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The present situation and trend prospect of collector in the experimental study of flotation barite ore

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Abstract: Barite is a primary source of barium, which is usually recovered by flotation. However, barite and fluorite, calcite and other embedded particle size is dense, often in the form of symbiosis, it is difficult to get efficient recovery from such mixed ore; and with the increase of mineral demand, efficient flotation separation is facing great challenges; Therefore, how to effectively improve the utilization value of barite has become the focus. Flotation reagent is the main research direction of barite flotation. Therefore, This study concentration on elucidation the adsorption mechanism and its influencing factors between collectors, collectors and minerals. It is pointed out that the essence of collector adsorption is the cationic action of the hydrophilic group and the mineral surface, which offsets a part of the residual bond force and weakens the alkylation of the mineral surface, thereby reducing the hydrophilicity of the mineral surface and improving the flotation effect. Secondly, the currently known inhibitors are briefly described. Subsequently, the properties of the collector were preliminarily characterized by calculation and analysis methods, and the theory was popularized to enhanced guidance the production.

Keywords: barite, fluorite, collector, DFT

1. Introduction

Barite is a non-metallic mineral with barium sulfate as the main component (Li et al., 2024; Yan et al., 2023, Gurpinar et al., 2024). It is widely used in oil and gas drilling mud weighting agents, preparation of barium-containing chemical products and barium alloys due to its excellent properties such as insoluble in water, acid, non-toxicity, absorption of X-rays and Y-rays, and stable properties (Staszczuk and Bilinski, 2005; Demeekul et al., 2016) (see Table 1 for other fields).

Among them, 80% of barite is used as weighting agent in natural gas and petroleum drilling fluid, and the remaining barite is used to produce electronic components, glass, polymer materials, wear-resistant materials and barium compounds.

Table 1. Application of barite in various fields

Field	Usage
Silver white pigment	Raw materials for paints and paints
Mortar and concrete	It is used to replace metal lead plate shielding nuclear reactor and so on.
Filler industry	Barite powder filler can increase the thickness, strength and durability of the paint film.
Cement industry	Mineralizer

Barite is the dominant mineral in China, which has the characteristics of rich resources, concentrated distribution and high grade. In nature, the genetic types of barite deposits are mainly sedimentary type (including volcanic sedimentary type), hydrothermal type and residual type (Martins et al., 2011). Table

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2 is the characteristics and distribution characteristics of barite ore types. The main large and super large deposits in China are usually single barite deposits, which belong to layered barite deposits.

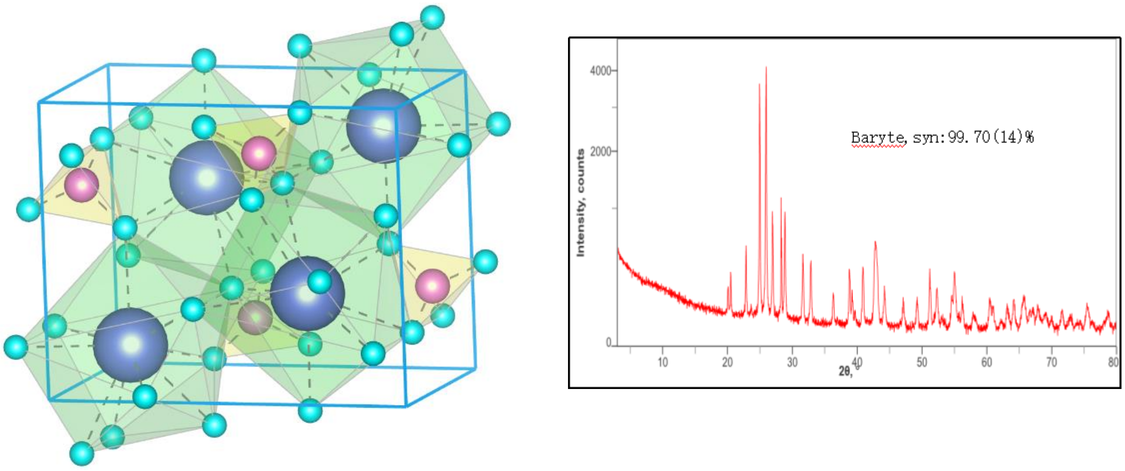


Fig. 1. Barite cell

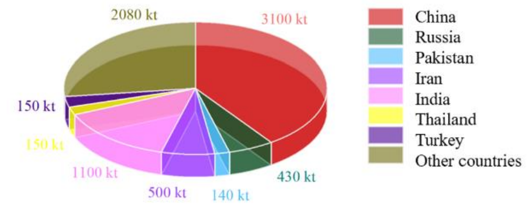
Table 2. Characteristics of main ore types of barite

Types of ores	Ore characteristics	Main minerals and associated minerals	Distribution spot
Sedimentary type	Stable layer	Siliceous, carbonate	Qinling,Shaanxi, Guizhou
Hydrothermal type	Densification	Barite, siderite, hematite	Hunan,Guizhou, Guangxi
Weathered residual type	The primary barite is weathered and accumulated with high grade	Quartz, barite, calcite	Southern city

According to the 2022 data from the US Geological Service, global barite reserves are diminishing in response to the demands of the oil and gas drilling industry (Fig. 1 illustrates barite reserves in major countries). The global consumption of barite is increasing (barite production is shown in Fig. 2, barite distribution is shown in Table 3). As the world 's second largest barite consumption country, China occupies a large proportion in the international export market (Hai, 2018), but the export products lack market competitiveness due to insufficient deep processing; in addition, with the expansion and accelerated consumption of various fields in China, the high-grade and easy-to-select barite is gradually depleted (Liu et al., 2023; Liu, 2023). Thus, the research on the resource development of low-quality barite ore has become the focus.

The properties of low-grade barite ore are complex, and its main gangue minerals are alkaline earth metal salt minerals such as fluorite and calcite (Yann e t al., 2018). The separation of low-grade barite is mainly flotation process (Zhao et al., 2022). However, the crystal properties and physical and chemical properties of barium ions on the surface of barite minerals and calcium ions on the surface of fluorite minerals are similar, which makes the flotation separation between barite and fluorite very difficult. The focus of this flotation is to identify surfactants with strong collecting power and high selectivity for valuable minerals (Jiang et al., 2024). As collector is the key to successful flotation (Wanjia et al., 2023), its performance evaluation is one of the most important steps in the collector development process. Zhao et al. (2014) conducted a flotation test on a low-grade barite in the southwest region, using sodium oleate as the collector, and a simple process of one roughing, three cleaning and one scavenging was carried out on the ore at the optimal grinding particle size of -0.074 mm, and a good separation effect was obtained.

Wang et al. (2014) took a low-grade barite ore in Myanmar as the research object and used sodium oleate as the collector to conduct a flotation test study. The test results showed that, under the conditions of grinding fineness of - 200 mesh 80% and sodium oleate 800 g/t, "two rough sorting, one closed sorting and two open sorting" were carried out. A marketable barite concentrate with 96.32% and 91.26% content was obtained.



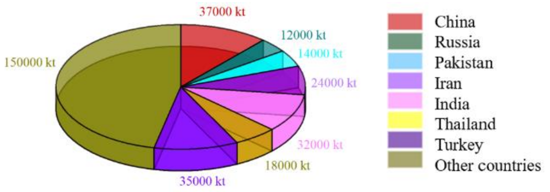


Fig. 2. Barite production in 2017/thousand tons Fig. 3.Barite reserves in 2017/thousand ton

Table 3. Distribution of barite minerals in China

Province	Reserves/million tons	Province	Reserves/million tons
National	3689.12	Chongqin	518.59
Liaoning	0.43	Sichuan	74.33
Jilin	0.43	Guizhou	4293.25
Zhejiang	732.79	Yunnan	206.85
Fujian	268.16	Shaanxi	213.02
Jiangxi	34.86	Gansu	1133.53
Shandong	52.9	Xinjiang	103.23
Hubei	495.27	Guanddong	1.91
Hunan	1443.69	Guangxi	1142.89

Data source: Ministry of Natural Resources of the People 's Republic of China 's ' National Mineral Resources Reserve Statistics in 2022'

