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FROM TRADITIONAL TO GREEN: EVOLUTION OF SHALE SWELLING INHIBITORS FOR SUSTAINABLE DRILLING

(Daripada Tradisional Ke Hijau: Evolusi Pencegahan Pembengkakan Syal Untuk Penggerudian Lestari)

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Abstract

The occurrence of shale swelling during water-based drilling operations poses substantial challenges to the stability of shale formations. Clay layer expansion is the primary cause of shale swelling, which results from interactions between clay minerals and drilling fluid components. The degree of expansion is determined by variables such as clay composition, ion exchange processes, osmotic pressure, ionic strength, temperature, and pressure. Therefore, this study explores various shale swelling inhibitors and meticulously investigates the underlying mechanisms. The effectiveness of conventional inhibitors, such as potassium chloride (KCl), ammonium chloride (NH_4Cl), and amine-based inhibitors, is well-established. However, it is important to note that these inhibitors do have certain limitations. Hence, the present work investigates a range of environmentally friendly inhibitors, including graphene oxide, ionic liquids, deep eutectic solvents, nanoparticles, nanocomposites, and biosurfactants. Graphene oxide exhibits notable efficacy in mitigating shale swelling and producing extensive, unbroken protective coatings. Ionic liquids, represented by 1-butyl-3-methylimidazolium chloride (BMIMCl), have demonstrated enhanced inhibitory characteristics in comparison to KCl, resulting in a reduction in bentonite swelling rates by 19.38%. Furthermore, it has been observed that deep eutectic solvents (DESs), such as NADES, exhibit remarkable inhibitory characteristics, resulting in a 49.1-62.8% reduction in the rate of swelling in clay samples. Nanocomposites, which involve the integration of single-walled carbon nanotubes (SWCNTs) and polyvinylpyrrolidone (PVP), have demonstrated successful mitigation of shale swelling and regulation of fluid loss. Moreover, biosurfactants such as chitosan-grafted l-arginine, flaxseed protein (FP), and flaxseed mucilage (FM), have exhibited potential as shale inhibitors that are both biodegradable and environmentally friendly. These findings contribute to ongoing efforts to improve the environmental sustainability of drilling operations and adhere to rigorous environmental protection standards. Nevertheless, more investigation, refinement, and practical application analysis are needed before they can be widely used.

Keywords: water-based drilling fluid, shale formation, shale swelling, inhibitors, environmentally friendly

Abstrak

Kejadian pembengkakan syal semasa operasi penggerudian berasaskan air menimbulkan cabaran besar kepada kestabilan pembentukan syal. Pengembangan lapisan tanah liat adalah punca utama pembengkakan syal, yang terhasil daripada interaksi antara mineral tanah liat dan komponen bendalir penggerudian. Tahap pengembangan ditentukan oleh pembolehubah seperti komposisi tanah liat, proses pertukaran ion, tekanan osmotik, kekuatan ion, suhu, dan tekanan. Oleh itu, kajian ini meneroka pelbagai perencat pembengkakan syal dan menyiasat dengan teliti mekanisme asas. Keberkesanan perencat konvensional, seperti kalium klorida (KCl), ammonium klorida (NH_4Cl), dan perencat berasaskan amina, adalah mantap. Walau bagaimanapun, adalah penting untuk ambil perhatian bahawa perencat ini mempunyai batasan tertentu. Oleh itu, kajian ini menyiasat pelbagai perencat mesra alam, termasuk graphene oksida, cecair ionik, pelarut eutektik dalam, nanopartikel, nanokomposit dan biosurfaktan. Grafin oksida mempamerkan keberkesanan yang ketara dalam mengurangkan pembengkakan syal dan menghasilkan salutan pelindung yang luas dan tidak pecah. Cecair ionik, yang diwakili oleh 1-butil-3-metilimidazolium klorida (BMIMCl), telah menunjukkan ciri-ciri perencatan yang dipertingkatkan berbanding dengan KCl, mengakibatkan pengurangan kadar pembengkakan bentonit sebanyak 19.38%. Tambahan pula, telah diperhatikan bahawa pelarut eutektik dalam (DES), seperti NADES, mempamerkan ciri-ciri perencatan yang luar biasa, mengakibatkan pengurangan 49.1-62.8% dalam kadar bengkak dalam sampel tanah liat. Nanokomposit, yang melibatkan penyepaduan tiub karbon berdinding tunggal (SWCNTs) dan polivinilpirolidon (PVP), telah menunjukkan kejayaan pengurangan bengkak syal dan pengawalan kehilangan bendalir. Selain itu, biosurfaktan seperti kitosan yang dicampurkan bersama l-arginin, protein biji rami (FP), dan lendir biji rami (FM), telah mempamerkan potensi sebagai perencat syal yang boleh terbiodegradasi dan mesra alam. Penemuan ini menyumbang kepada usaha berterusan untuk meningkatkan kelestarian alam sekitar operasi penggerudian dan mematuhi piawaian perlindungan alam sekitar yang ketat. Namun begitu, lebih banyak penyiasatan, penghalusan, dan analisis aplikasi praktikal diperlukan sebelum ia digunakan secara meluas.

