primary purpose of using cationic surfactants is to reduce the electrostatic repulsion between particles. At the same time, the addition of polymer flocculants promotes the formation of larger flocs, thereby reducing turbidity and accelerating the sedimentation rate.

$$V_g = \frac{1}{18}\frac{(\rho_1\text{-}\rho_2)g}{\eta}R^2 \tag{4}$$

In the equation, V_g represents the sedimentation velocity, ρ_1 is the density of the solid particles, ρ_2 is the density of the liquid, R denotes the particle radius, g stands for the gravitational acceleration, and η is the dynamic viscosity of the liquid.

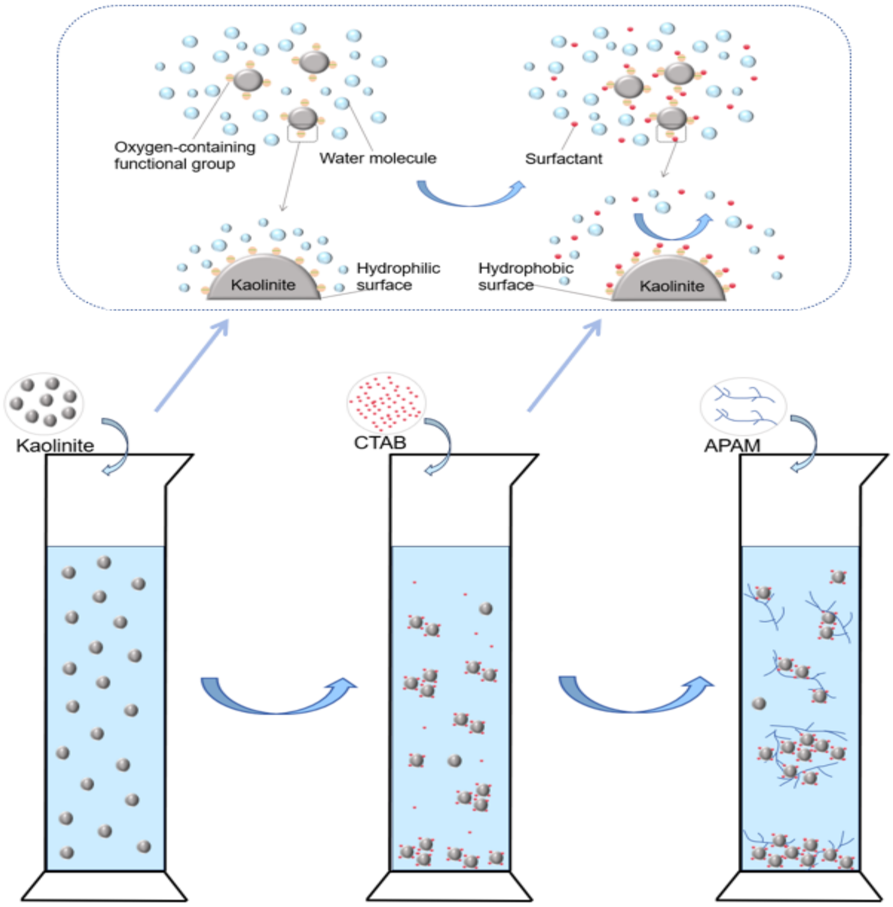


Fig. 11. Sedimentation mechanism

5. Conclusions

Different types of cationic surfactants and flocculants have varied effects on settling kaolin particles. Under single-agent conditions, APAM performs better than NPAM and CPAM, and CTAB outperforms TTAB, DDA, and DTAB. Specifically, APAM exhibits optimal settling performance at a dosage of 20 mg/L, while CTAB achieves the best performance at a concentration of 2×10^{-4} mol/L. When used alone, APAM results in higher turbidity, which CTAB significantly reduces; however, the settling rate is slower. In combination, the order of additive addition significantly affects settling performance, with better results observed when CTAB is added first, followed by APAM. Combined experiments achieve optimal settling performance with APAM at 20 mg/L and CTAB at a concentration of 1.5×10^{-4} mol/L, accelerating settling rates and reducing supernatant turbidity. Analysis combining aggregate imaging, contact angle testing, and Zeta potential testing reveals that cationic surfactants alter particle surface properties by reducing surface electronegativity and increasing hydrophobicity, thereby reducing interparticle repulsion, promoting aggregation, and lowering turbidity. At a CTAB concentration of 2×10^{-4} mol/L, the absolute Zeta potential of particles is 3.83 mV, and the contact angle is 23.5°. Flocculants act through adsorption bridging to increase aggregate particle size, enhancing settling rates. For APAM at a dosage of 20 mg/L, the average aggregate area is 891.07666 μm^2. When CTAB and APAM are combined, the maximum aggregate area can reach 77066.984 μm^2, with the average aggregate area increasing to 5017.6079 μm^2.

Acknowledgments

This research has been supported by the National Natural Science Foundation of China (Grant No. 52374265), Hebei Provincial Science and Technology Department (Grant No. 236Z4106G), Hebei Provincial Natural Science Foundation of China (Grant No. E2022209108), and Hebei Provincial Department of Education Key Project (Grant No. ZD2022059).

References

XU, Y., 2024. *The Growing Demand for Mineral Resources in China.* China Gold News, 2024-05-24 (002).

LI, H. M., 2015. *Mineral Processing Wastewater Treatment Methods and Application.* Hydrometallurgy, 34 (06): 439-443.