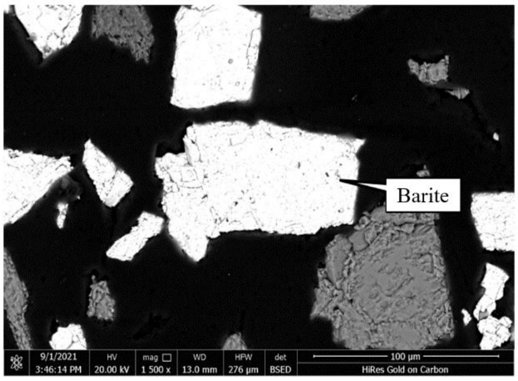


Fig. 4. Fluorite and barite conjoined

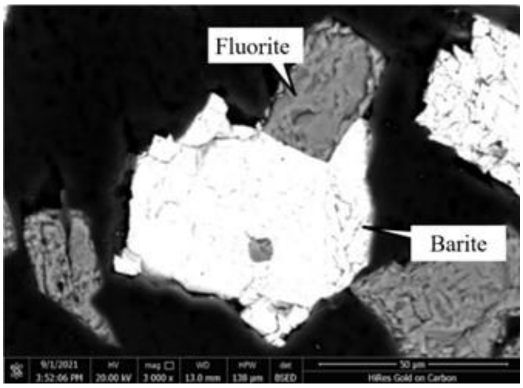


Fig. 5. Barite wrapping other minerals

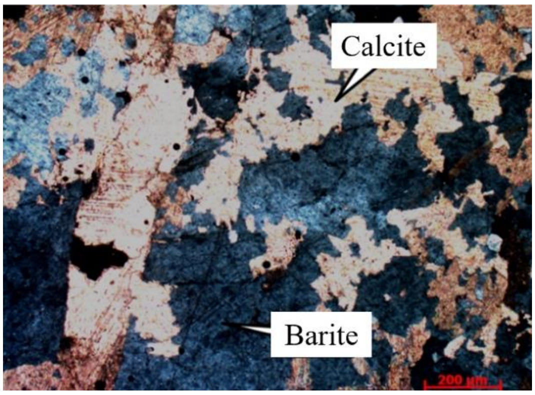


Fig. 6. Calcite is distributed among barite grains

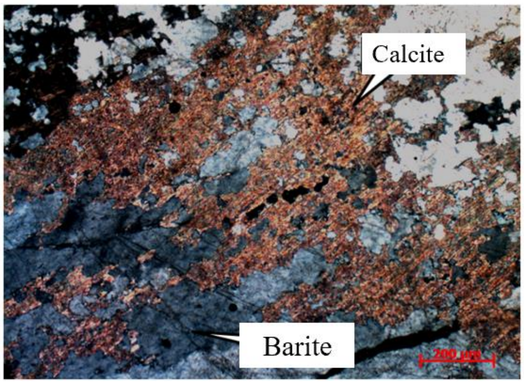


Fig. 7. Calcite is distributed among barite grains

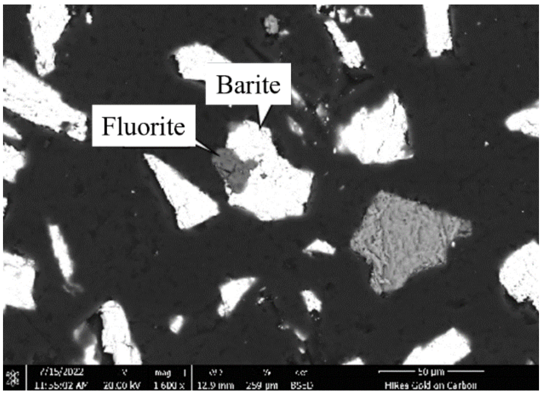


Fig. 8. Fluorite and barite conjoined

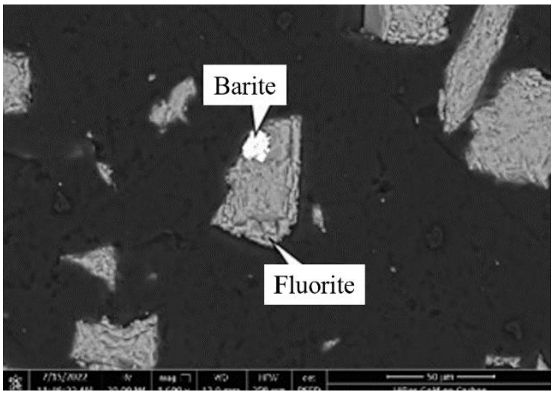


Fig. 9. Fluorite and barite conjoined

However, in the current flotation test, the conventional collector system is difficult to effectively separate it (Dui et al., 2019), new, synthetic, modified and compounded environmentally friendly collectors have become new research hotspots; Jiang et al. (2024) studied the mechanism of 1-octadecyl ester-1,2-benzenedicarboxylic acid (OEBA) as a collector for fluorite, calcite and barite. In the mixed mineral test, under the condition of neutral pH, 2.75×10^{-6} mol ·L^{-1} OEBA floated more than 80.0% barite from the mixture, and the separation efficiency of fluorite, calcite and barite was very high. During the study of barite ore, Lu et al. (2020) found that dodecyl phosphate is also a promising collector for barite flotation. Therefore, the flotation test of barite was carried out by using dodecyl phosphate as collector. The results show that the flotation recovery of barite can reach 95% in a wide pH range. Through various test results, it was found that lauryl phosphate replaced water and adsorbed on the surface of barite.

As one of the important reagents to adjust the difference of mineral surface hydrophobicity, collector is one of the reagents in flotation. In the study, we can use the first principle calculation to get the structure of the collector and then analyze the molecular properties of the collector. Duan et al. (2021) synthesized a new collector octylamine-bis (butyric acid hydroxamic acid) (OBHA) with macromolecular structure and two functional groups based on the molecular design of flotation reagent theory. The selective adsorption mechanism of OBHA was studied by DFT calculation. The results showed that OBHA matched well with the surface of barite, thus improving the selectivity. Then, the adsorption of flotation reagents (collectors, inhibitors and activators) was studied by density functional theory (DFT). Or it is necessary to determine the interaction mechanism of the collector and reveal the adsorption process of the collector (Duan et al., 2021). In the study of the separation of barite, fluorite and calcite by Ren et al. (2017), MD was used to simulate the crystal structure specificity of the inhibitor molecules of different minerals, and the adsorption energy of the three types of ores before and after the inhibitor was obtained. On the basis of the experiment, calculation is added to realize the separation of barite, fluorite and calcite.

2. Collector

2.1. Fatty acid collectors

Typical barite flotation collectors include anionic collectors such as fatty acids, alkyl sulfates and alkyl sulfonates, cationic collectors represented by amines, and amphoteric collectors between them (Zhang et al., 2023). Among them, the main fatty acid collectors are oleic acid, naphthenic acid and oxidized paraffin soap. The main mechanism of action is that carboxyl functional groups can form complexes with metal ions on the surface of various minerals, and can form insoluble compounds with alkaline earth metals and heavy metal ions (Liu et al., 2021).