Kata kunci: cecair penggerudian berasaskan air, batuan syal, pembengkakan syal, perencat, mesra alam sekitar

Introduction

Oil drilling is a challenging industrial process for finding and extracting hydrocarbon resources such as crude oil and natural gas. It entails drilling a borehole or wellbore through the earth's crust to reach reservoirs containing these valuable resources. The fundamental goal of oil drilling is to extract these resources safely and efficiently for use in a variety of applications such as energy production, transportation, and petrochemical manufacturing. To facilitate this process, drilling fluids plays a pivotal role. Drilling fluids, often known as drilling muds, are multipurpose fluids that are essential to the oil and gas drilling industry. These specialty fluids are painstakingly designed to accomplish a variety of critical duties during the drilling operation. Drilling fluids operate as cooling and lubricating agents while the drill bit bores into the earth's crust, minimizing the adverse effects of heat and friction on the drill bit. At the same time, they efficiently transport the rock cuttings generated during drilling, preventing obstructions, and keeping a clear wellbore. Drilling fluids also play an important role in preserving wellbore stability by exerting hydraulic pressure on the wellbore walls, preventing the entrance of formation fluids, which could cause well control concerns and blowouts. By preserving the integrity of cuttings for examination, they enable geologists and geophysicists to examine subsurface formations. Additionally, drilling fluid density is altered to give the drill string buoyancy, preventing it from getting stuck in the wellbore and promoting efficient drilling operations. In addition, these fluids contain corrosion inhibitors to protect drilling equipment and minimize formation damage, making them essential to the oil and gas industry's pursuit of safe, efficient, and environmentally responsible drilling practices.

Essential to the oil and gas drilling process, drilling fluids comprise a wide variety of formulations tailored to specific well conditions. These fluids are divided into three primary categories. First, water-based drilling fluids use water as their primary base fluid, which is frequently combined with additives. These compounds, which may include clays, polymers, and salts, serve to improve the viscosity, lubrication, and shale inhibition properties of the fluid. Second, oil-based drilling fluids use oil as their base fluid. These fluids are highly valued for their resistance to high-temperature and high-pressure drilling environments and their ability to provide superior lubrication for the drill bit. Lastly, gas-based drilling fluids, such as air or nitrogen, employ gases as the base fluid. They excel in specific drilling scenarios, such as excavating coalbed methane. The selection of drilling fluid type is influenced by geological formations, well conditions, and environmental factors, and selecting the optimal formulation is essential for optimizing drilling performance and ensuring wellbore stability [1]. Each type provides a distinct combination of ingredients and functions to address the difficulties encountered during drilling operations.

In addition to the three main categories of drilling fluids, there is another important category known as synthetic drilling fluids. Synthetic drilling fluids, also known as synthetic-based muds (SBMs), are composed of synthetic or man-made base fluids as opposed to conventional oil or water. These base fluids can include esters, olefins, and other hydrocarbons that are synthetic. Drilling operations benefit from several advantages when synthetic drilling fluids are used. They are highly stable at elevated temperatures, making them ideal for excavating in high-temperature environments, such as offshore deep wells. Additionally, synthetic fluids have excellent lubricating properties, reducing equipment wear and extending their lifespan. Moreover, they have less of an impact on the environment than oil-based lubricants because they do not contain crude oil. When drilling through sensitive formations where contamination from conventional drilling fluids could cause significant damage, synthetic drilling fluids are particularly advantageous [2]. Synthetic drilling fluids are a valuable option for optimizing drilling performance while mitigating environmental impact in certain drilling scenarios due to their adaptability, stability, and environmental benefits. However, synthetic drilling fluids can be more expensive than their conventional equivalents, which can impact their selection based on the budget and drilling conditions of a project.