LIU, W. L., ZOU, D. X., ZHANG, R., MA, Z.H., 2021. *Application of Flocculant in Reducing Suspended Matter Content in Tailings Recycling Water of Beneficiation.* Baogang Technology, 47 (04): 13-16.

CHEN, J., MIN, F. F., LIU, L. Y., PENG, C. L., LU, F. Q., 2016. *Hydrophobic Aggregation of Fine Particles in High Muddied Coal Slurry Water.* Water Science and Technology, 73 (3): 501-510.

KANG, X., XIA, Z., CHEN, R., SUN, H., YAMG, W., 2019. *Effects of Inorganic Ions, Organic Polymers, and Fly Ashes on the Sedimentation Characteristics of Kaolinite Suspensions.* Applied Clay Science, 181: 105220-105220.

YU, F., LIU, C. J., ZHANG, L. F., WU, G. Y., MA, Y. H., LU, T., LIU, H. N., WANG, T., 2023. *Study on Improvement of Surface Flocculation Process of Kaolinite by Cationie Surfactant.* Nonferrous Metals Engineering, 13 (04): 88-92.

WANG, X., QU, Y., HU, W., CHEN, J., ZHAO, X., WU, M., 2008. *Particle Characteristics and Rheological Constitutive Relations of High Concentration Red Mud.* Journal of China University of Mining & Technology, 18 (2): 266-270.

LUO, J. Q., 2021. *Influence mechanism of inorganic salts on settling behavior of fine clay and regulation of interfacial hydrophobicity.* China University of Mining and Technology.

ALAM, N., OZDEMIR, O., HAMPTON, A. M., NGUYEN, V. A., 2010. *Dewatering of Coal Plant Tailings: Flocculation Followed by Filtration.* Fuel, 90 (1): 26-35.

ZHANG, J. R., 2018. *Application of coagulant and flocculant in coal slurry treatment in coal preparation plant.* Shanxi Chemical Industry, 38 (05): 217-218+224.

CHEN, J., 2017. *Characteristics and mechanism research on hydrophobic aggregation of fine particles in high muddied coal slurry water.* Anhui University of Science and Technology.

LINGYUN, L., LIANG, S., WEIRONG, L., FANFEI, F., FANGQIN, L., 2018. *Study on the Aggregation Behavior of Kaolinite Particles in the Presence of Cationic, Anionic and Non-Ionic Surfactants.* PloS One, 13 (9): e0204037.

AREF, M. A., 2022. *Colloidal and Sedimentation Behavior of Kaolinite Suspension in Presence of Non-Ionic Polyacrylamide (PAM).* Gels, 8(12): 807-807.

HUANG, W. H., 2023. *Study on Enhancing the Sedimentation of Coal Slurry Water by Regulating the Hydrophobicity of Kaolinite Surface.* Guizhou University.

PENG, K., HUANG, Z., ZHANG, Y., 2024. *Contrasting Aqueous Dispersion State of Kaolinite with Different Organic Modification Surfactants*. JOM.

HU, Y., YANG, Q., KOU, J., SUN, C., LI, H., 2020. *Aggregation Mechanism of Colloidal Kaolinite in Aqueous Solutions with Electrolyte and Surfactants*. PLoS One, 15(9).

PENG, Y., XIANZHI, H., FUTING, Z., YANG, B., WANG, Q., CHEN, Y., CHEN, S., 2020. *Synergistic Enhancement of Fine-Kaolinite-Particle Hydrophobic Agglomeration by Combining Dodecylamine with Octanoic Acid.* Minerals Engineering, 155(7): 106444.

YANG, Y. L., 2022. *Study on the Effect of Compound Reagents on the Settling and Dewatering Characteristics of Montmorillonite.* Guizhou University.

ZHANG, X., HU, Y., LIU, R., 2008. *Hydrophobic Aggregation of Ultrafine Kaolinite*. Journal of Central South University of Technology, 15(3): 368-372.

BIAN, C. S., 2017. *Study on the Settlement Characteristics and Model of Coal Slurry Containing Kaolinite.* China University of Mining and Technology.

MIN, F. F., REN, B., CHEN, J., LIU, C. F., PENG, C. L., 2020. *Mechanism and experimental study on promoting coal slime dewatering based on weakening of hydration layer.* Journal of China Coal Society, 45 (01): 368-376.

GUO, Y. T., 2022. *Effect of Surface Hydrophobic Modification on Sedimentation and Filtration of Highly Slimed Coal Slurry.* Taiyuan University of Technology.

LIU, Z. S., HE, J., NIE, Q., CUI, J. X., XIAO, Y., ZHAO, L. Z., XU, W. W., 2015. *Studies of coagulation mechanism for sludge and sludge water*. China Building Materials Science & Technology, 24 (06): 23-24.

SRIDHARAN, A., JAYADEVA, M. S., 1982. *Double Layer Theory and Compressibility of Clays*. Géotechnique, 32(2): 133-144.

YAN, Y. Z., 2023. *Micro-mechanism analysis of hydration and expansion of expansive soil based on Diffuse double-layer theory and Soil Sorptive Potential theory*. Xinyang Normal University.

HUANG, W., CHENG, W., 2023. *Study on the Mechanism of Metal Cations Affecting the Settling of Kaolinite Particles*. Mining Research and Development, 43 (10): 209-216.

LI, F., ZHANG, S., ZHAO, Y., 2005. *Coagulants and Flocculants*. Beijing: Chemical Industry Press, pp. 3-6.