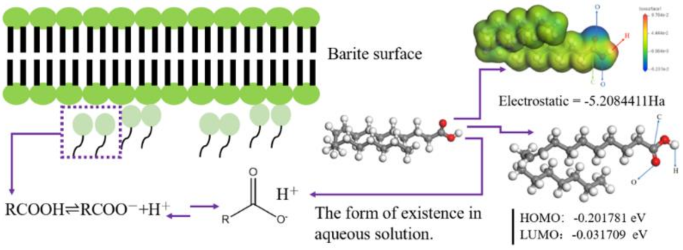


Fig. 10. Adsorption mechanism of oleic acid on barite surface

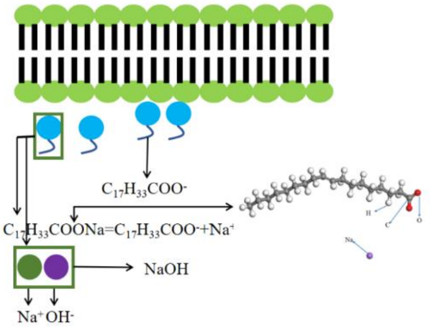


Fig. 11. Adsorption mechanism of sodium oleate on barite surface

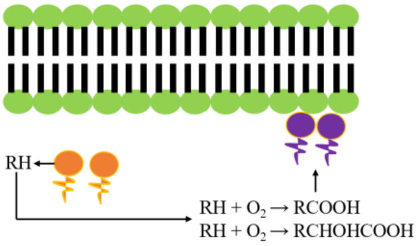


Fig. 12. Adsorption mechanism of oxidized paraffin soap on barite surface

Oleic acid has strong collecting ability and low price; in the neutral environment, oleic acid is mainly adsorbed on the surface of barite by chemical adsorption (Yue, 2001); however, due to the poor selectivity, a large number of inhibitors need to be added in the flotation test (Zhao et al., 2014). Fig. 10 is the mechanism of adsorption of oleic acid on the surface of barite when it is used as collector. Sodium oleate is a commonly used collector at present. Sodium oleate is more stable than oleic acid (Fig. 11). The reason is that-COOH in oleic acid is easily decomposed into carboxylate anions and positively charged hydrogen ions (protons), and carboxylate ions are stabilized by resonance. The negative charge left after the deprotonation of the carboxyl group is delocalized between the two electronegative oxygen atoms in the resonant structure. Ren et al. (2017) used valerian extract and sodium fluosilicate as inhibitors and sodium oleate as collector to selectively float barite, fluorite and calcite. Valerian extract has a good separation effect on three minerals. Zhao (2014) et al. studied a low-grade barite in Southwest China, using sodium oleate as collector, the flotation test of barite was carried out under the condition of grinding particle size of -0.074 mm, and a barite concentrate with $BaSO_4$ content of 98.21% and recovery of 80.71% was obtained. Sodium oleate can be adsorbed on the surface of positively charged minerals by electrostatic interaction. At the same time, sodium oleate can also undergo chemical adsorption on the surface of minerals (Sun 2014), that is, precipitation is formed by chemical reaction between polar groups and metal cations on the surface of minerals. These two adsorption forms play a decisive role in the flotation behavior of minerals (Leng and Zhang, 2023). Oxidized paraffin soap is an industrial product, and its harvest is divided into fatty acids, which is similar to the mechanism of oleic acid. The difference is that the oxidized paraffin soap does not require high pH (Song, 1994); Fig. 12 is the mechanism diagram of the adsorption of oxidized paraffin soap on the surface of barite. Naphthenic acid exists in the alkali residue produced in the process of petroleum refining, which is cheap and the collection capacity is less affected by temperature (Wang et al., 1996). Wang et al. (1996) used naphthenic acid as collector to float fluorite and barite. Under the condition of pulp concentration of 5.7 and naphthenic acid concentration of 2.5×10^{-5} mol/L, barite and fluorite were effectively separated. The carboxyl group in fatty acid collectors can interact with barium ions (Jiang et al., 2020).

The collector mainly acts on the mineral surface and is an important reagent to adjust the hydrophobicity difference of the target mineral surface. DFT was used to optimize the structure of the collector in aqueous solution to analyze the molecular properties of the collector. Lin et al. (2023) used DFT to calculate the electrostatic diagram and orbital diagram of the collector pectin, and obtained that the possible active sites of pectin were -COOC-, -OH and C-O-C oxygen atoms, which also indicated that the area of cation adsorption on the mineral surface was -COO-, -OH and C-O-C in the pectin molecule. Using density functional theory (DFT) to analyze the chemical properties of collectors at the atomic level, the mechanism of action of collectors can be preliminarily understood. Fig. 13 is the structural formula of three types of collectors. The structure and performance of collectors determine one of the important indicators of flotation. The frontier orbital and charge distribution are important indicators for inferring the reactivity of a class of collectors. To this end, the Materials studio software DMol3 template was used to design and model the three barite collectors, and then the software was used to optimize the built pharmaceutical model. The structure optimization and frequency calculation parameters are GGA/PBE under DFT method, and the global optimal reagent conformation without imaginary frequency is obtained.

Fig. 13 (left 1) is the oleic acid structural formula. It can be seen that one end of -COOH in oleic acid is a polar group, and $-CH_3$ is a non-polar group. In the flotation process, -COOH will be adsorbed on the mineral surface, and the non-polar end will be outward, which makes the mineral particles hydrophobic and play a collecting role. The existence of double bonds in the non-polar group of oleic

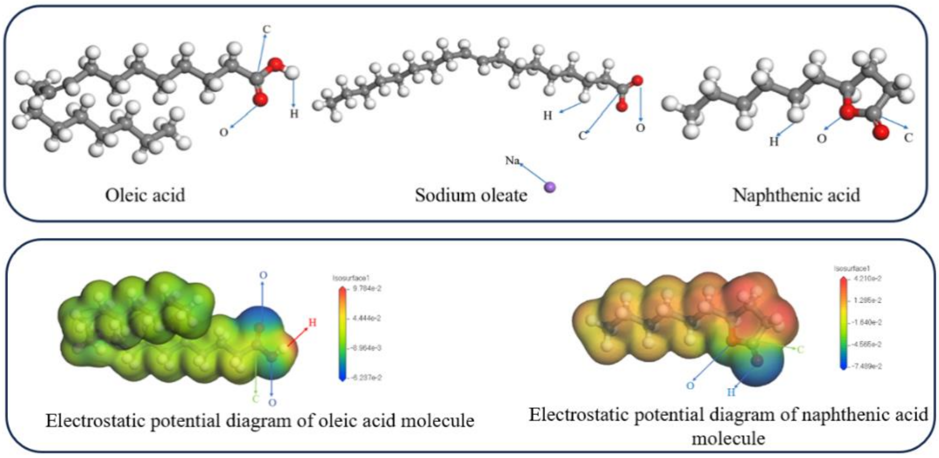


Fig. 13. Structure of fatty acid collectors and electrostatic potential Fig.s

acid is one of the factors that oleic acid has good collecting ability (Chen, 2008). The chemical adsorption of flotation collector on mineral surface refers to the interaction between collector and mineral surface in the form of ionic bond or covalent bond, and there is charge transfer between them. For this purpose, the electrostatic potential of oleic acid and naphthenic acid was calculated and the electrostatic potential diagram was drawn as shown in 7. Oleic acid has active carboxyl group (-COOH), which is distributed in the negative electrostatic potential region. In addition, because oleic acid has a hydrocarbon group (-CH_3), and the collection performance will increase with the increase of the carbon chain of the hydrocarbon group, the influence of the aggravation effect and the enhancement of the association energy between the hydrocarbon chains will reduce the percentage of ionic bonds on the mineral surface of oleic acid, increase the covalent bonds, and make the adsorption more reliable. Oxygen atom is the bonding ion of oleic acid and barite surface (Li et al., 2023). According to the calculation of electrostatic potential, oxygen in oleic acid molecule has strong reactivity. Sodium oleate is more stable than oleic acid because -COOH in oleic acid is easily decomposed into carboxylate anions and positively charged hydrogen ions (protons), and carboxylate ions are stabilized by resonance. The negative charge left after the deprotonation of the carboxyl group is delocalized between the two electronegative oxygen atoms in the resonant structure.

The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) determine the electron gain and loss and transfer ability of the molecule, and determine the spatial orientation of the intermolecular reaction and other important chemical properties. For this reason, the frontier orbitals of fatty acid collector molecules were calculated in the DMol3 module of Materials studio.

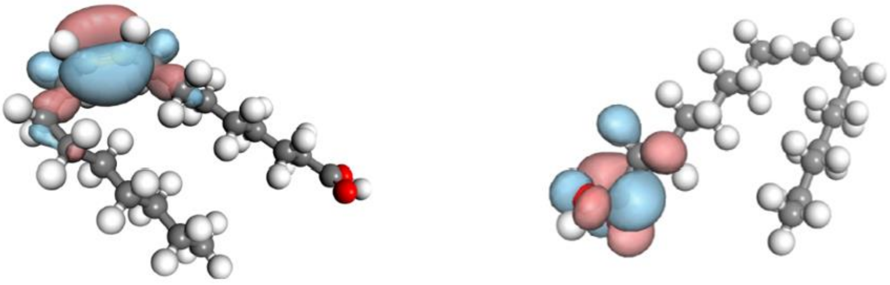

Oleic acid: HOMO Oleic acid: LUMO

Fig. 14. Orbital graph

Table 4. Highest atomic orbital and lowest occupied orbital energy

	HOMO	LUMO	ΔE (eV)
Oleic acid	-0.201781	-0.031709	0.170071
Naphthenic acid	-0.219144	-0.026654	0.19249

It can be seen from Table 4 that the HOMO value of oleic acid is − 0.201781 eV, the LUMO value is − 0.031709 eV, the HOMO value of naphthenic acid is − 0.219144 eV, and the LUMO value is − 0.026654 eV. Both HOMO and LUMO values are very small, indicating that the ability of the molecule itself to provide or obtain electrons is relatively low; HOMO is the easiest to lose, so it is the most lively; LUMO has lower energy in all unoccupied orbitals, indicating that it is easier to accept electrons. When a substance undergoes a chemical reaction, it usually occurs at HOMO and LUMO. It can be seen that the electron gain and loss and transfer ability of the substance are determined by HOMO and LUMO. The band gap ΔE (oleic acid) < ΔE (naphthenic acid), indicating that oleic acid is more easily excited.

Oleic acid and naphthenic acid have the advantages of strong collecting ability and less dosage, but the selectivity to barite is poor, and the flotation effect depends largely on the concentration of fatty acid anions in the medium, and the concentration of fatty acid anions is related to the pH of the medium (Fan et al., 2022). When the concentration of H^+ in the medium is high and acidic, electrostatic adsorption occurs between fatty acid collectors and anions on the surface of minerals. When the concentration of OH- in the medium is high and alkaline, the metal cation in the medium reacts with RCOO- to form fatty acid soap chemically adsorbed on the surface of the ore. The long-chain alkyl R-end of fatty acid anionic surface modifier is similar to the polymer structure, and the two have good affinity (Huang et al., 2013); the -COOH at the other end of the molecule can undergo physical and chemical adsorption with barite, making the non-polar group face the water, and the surface of the barite is hydrophobic (Zhu et al., 2022). However, with the increase in the price of anionic surface modifiers, it is urgent to find a more cost-effective modifier alternative.