Particularly when considering the sustainability and environmental impact of drilling operations, the significance of water-based drilling fluids which consist predominantly of water as their base fluid, has risen in popularity. As industry endeavors to reduce its carbon footprint and minimize drilling's environmental impact, water-based fluids have emerged as a sustainable solution. However, water-based drilling fluids present their own set of challenges particularly when drilling through shale formations, where problems such as shale swelling can compromise wellbore stability [3]. Shale formations are characterized by their high concentration of clay minerals, notably smectite and montmorillonite clay minerals, which are recognized for their swelling properties. When drilling fluids containing water meet clay minerals, the water is absorbed, causing the clay to expand. This expansion, also known as shale swelling, can exert pressure on the wellbore walls and result in a few problems. Increased pore pressure within the formation can result in wellbore instability, which can lead to wellbore expansion and other problems such as blocked pipe incidents, lost circulation, and decreased drilling efficiency. Inefficient cuttings conveyance may also exacerbate drilling challenges. To combat these issues, shale inhibitors or shale stabilizers are added to water-based drilling fluids by the drilling industry. These additives are designed to minimize the interaction between the drilling fluid and shale minerals, thereby reducing swelling and sustaining the stability of the wellbore.

Shale swelling inhibitors are chemical additives used to combat the swell of clay minerals in shale formations during drilling operations. Potassium chloride (KCl) and amine-based inhibitors are two popular types of traditional shale swelling inhibitors. KCl prevents clay swelling by increasing the ionic strength of the drilling fluid, thereby decreasing the water absorption capacity of clay minerals. On the other hand, amine-based inhibitors function by adsorbing onto clay surfaces and modifying their chemical properties to render them less susceptible to hydration. Although these inhibitors have historically played a role in sustaining the stability of the wellbore, they have significant limitations related to conventional drilling methods. The release of KCl and certain amine-based inhibitors can contaminate soil and water, raising environmental concerns about the sustainability of these conventional approaches. In addition, these inhibitors may not function optimally under high-temperature or high-pressure drilling conditions, restricting their applicability for modern unconventional resources. There is also limited compatibility with some drilling fluid formulations containing polysaccharides or polyanionic cellulose, further reducing the scope of usable formulations. The high cost of these traditional inhibitors additionally influences selection criteria, driving demand for more affordable shale swelling options.

To mitigate these drawbacks, the industry has shifted focus toward more sustainable and environmentally friendly approaches that align with stringent environmental regulations. The "green criteria" for new shale swelling inhibitors place priority on reduced toxicity, biodegradability, and minimizing environmental impact. This context encompasses not only environmental sustainability but also improved performance and adaptability under diverse drilling conditions. Alternatives like Graphene Oxide (GO) demonstrate promise for reducing shale swelling with less risk of ecological damage. Ionic Liquids (ILs) boast superior inhibition properties and a lower environmental footprint compared to conventional options. Emerging solvents like Deep Eutectic Solvents (DESs) effectively prevent swelling. Furthermore, biosurfactants, nanomaterials, and natural biomolecules offer environmentally conscious solutions to promote wellbore stability with minimal toxicity.

Shale swelling mechanism

The enlargement of shale during drilling with water-based drilling fluids is a complex process governed by several interrelated factors. Shale swelling is triggered when shale is exposed to drilling fluid with a different chemistry that causes clay minerals to absorb and adsorb water [4]. This typically occurs when shale formations that were confined in situ underground at high stresses are excavated and exposed to surface conditions or water infiltration. At the molecular level, as pore waters and moisture infiltrate into the shale, water molecules first get attracted to and bonded to the surfaces of clay mineral particles like montmorillonite or illite. These clays have an affinity for water and the additional mass intake causes them to expand their layered structures. These interactions between water and clay minerals are crucial to the phenomenon of shale expansion [5]. According to Alcázar-Vara and Cortés-Monroy, shale swelling occurs in three distinct stages: stage 1: surface hydration and inter-crystalline swelling; stage 2: intra-crystalline swelling from moisture ingress between mineral layers and stage 3: osmotic swelling from diffused double-layer expansion [6].