Although fatty acid collectors have strong collection effect in the case of small dosage, they are expensive to use, sensitive to the temperature of the flotation system, and can not be used in low temperature environment, and can not be selectively adsorbed for different minerals, and are easily affected by metal ions. Usually, in order to achieve better flotation results, it is necessary to combine other types of collectors (amines or sulfates) (Bai et al., 2024).

2.2. Alkyl sulfate collector

Alkyl sulfate is an anionic collector. The commonly used alkyl sulfate collectors include sodium dodecyl sulfate, sodium dodecyl sulfonate and sodium dodecyl benzene sulfonate (Lu et al., 2020). Fig. 16 shows the molecular structure of three common anionic collectors.

The three types of alkyl sulfates are mainly chemically adsorbed on the surface of barite, thereby changing the flotation performance of barite. Dodecyl sulfate (sodium) is similar to fatty acid soap in nature. In the study of barite fluorite minerals, Shi et al. (2018) used sodium dodecyl sulfate as collector to carry out mixed flotation of one roughing and one scavenging, and obtained barite concentrate with yield of 52.44%, $BaSO_4$ grade of 94.83%, $CaCO_3$ content of 1.50% and recovery of 97.00%. In the study of a low-grade barite ore, Xu et al. (2023) used 2000 g/t Na_2CO_3 as the regulator, 1000 g/t water glass as the inhibitor, and 2000 g/t sodium dodecyl sulfate as the collector to carry out the open-circuit flotation experiment, and obtained a flotation barite concentrate with a $BaSO_4$ grade of 91.36%, and the recovery rate was 73.83%. In the sodium dodecyl sulfate system, minerals (barite, fluorite) are chemically reacted with the $-SO_3-$ group in the sodium dodecyl sulfate molecule (Huang et al., 2013). The recovery rate of sodium dodecyl sulfate under acidic and weak alkaline conditions is better than that under alkaline conditions (Chen et al., 2020). Wang et al. (2020) used sodium dodecyl sulfonate as collector in the study of flotation separation behavior and mechanism of fluorite, barite and calcite. Under the optimum experimental conditions, sodium dodecyl sulfonate has the advantages of small dosage and better selectivity. Jiang et al. (2020) carried out the flotation test of barite with four existing collectors. It was found that the sodium dodecyl sulfonate had the strongest ability to recover, and the recovery rate of barite was maintained at about 95% when the dosage was 0.8 mg/L and the pH was 9.0~9.5. The chemical adsorption of Ba^{2+} and $C_{12}H_{25}OSO_3-$ on the surface of barite minerals may produce relatively stable barium dodecyl sulfonate on the surface of minerals, which is similar to the mechanism of sodium dodecyl sulfate acting on the surface of barite.

The recovery effect of sodium dodecyl sulfate and sodium dodecyl sulfate on barite is equivalent. Some researchers use the mixed reagent of the two to carry out the flotation test of barite, and the result is due to the single alkyl collector. Usually, alkyl sulfate collectors are rarely used alone, and generally form a combined inhibitor with fatty acid collectors to effectively improve the collection efficiency and selection performance.

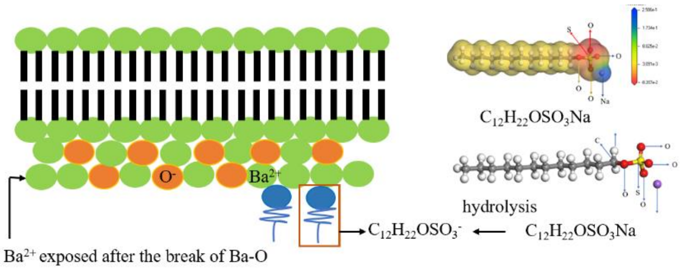


Fig. 15. Adsorption of sodium dodecyl sulfonate on Barite surface

Fig. 15 is a mechanism diagram of sodium dodecyl sulfate adsorbed on the surface of barite. The barite is an island sulfate mineral. In the strong acidic medium, the number of barium ions on the surface of the barite increases, which increases the positive charge on the surface of the mineral (Wang et al., 2020); in alkaline medium, the formation of various hydroxyl complexes reduces the number of barium ions on the surface, and the corresponding number of SO_4^{2-} and HSO_4^- increases, thus showing strong negative charge (Jiang et al., 2020). In the flotation process, the Ba-O bond is stronger than the S-O bond and is more likely to break, which makes it easy to expose a large number of positively charged Ba^{2+} ions and negatively charged O^- ions on its surface. When sodium dodecyl sulfonate was added, the Ba^{2+} ion on the surface of barite mineral was chemically adsorbed with $C_{12}H_{25}OSO_3^-$, and relatively stable barium dodecyl sulfonate was formed on the surface of the mineral, and the hydrocarbon group extended outward towards the medium to make the mineral hydrophobic.

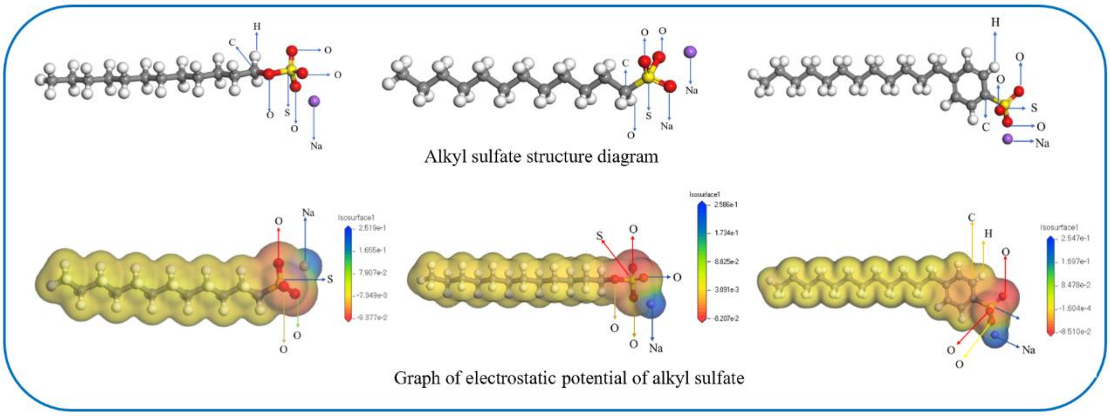
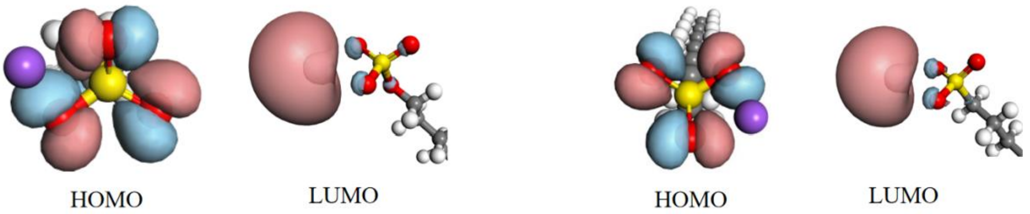


Fig. 16. Molecular structure of alkyl sulfate

Fig. 16 shows the molecular structure of alkyl sulfate and its electrostatic potential diagram. From left to right, they are sodium dodecyl sulfate, sodium dodecyl sulfonate and sodium dodecyl benzene sulfonate. The hydrophilic group of the three is -SO3-, and the hydrophobic group is -RO-. From the electrostatic potential diagram of the three collector molecules, it is easy to find that the negative area is concentrated in the vicinity of sulfate ion and dodecyl chain, while the vicinity of sodium atom shows positive electric characteristics. Therefore, for the classical electrostatic weak interaction such as hydrogen bond, sulfate and dodecyl chain can be considered as the dominant hydrogen bond acceptor and donor of this molecule, respectively. This is one of the reasons why the flotation recovery rate of single minerals will increase to a certain extent. From the electrostatic potential diagram of the three collector molecules, it is easy to find that the negative area is concentrated in the vicinity of sulfate ion and dodecyl chain, while the vicinity of sodium atom shows positive electric characteristics. The above electrostatic potential diagram shows that the electrostatic potential around the S atom is negative that is, the positively charged particle has strong interaction with it and is easy to get close to it. The positive charge around the Na atom tends to converge with the OH- in the pulp. Based on this, the preliminary selection of the collector was made through the molecular reaction site, molecular interaction and molecular recognition.