When shale comes into contact with water, the first stage of swelling occurs through capillary absorption of the water into the pores between the clay mineral particles (inter-crystalline pores) as shown in Figure 1. This stage corresponds to inter-crystalline swelling. As the water molecules enter the pores, they become attached to the surface of the clay mineral particles through hydrogen bonding and other surface forces. In sodium montmorillonite clay, the water dipoles readily attach to the siloxane cavities exposed on the edges of the clay mineral layers, as well as to cations like Na^+ adsorbed on the surface. The affinity for water absorption depends on the specific surface area available for bonding and the nature of the interchangeable cations present. Cations like Ca^{2+} attract fewer water molecules than cations like Na^+. The absorbed water forms a hydration shell around the particles, forcing them apart and leading to volumetric expansion and inter-crystalline swelling. The rate and amount of swelling depend on factors like the permeability of the shale, the availability of surface area for water bonding, shale mineralogy, and cation exchange capacity. Tight shales with low permeability and surface area tend to absorb less water and swell less. Highly reactive shales containing montmorillonite as the predominant clay mineral, with high cation exchange capacity, tend to imbibe larger amounts of water and exhibit greater inter-crystalline swelling.

The second stage of swelling occurs as water penetrates between the layered structural packets within the clay mineral particles themselves, known as intra-crystalline swelling. This process is most significant in smectite group clay minerals like montmorillonite, where the layered packets are held together only by relatively weak van der Waals forces. For instance, in montmorillonite clay, water dipoles can penetrate between the 2:1 layered silicate sheets that make up its structure. The extent of penetration and separation of the sheets depends heavily on the exchangeable cations present. Sodium montmorillonite will hydrate extensively, with unlimited swelling possible as water freely enters the interlayer spaces. On the other hand, calcium montmorillonite has limited swelling due to the stronger binding of Ca^{2+} ions holding the sheets more tightly together. The intrusion of water leads to an increase in the basal spacing between the stacked sheets and a many-fold volumetric expansion - the intra-crystalline swelling. The presence of even small amounts of swelling clays like montmorillonite in shale can result in substantial overall swelling behavior.

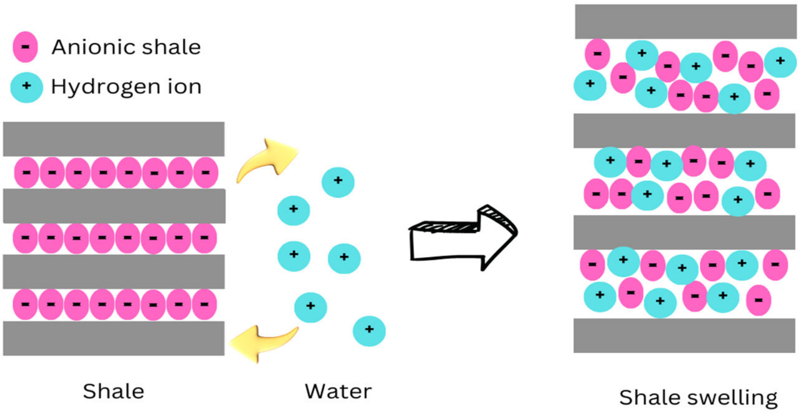

Figure 1. Surface hydration or inter-crystalline swelling

For the last stage, the introduction of water into the shale also induces osmotic pressure within the clay structure [7]. This osmotic pressure forces more water into the interlayer spaces, causing the clay layers to separate and swell. The degree of swelling increases as the osmotic pressure created by the drilling fluid rises, which is affected by variables including water content and salt concentration [8]. The ionic strength of the drilling fluid, which is determined by the concentration of salts such as potassium chloride (KCl) and calcium chloride ($CaCl_2$), can substantially influence the behavior of shale swelling [9]. The negatively charged surfaces of shale minerals attract positively charged ions or cations present in the drilling fluid. This exchange process results in the adsorption of cations onto the surfaces of clay minerals, which causes the clay strata to expand. Due to this, the distance between the strata grows, which contributes to the swelling effect [10]. Nevertheless, it was reported that higher salt concentrations in the drilling fluid somehow diminish the water's ability to permeate clay layers, thereby mitigating swelling to some extent [11]. Moreover, it was found that temperature and pressure also play a significant role in shale swelling. In a wellbore, elevated temperatures and pressures can intensify the absorption of water by shale minerals and the concurrent expansion of clay layers. These downhole conditions can have a significant effect on the amount of shale swelling encountered during drilling [12, 13]. Therefore, chemical inhibitors, such as surfactants or polymers, are frequently included in drilling fluid formulations to combat shale expansion issues. These shale inhibitors alter the surface properties of the shale, reduce water absorption, and prevent clay layers from expanding, as shown in Figure 2. By understanding the relevant factors, drilling engineers and fluid specialists can devise more effective strategies for combating shale swelling and preserving wellbore stability. It was concluded that the rate and magnitude of volume expansion depend on shale mineralogy, permeability to water, and pore pressures. This information guides the selection and formulation of drilling fluid additives intended to inhibit shale swelling. In addition, it permits the optimization of drilling parameters, such as temperature and pressure, to minimize the amount of edema encountered during operations. The ultimate objective is to improve drilling efficiency, reduce operational difficulties, and ensure the safety and integrity of wellbore systems. In addition, this understanding contributes to ongoing efforts in the oil and gas industry to develop environmentally sustainable drilling practices by minimizing the environmental impact of shale swelling and the use of drilling fluid additives.