Table 5. Highest atomic orbital and lowest occupied orbital energy

	HOMO	LUMO	ΔE (eV)
Sodium dodecyl sulfate	-0.202067	-0.59244	-0.390
Sodium dodecyl sulfate	-0.19866	-0.057436	0.140
Sodium dodecyl benzene sulfonate	-0.202067	-0.059244	0.143



Sodium dodecyl sulfate ($C_{12}H_{25}SO_4Na$) Sodium dodecyl sulfonate ($C_{12}H_{25}SO_4Na$)

Fig. 17. Orbital graph

Table 5 shows the highest occupied orbital, the lowest unoccupied orbital and the energy gap of the three alkyl sulfates. It can be seen from the table that the HOMO value of the dodecyl sulfate molecule is -0.202067 eV, and the LUMO value is - 0.59244 eV. The HOMO value of sodium dodecyl sulfonate is -0.19866 eV, and the LUMO value is -0.057436 eV. The HOMO value of sodium dodecyl benzene sulfonate is - 0.202067 eV, and the LUMO value is -0.059244 eV. The HOMO and LUMO orbitals also help to predict the behavior of molecules in different chemical reactions. From the energy gap difference of the three, it can be obtained that the sodium dodecyl benzene sulfonate molecule is more stable, and its stability is: sodium dodecyl benzene sulfonate > sodium dodecyl sulfonate > sodium dodecyl sulfate (Jiang et al., 2020).

2.3. Phosphonic acid collectors

Phosphonic acids have a structure in which the P atom is directly connected to the C atom (Liu et al., 2012), and the hydrophilic center atom is P (Huang et al., 2013). Phosphonic acid collectors include alkyl α-hydroxy 1,1-diphosphonic acid, α-aminodiphosphonic acid and β-aminoalkylphosphonic acid. The flotation recovery effect of barite is better in weak alkaline environment, and there are both physical adsorption and chemical adsorption on the surface of barite.

Hu and Wang (1990) studied the enrichment properties of a-amino arylphosphonic acid on fluorite, barite and scheelite. The results of flotation test showed that the collected active substance of LN 11-2 was ((R1) (R) NCH (Rs) POH)$^-$. Through the analysis, it is found that the coordination covalent bond is formed between P = O and calcium or barium atoms, which indicates that the mechanism of ln11-2 in barite is mainly chemical adsorption. Lin and Cui (1993) used alkyl-radial 1,1-diphosphate code as collector to separate barite fluorite by flotation at a lower dosage. In the study of barite flotation, Lu et al. (2020) used dodecyl phosphate collector to analyze the adsorption state on the surface of barite, and used contact angle, Zeta potential and molecular dynamics simulation (MDS) method. Molecular dynamics simulation and experimental results show that lauryl phosphate instead of water is super adsorbed on the surface of barite.

According to the different electronegativity of atoms, the order of electronegativity of the three atoms is N>C>P. Therefore, the electron-donating ability of the single bond O atom of the phosphonate collector is stronger than that of the carboxylic acid collector (Marion et al., 2020). Although the organic phosphonic acid collectors are chelating collectors, the selectivity is relatively strong. However, the production cost is high, so the wide range of applications is limited.

2.4. Amine collectors

Amine collectors belong to the category of cationic collectors, and cationic collectors are mostly organic compounds containing N (Wang et al., 2020). Common amine collectors include alkylamines, sulfonated butyramides, etc., mainly in the form of electrostatic adsorption, semi-gel beam adsorption, molecular adsorption and exchange adsorption. The mechanism of action is that metal cations may be adsorbed on the surface of minerals by carboxyl complexes and hydroxides.

The amine collector hydrolyzes in water to form -NH_3^+ groups, which are positively charged and adsorbed on the mineral surface. The hydrophobic part of the hydrocarbon group is very strong, making the mineral surface hydrophobic. Under certain medium conditions, -NH_3^+ groups can effectively capture the negative silicate minerals and metal oxide minerals. The cationic surfactant has strong semi-micellar adsorption on the surface of the mineral, and further forms the adsorption group of the mineral and the collector molecule, which is less affected by temperature when used. There is basically no disadvantage of weakening harvesting capacity under low temperature conditions. When the acidity is too strong, the concentration of amine cations (RNH_3^+) in the pulp is too high, and the amine cations interact with each other through hydrogen bonds, reducing or even losing the adsorption with mineral particles, and can not achieve good separation effect.

In the study of a low-grade barite ore, Xu et al. (2023) used 2000 g/t Na_2CO_3 as the regulator, 1000 g/t water glass as the inhibitor, and 2000 g/t sodium dodecyl sulfate as the collector to carry out the open-circuit flotation experiment, and obtained a flotation barite concentrate with a $BaSO_4$ grade of 91.36%, and the recovery rate was 73.83%. Wei et al. (2023) introduced two 2-hydroxy-3-chloropropyl groups into the dodecylamine collector to prepare a new cationic collector N, N-bis (2-hydroxy-3-chloropropyl) dodecylamine (BHCPDA) in the reverse flotation test of apatite and quartz. The adsorption capacity of BHCPDA on the surface of apatite was higher than that of DDA.

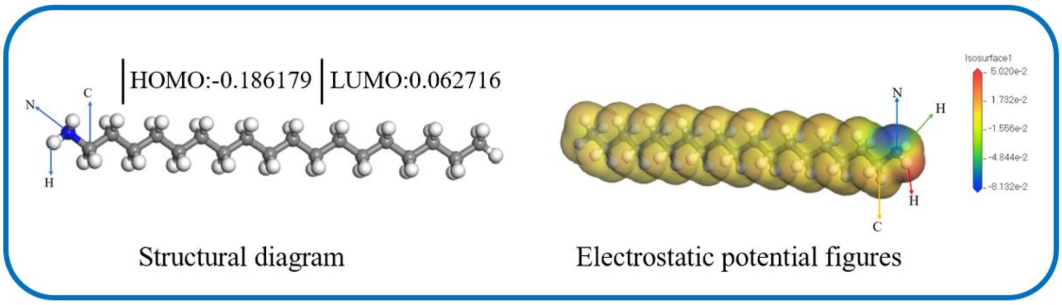


Fig. 17. Structure and electrostatic potential diagram of alkyl collectors

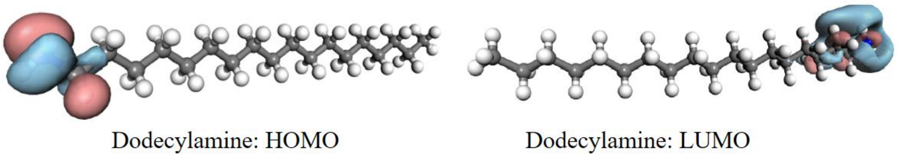


Fig. 18. orbital graph

In dodecylamine, -NH_3 and-CH_3 are functional groups, and-NH_3 is beneficial to the collection of barite (Wang et al., 2020). For the same mineral, the strength of the electrostatic action is proportional to the charge of the adsorbent atoms. On the right of the Fig. is the electrostatic potential diagram of the alkyl group. It can be seen from the Fig. that the nitrogen atom is negatively charged and has a large intensity. The electron density criterion indicates that the higher the group charge density, the more the net charge, and the stronger the collecting ability (Dirnuur 2023). In addition, we can increase the size of the polar group of the collector to increase the steric hindrance effect of the adsorption of the reagent and the mineral surface, and improve the flotation selectivity of the reagent (Wang et al., 2020).

2.5. Mixed collectors

Wang (2019) used a mixture of sodium dodecyl sulfate and sodium dodecyl sulfonate as a flotation combined collector to conduct flotation experiments on barite minerals. The barite concentrate with $BaSO_4$ grade of 81.02% was obtained, and the barite recovery was 83.04%. The adsorption mechanism in the flotation process was studied by Zeta potential and infrared spectroscopy. Wang et al. (2008) used a mixed collector (sodium dodecyl sulfate + sodium oleate) to obtain a barite concentrate with a grade of 91.68% and a recovery of 80.43%. Fen et al. (2023) used NaOL/CTAB mixed collector for mineral flotation test. The results showed that the surface activity and molecular arrangement density of the mixed collector were higher than those of the single collector, indicating that the mixed collector had synergistic effect. Compared with a single collector, the mixed collector has stronger surface activity and hydrophobicity. Lenzo et al. (1995) used Aero825-845, a combination collector, to carry out flotation tests on barite, and obtained a barite concentrate with a grade of 96.5% and a recovery rate of 77.5%. Liu et al. (Yan et al., 2023) used a mixed collector for mineral flotation. The results showed that NaOL and DDA had a co-adsorption effect on the mineral surface, and the introduction of metal ions enhanced the effect of mixed adsorption. Gao et al. (2017) obtained a barite concentrate with a grade of 96.95% and a recovery rate of 80.22% by using a mixed collector of dodecylamine, hexadecylamine and sodium dodecylsulfonate.

2.6. New collectors

Jiang et al. (2024) used a newly synthesized 1-octadecyl ester, 1, 2-phenyl dicarboxylic acid (OEBA) as a collector for flotation separation of fluorite, barite and calcite. By infrared analysis, the C-H tensile vibration peak at 2924 cm-1 of OEBA appears on the surface of barite, indicating that OEBA has adsorption effect on barite. AFM analysis shows that the RMS roughness Rq of barite changes from 0.329 nm to 0.351 nm at pH ~ 9.0, and a large number of aggregates cover the entire surface of barite. At pH ~ 11.0, OEBA is captured on the entire surface of barite. Fig. 19 shows the OEBA structural formula.

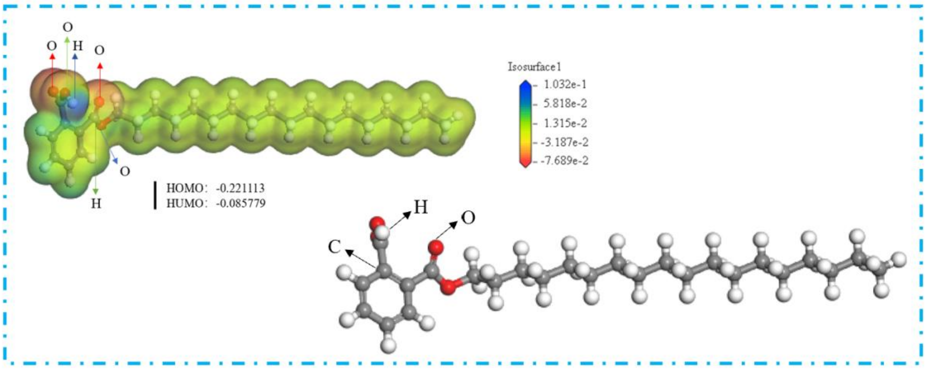


Fig. 19. OEBA structure and its electrostatic potential diagram

Yan et al. (2023) synthesized a new type of oleic acid hydroxamic acid collector and applied it to flotation when they studied the flotation separation of fluorocarbon and barite. Under the condition of pH 8, 30 mg/L OLHA and 20 mg/L SHMP can realize the effective separation of fluorocarbon and barite. Studies have shown that new fatty acid collectors can not only reduce the amount of reagents used in the flotation process and achieve low-cost reagents, but also achieve excellent flotation results in low-temperature environments, and their performance is much better than conventional oleic acid reagents. Zhang et al. (2023) used CY-30 as collector for barite flotation, and obtained the separation indexes of $BaSO_4$ grade and recovery rate of 93.55% and 87.85% respectively through closed-circuit test. Liu et al. (2024) carried out micro-flotation experiments on barite under a new collector (α-BLA) system, and obtained barite concentrate with grade of 81.12% and recovery of 87.74%。 When Papini et al. (2001) introduced ether groups to the alkyl group, liquid ether amines were formed, which dispersed uniformly in the pulp and had remarkable flotation effect on minerals.

3. Depressant

The inhibitor can create a hydrophilic film on the surface of the ore particles, and also has the effect of removing activated ions. In this paper, inhibitors and their mechanism of flotation were reviewed.

3.1. Macromolecular compound

Starch, as a renewable and biodegradable polymer (Yang and Wang, 2019), has many applications in the flotation separation of salt ores (Yang et al., 2020). The starches commonly used in industry are corn starch, potato starch and cassava starch. Because starch molecules have many branches and have a high degree of bending, when starch is adsorbed on the surface of minerals, it will cover up the collector that has been adsorbed on the surface of minerals, so that the hydrophobic film on the surface of minerals cannot play a role, even if the collector adsorbed on the surface of minerals does not desorption. There are also many hydrophilic functional groups (-OH, -O-, and -COOH, etc.) on the surface of minerals that make the surface of minerals hydrophilic, thus producing an inhibitory effect on minerals. Modified starch is a new type of modified starch, which overcomes the defects of ordinary starch in industrial application. In essence, starch molecules are cut off, rearranged, oxidized and introduced chemical groups. It is prepared by introducing carboxyl, sulfonic acid and other groups, which has the characteristics of solubility, water holding capacity and other characteristics that ordinary starch does not have. Wu and Gong (1989) et al. used starch and modified starch as inhibitors to separate fluorite and barite in the flotation separation experiment of fluorite and barite. The results showed that the inhibition and selectivity were obviously related to the causticization of starch. Carboxymethyl starch has a certain inhibitory effect, and the inhibitory effect of caustic starch is the strongest, and the inhibition of barite is far more than the inhibition of fluorite. Yang et al. (2020) used gelatinized starch as inhibitor (GS) to separate barite fluorite. The results of single mineral test showed that with the increase of GS dosage, the flotation recovery rate of barite decreased significantly from 90% to less than 5%. The presence of gelatinized starch has little effect on fluorite. The C-O bond (286.44 eV) of the gelatinized starch treated barite was significantly stronger than that of fluorite by XPS analysis. These results indicate that starch is adsorbed on the surface of barite. The adsorption of GS on the surface of barite is mainly dominated by hydrogen bonds.

Fig. 20 shows the adsorption diagram of gelatinized starch on the surface of barite. Yang et al. (2020) used gelatinized starch as inhibitor (GS) to separate barite fluorite. The results of single mineral test showed that with the increase of GS dosage, the flotation recovery rate of barite decreased significantly from 90% to less than 5%. The presence of gelatinized starch has little effect on fluorite. The C-O bond (286.44 eV) of the gelatinized starch treated barite was significantly stronger than that of fluorite by XPS analysis. These results indicate that starch is adsorbed on the surface of barite. The adsorption of GS on the surface of barite is mainly dominated by hydrogen bonds. Fig. 20 shows the adsorption diagram of gelatinized starch on the surface of barite.

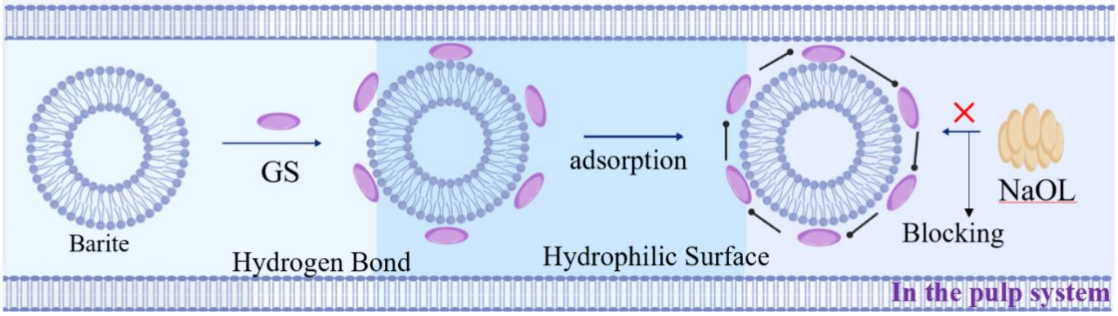


Fig. 20. A schematic diagram of the interaction mechanism between GS, NaOl and barite

Caustic starch is made by destroying the aldehyde group at the end of the starch molecule to form an organic acid group (Pugh and Stenius, 1985). Zhang (2000) showed that the chemical adsorption of caustic starch on the surface of barite would strongly inhibit the floating of barite. When starch macromolecules are decomposed and hydrolyzed under the action of heating, acid or amylase, they will be converted into dextrin, an intermediate substance of small molecules. Its chemical composition is basically similar to that of starch. It is generally believed that it is strongly adsorbed on the surface of hydrophobic minerals through hydrophobic bonding adsorption and mineral action (Li and Yang, 2020). Li Ye et al. (Wang et al., 2017) studied the adsorption characteristics of dextrin on the surface of barite, and found that dextrin was greatly affected by pH, and dextrin was easily adsorbed on the surface of barite under pH of 9.7 or strong acid. X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES) analysis show that Ba^{2+} is easily exposed on the surface of barite after the bond is broken, which is conducive to the chemical interaction between dextrin and Ba2+. At the same time, the radius of (SO$_4$)$^{2-}$ complex anion on the fracture surface of barite is large, and the attraction of complex anion to Ba^{2+} ion is weak, which is also conducive to the chemical interaction between dextrin and Ba^{2+} ion.

Wu and Gong (1989) studied the flotation of fluorite and barite minerals by ordinary corn starch, carboxymethyl starch, dextrin and starch with different caustic ratios. The results of pure mineral test showed that the inhibitory effect of starch was related to the causticization of starch. The actual mineral test showed that the inhibitory effect of ordinary corn starch and dextrin barite was not obvious, carboxymethyl starch had a certain inhibitory effect, and caustic starch had the strongest inhibitory effect on barite.