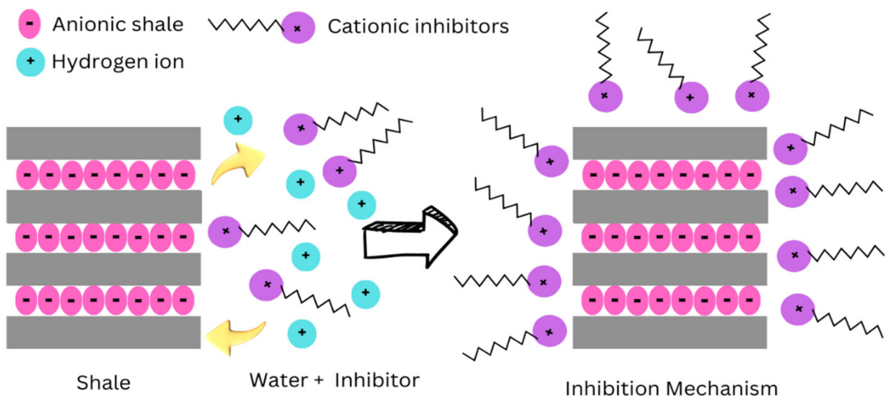

Figure 2. Shale inhibition mechanism by shale swelling inhibitors

Traditional shale swelling inhibitors

Potassium chloride (KCl) is the earliest and most extensively used shale swelling inhibitor for water-based drilling fluids. KCl inhibits the swelling of shale through an ion exchange mechanism. It does this by exchanging the Na^+ ions in the montmorillonite clay layers with K^+ ions that are weakly hydrated, as shown in Figure 3. This exchange of ions decreases the clay's affinity for water, preventing expansion and preserving the wellbore's integrity. Previously, it was found that by using KCl as the shale inhibitor, the activity of the drilling fluid increased, and the contact angles between the fluid and the shale increased, indicating a higher absorption rate [14]. According to the study, the ability of the drilling fluid to inhibit was inversely proportional to its ability to hydrate the surface. Osmotic hydration data showed that the shale had the lowest negative extreme swelling ratio with KCl, indicating its superior inhibitory effect, while the KCl drilling fluid displayed the highest surface adsorption rate. Moreover, another study found that KCl had an inhibitory effect on the mechanical properties of the samples, increasing their compressive strength and elastic modulus while decreasing their Poisson's ratio [15]. However, the results demonstrated that the clay content and presence of microcracks and bedding fissures in shale had a significant impact on the inhibitory effect of KCl on hydration. In addition, it was found that the relationship between KCl concentration and expansion rate is negatively exponential [16]. As the KCl concentration increased, the swelling rate decreased. When the concentration of KCl was 6%, the rate of swelling tended to be stable. The ultimate rate of swelling decreased from roughly 2% to 0.5% as shown in Figure 4. This high concentration increased the density of the drilling fluid, making it less suitable for use under specific drilling conditions.