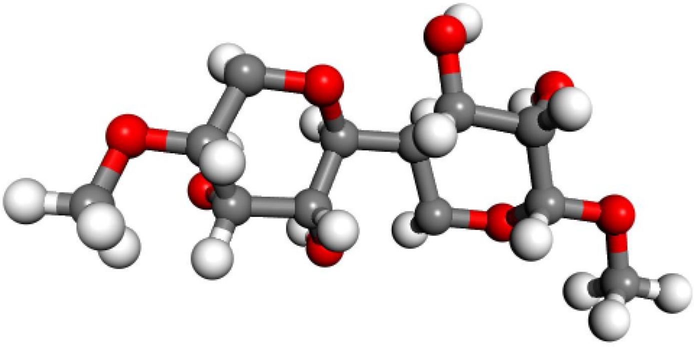


Fig. 21. Molecular structure of carboxymethyl cellulose

Carboxymethyl cellulose is obtained by the reaction of monochloroacetic acid or its sodium salt with cellulose. Cao and Ji (2006) studied the inhibition behavior of carboxymethyl cellulose in the separation of niobium minerals. The experimental results also showed that carboxymethyl cellulose as an inhibitor of gangue minerals removed most of the carbonate minerals, phosphate minerals such as dolomite, calcite, barite, monazite, apatite, quartz, feldspar and most of fluorite. When carboxymethyl cellulose is used as an inhibitor of barite, its carboxyl anion and Ba^{2+} on the surface of the barite lattice electrostatically attract the alkyl group in the carboxymethyl cellulose molecule and water to form a water film through hydrogen bonding, thereby exerting an inhibitory effect. Some scholars believe that carboxymethyl cellulose is incompletely ionized into carboxymethyl cellulose anion in aqueous medium, which is in a molecular flocculent state. This micelle is negatively charged and easily attracts positively charged minerals by electrostatic attraction, so the minerals are adsorbed to the micelle and inhibited (Li et al., 1997).

The role of lignosulfonate is to selectively cover the surface of gangue minerals such as barite to make it hydrophilic, or it may be the difference in coverage. The adsorption amount on the surface of fluorite is less, while the adsorption amount on the surface of gangue minerals such as barite is more. Sodium lignosulfonate is a typical inhibitor for the flotation of Mountain Pass rare earth ore, which has a strong inhibitory effect on barite.

Tannic acid, also known as tannic acid, contains a plurality of adjacent phenolic hydroxyl functional groups in the molecule, which is non-toxic and easy to be biological. Due to the advantages of degradation and low price, it has a wide range of applications in mineral separation and secondary resource recovery. Yao et al. (Dirnuur, 2023) used tannin to study the inhibition effect of barite and calcium-containing silicon-containing minerals under different collector systems. Under the combined fatty acid collector system, when the amount of tannic acid was 2.5 mg/L, barite and calcium-containing carbonate minerals, silicon-containing minerals have good flotation differences. The mechanism research results show that the adsorption of tannic acid on the surface of barite is much weaker than that on the surface of calcium carbonate minerals by controlling the amount of tannic acid.

From the perspective of the structure of tannins, most tannins have polar groups (alkyl groups or carboxyl groups) at their ends. When tannins interact with barite, the carboxyl group (or hydroxyl group) at one end is fixed on the surface of the barite by adsorption (or combination), and the hydroxyl group (or carboxyl group) at the other end is outward and adsorbed with water molecules to be hydrophilic, so that the barite is inhibited (Cao and Ji, 2006). Similar to tannin inhibitors, tannin extract is a polyphenol derivative with tannin as the main component. (Man, 1991); the chemical structures of tannins from different plant sources are often quite different, and the molecular structure is more complex, all of which have a glucopyranose structure of gallic phenol. In the study of flotation behavior of fluorite, barite and calcite by Chi (2024), sodium oleate was used as collector and tannin extract was used as inhibitor. Under the conditions of 8.0 × 10-5 mol/L, 5 mg/L and pH 6, the recovery rates of the three minerals were 86.14%, 15% and 49.49%, respectively, which effectively inhibited barite.

The inhibition mechanism of organic inhibitors on gangue minerals : the main hydrocarbon chain or branch chain is adsorbed on the surface of hydrophobic minerals ; the hydroxyl groups are ionized or form hydrogen bonds to interact with the mineral surface; strong hydrophilic hydration polar groups (such as SO_3^{2-}, COO-, etc.) make the mineral surface more hydrophilic; anionic functional groups (such as carboxylate or sulfate) form polymers with metal cations on the surface of minerals, which hinder the adsorption of agents. The functional groups, charge density and molecular weight of organic inhibitors greatly affect the effectiveness of inhibitors.

3.2. Inorganic salts

The commonly used inorganic salt inhibitors mainly include silicates, sulfates, phosphates, sodium carbonate, ferric chloride, etc. Therefore, this paper mainly reviews the application of the above inhibitors in barite flotation.

Common inhibitors contain COOH, SiO_3, PO_4 and OH groups, which interact strongly with Ca^{2+}. Water glass (WG) is the most common inorganic inhibitor, which can form binding complexes with metal ions through its silicate groups, so that the mineral surface is hydrophilic (Shi, 2012). In the process of foam flotation separation, fluorite is easily affected by the mud coating of fine barite. Therefore, In the process of foam flotation separation, fluorite is easily affected by the mud coating of fine barite. Therefore, Liu (2011) used water glass as dispersant, sodium oleate as collector and GS/NaOl reagent scheme to eliminate the negative effects of barite slime on fluorite flotation. In the fluorspar and barite slime system, WG and GS were added first, and the grade and recovery of CaF_2 were increased to 92.26% and 85.93%, respectively, which improved the flotation separation performance of fluorspar and barite slime. The results of zeta potential measurement, sedimentation test and DLVO calculation show that the surface charges of barite mud and fluorite are opposite, resulting in the cross-coagulation between the two minerals. After the addition of dispersant WG, since both barite slime and fluorite are negatively charged, electrostatic repulsion is generated between them. Under the condition of this reagent, the adsorption of GS on the surface of barite does not affect the interaction between fluorite and the collector NaOl, and improves the separation performance of fluorite and barite mud. The diagram shows the surface mechanism of water glass adsorption of barite. Water glass (WG) is a commonly used and effective inhibitor in actual flotation due to its low price (Isabel et al., 2023). In order to improve the separation performance, water glass is usually acidified to generate acidified water glass (AWG). The acidified water glass reaction formula is shown in Eq. (1).

$$NaSiO_3 + H_2SO_4 \rightarrow H_2SO_3 + 2Na + SO_4^{2-} \tag{1}$$

As a barite inhibitor, the SiO(OH)3-component in water glass (the main inhibitor of calcium carbonate gangue minerals) (Wei et al., 2023) forms covalent bonds or hydrogen bonds on the surface of minerals, while its $Si(OH)_4$ component interacts with minerals only through hydrogen bonds. In addition, the acidified water glass can be selectively adsorbed on the surface of the barite, hindering the adsorption of the anionic collector sodium oleate, thereby selectively inhibiting the barite and playing a good separation role.

Li et al. (2017) used aluminum sulfate as an inhibitor to study the flotation of barite. The pH of the pulp was adjusted to 6 by separation flotation. Sodium silicate, aluminum sulfate and tannin extract were used as inhibitors, and sodium oleate was still used as collector. The process adopted one roughing, five cleaning and two scavenging, and finally fluorite and barite concentrates were obtained.

Phosphate is an inorganic agent containing PO_4^{3-} tetrahedra in the molecule. Common polyphosphates include sodium hexametaphosphate (SHMP, $(NaPO_3)_6$), sodium pyrophosphate (SP, $Na_4P_2O_7$), trisodium phosphate (TSP, Na_3PO_4) and sodium tripolyphosphate (STPP). Yuan et al. (2022) used phosphate as an inhibitor to investigate the adsorption between barite and phosphate. The surface adsorption mechanism of the interaction between DTPMP and barite at low phosphate concentration. From the perspective of nucleation inhibition, compared with the concentration of DTPMP in aqueous phase, the fractional coverage on the particle surface has a better linear relationship with the logarithm of barite induction time. According to the desorption experiment, the release of DTPMP from the barite

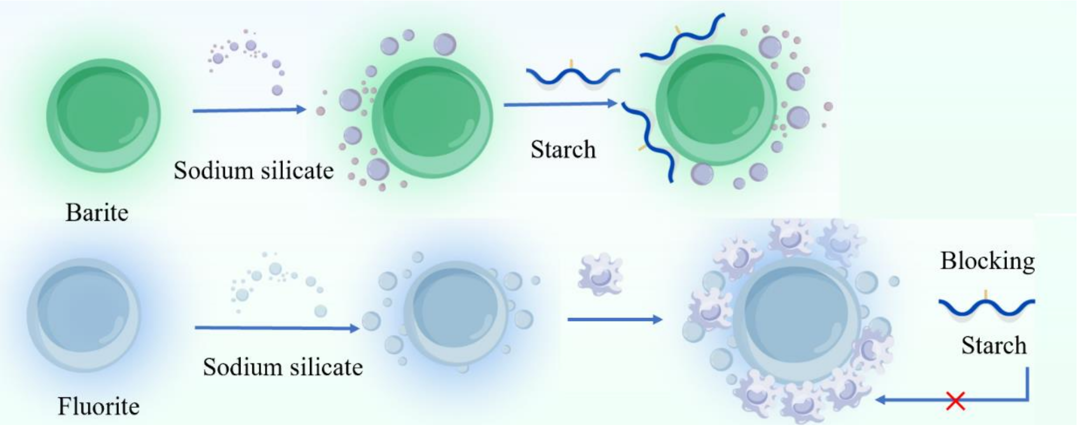


Fig. 22. Adsorption mechanism of water glass on barite surface

surface was controlled by the dissolution kinetics of the formed Ca-DTPMP precipitate. Sodium tripolyphosphate is a linear polyphosphate. The three phosphates in the molecule are arranged in a straight chain and contain two terminal phosphates. For Ba^{2+} in barite slurry, when the concentration of sodium tripolyphosphate is 1.6×10^{-5} mol/L, the concentration of Ba^{2+} changes little, only a slight decline, and then with the increase of sodium tripolyphosphate concentration, the concentration of Ba^{2+} gradually increases. Unlike fluorite, the solubility of barite is smaller, and there is only a small amount of free Ba^{2+} in the pulp. When 1.6×10^{-5} mol/L sodium tripolyphosphate is added, Ba^{2+} in the pulp can be fully precipitated. When the concentration of sodium tripolyphosphate increases, the precipitation is converted into a soluble complex, which promotes the dissolution of Ba^{2+} from the mineral surface (Xu et al., 2023). Sodium hexametaphosphate (SHMP) is a linear inorganic compound, and its adsorption on the mineral surface can aggravate the steric hindrance effect between particles. Under the condition of using OHA as flotation collector, three phosphate inhibitors, sodium tripolyphosphate, sodium trimetaphosphate and sodium hexametaphosphate, have a certain inhibitory effect on barite. Sodium hexametaphosphate, trisodium phosphate and acidic water glass have been reported as inhibitors of barite. However, the use of these inhibitors usually causes serious pollution to the ecosystem, so it is still necessary to find an effective green barite inhibitor (Xu et al., 2023).

3.3. Mixed inhibitors

Li et al. (2017) used the synergistic effect between the inorganic inhibitor CYD-1 and the organic inhibitor CYD-2 to separate the low-grade fluorite-barite symbiotic minerals. This not only strengthens the inhibition of barite, but also significantly improves the selectivity of collector to fluorite, and realizes the efficient separation of fluorite and barite. Sosa et al. (2021) explored a series of homologous polycarboxylic acids as crystallization inhibitors for barium sulfate (barite). Through crystallization, time-resolved microscopy and scattering measurements, it was shown that hydroxycitrate (a naturally derived small molecule) effectively inhibits barite nucleation. In addition, combined with microfluidic and atomic force microscopy measurements, it was found that hydroxycitrate completely inhibited growth by forming a disordered layer on the surface of barite.

3.4. New inhibitors

Xia et al. (2023) used gellan gum as an inhibitor to study the flotation of barite in high-density drilling fluid. The flotation process of “one roughing, two cleaning and one scavenging” was adopted. The dosage of sodium dodecyl sulfate was 700 g/t, and the dosage of gellan gum was 700 g/t. The barite concentrate with a comprehensive recovery rate of 86.49%, a comprehensive grade of $\geqslant$ 90%, and a mixed concentrate density of $\geqslant$ 4.2 g/cm^3 can be obtained. The wettability and Zeta potential tests showed that the adsorption between gellan gum and barite was in the form of hydrogen bond.

Long et al. (2022) used a new inhibitor gellan gum to inhibit barite. Under the condition of pH 7.5, 15 mg/L GG was used as an inhibitor to achieve efficient flotation separation of fluorite and barite. Under these conditions, the flotation test of artificial mixed minerals was carried out, and a high-quality concentrate with CaF_2 grade of 85.24% and recovery of 86.73% was obtained. In addition to the flotation test, Zeta potential, Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS) confirmed that GG was chemically adsorbed on the surface of barite, and strongly hindered the adsorption of NaOL on the surface of barite, achieving the separation of barite fluorite. The Fig. is the mechanism model of inhibitor adsorption on barite minerals.

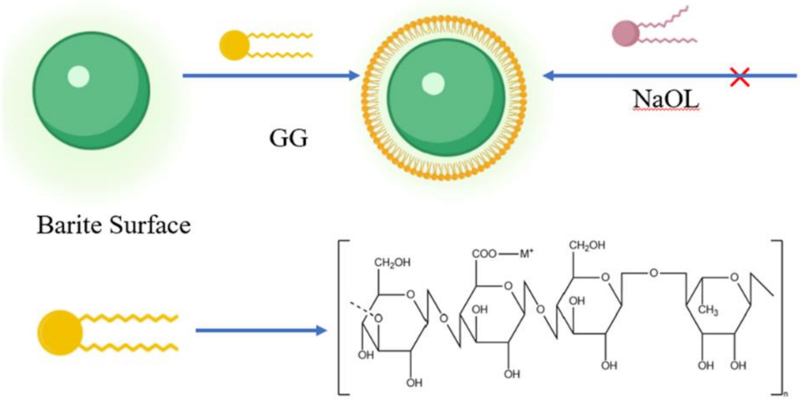


Fig. 23. Barite separation model

Chi (2021) studied the flotation separation of barite by using sodium oleate as collector and naphthalene sulfonate polymer EM as inhibitor. When the pulp pH value is 6, the dosage of naphthalene sulfonate polymer organic matter EM is 20 mg/L, and the dosage of sodium oleate is 8.0×10^{-5} mol/L, the floatability difference between barite and fluorite and calcite is the most obvious. The adsorption mechanism of EM inhibitor on the surface of barite was discussed by Zeta potential and infrared. The results showed that the naphthalene ring in EM and the S = 0 group in sulfonate produced complexation reaction on the surface of barite, which strongly hindered the adsorption of collector sodium oleate on its surface. Therefore, the inhibitor EM had the strongest selective inhibition effect on barite, thus realizing the flotation separation of barite and other minerals. The mechanism diagram of EM adsorption on barite surface is shown in the Fig. 18.

In the study of comprehensive recovery of barite and fluorite from a tailings in Yunnan by Long et al. (2022), a fluorite concentrate with a grade of 95.61% and a recovery of 82.14% and a barite concentrate with a grade of 94.01% and a recovery of 77.83% were obtained by using a self-made inhibitor BFN-3 in a full flotation closed circuit process. The comprehensive utilization of resources is realized. Zhou et al. (2017) studied the associated ore of high calcium fluorite-barite, used the compound high-efficiency reagent EMY-326F as the barite inhibitor, and obtained the barite concentrate with grade of 89.03% and recovery of 81.95% by the process of mixed flotation-rock table gravity separation, and achieved good beneficiation indexes.

Xiao et al. (2023) and others used different types of inhibitors to study the recovery rate of barite. The results showed that the grade change of barite was blank > maltodextrin > tannin > caustic starch > new inhibitor KP. Therefore, the new inhibitor KP is used as a barite inhibitor, which can effectively reduce the content of barite in fluorite concentrate and greatly improve the recovery rate of fluorite.

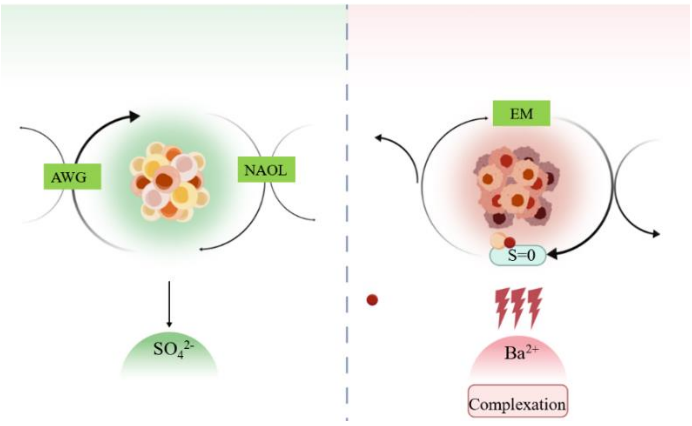


Fig. 24. Mechanism of EM and sodium oleate on mineral surface

4. Conclusion

China's barite resources are abundant, but the resource grade is low and the properties are complex. The physical and chemical properties of its gangue minerals are similar to those of barite ore, so it is difficult to separate barite by flotation. How to efficiently and comprehensively utilize associated barite ore is a key problem to be solved in the future.

The flotation method has a good separation effect, but the cost is high, and a large amount of flotation agent is needed. After the beneficiation operation, it is also accompanied by the problem of waste liquid treatment. Therefore, the development of efficient, selective and environmentally friendly flotation agents is the development trend of flotation technology in the future. At present, the utilization rate of barite can be improved by introducing other elements or functional groups, changing the molecular structure, and the synergistic effect and co-adsorption between combined flotation agents.

Some flotation mechanism research is not deep enough, and related theories need further study. Therefore, molecular simulation software, flotation solution chemistry, surface dissolution calculation and other methods can be used to explain the flotation mechanism with the help of modern detection methods (quartz Tianping), so as to expand the development scope of low-grade barite mineral resources.

Acknowledgements

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