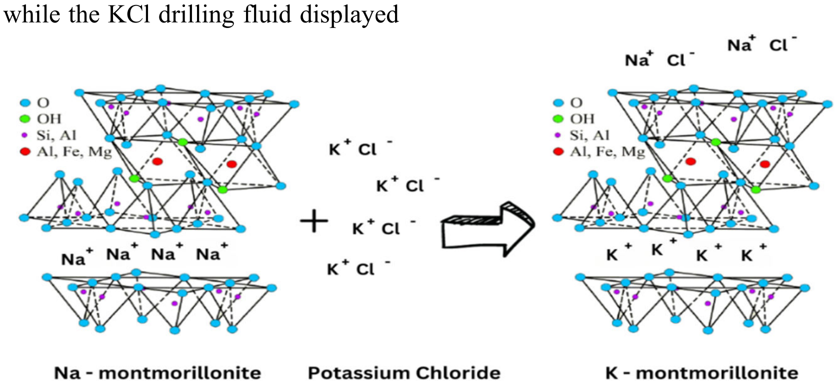

Figure 3. The replacement of Na^+ with K^+ within the montmorillonite structure

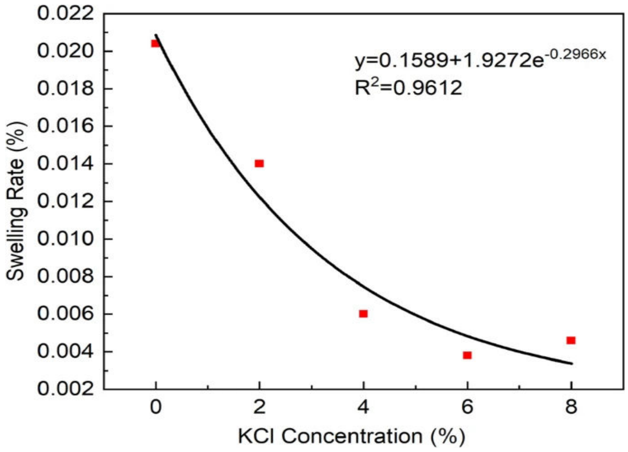

Figure 4. Final swelling rate of mudstone samples in relation to KCl concentration [16]

As a result of these limitations, various possible replacements for KCl have been investigated. Ammonium chloride (NH_4Cl), in contrast, functions as a shale inhibitor by facilitating the exchange of ammonium ions with the cations present on the surface of clays [17]. This ion exchange aids in preventing clay hydration and subsequent swelling. The NH_4^+ ion from NH_4Cl can replace Na^+ and other cations between the layers of the clay minerals. Since NH_4^+ has a lower hydration energy and tendency to attract water molecules compared to Na^+, the overall water uptake by the clay is reduced, thereby diminishing the swelling potential. According to a previous study, NH_4Cl is notably effective in stabilizing clays that are sensitive to potassium ions [18]. Moreover, NH_4Cl helps to establish an osmotic balance between the drilling fluid and the shale formation [19]. By controlling the water activity in the drilling fluid, the drive for water molecules to move into the shale and cause swelling is reduced. The presence of NH_4^+ ions also stabilized the clay structure by reducing the repulsive forces between the clay platelets [20]. This contributes to a reduction in the swelling and dispersion of the clays. Nevertheless, despite its benefits, the environmental impact of NH_4Cl, particularly its potential to contribute to eutrophication, and its corrosive nature are significant concerns. To surmount these issues, NH_4Cl is often used alongside corrosion inhibitors and advanced waste management techniques to minimize its environmental footprint.

The investigation of ammonium cations with similar hydration volumes to potassium ions (K^+) is a prominent strategy. This research led to the development of a variety of amine-based shale inhibitors, including polyetheramine, polyetherdiamine, polyvinylamine, and quaternary amine compounds. Amine-based shale inhibitors have emerged as a prospective alternative to potassium chloride (KCl) in water-based drilling fluids due to their ability to inhibit shale swelling effectively while mitigating some of the environmental concerns associated with KCl. Polyamines are particularly effective in inhibiting the swelling of smectite clays commonly found in shale formations. They work by adsorbing onto clay surfaces and neutralizing the charges that cause clay particles to repel each other and swell. In addition, amine-based inhibitors can inhibit shale at lower concentrations than KCl, which can aid in mitigating problems associated with drilling fluid density and disposal. Previously, the function of polyether amine as a shale inhibitor in the production of shale hydrocarbons has been studied [21]. The study demonstrated that the pH of polyether amine solution can influence its shale-inhibiting properties. Besides, it was found that polyether amine-derived bis-quaternary ammonium salt demonstrated superior shale inhibition performance compared to conventional stabilizers. The mechanism entails strong adsorption, an increase in hydrophobicity, and the reduction of clay particle repulsion by positive charges. This research provided an effective shale inhibitor, which is crucial for the efficient and sustainable development of shale gas and hydrocarbons. Moreover, the application of ammonium-malic salts (AMS) as inhibitors for shale swelling has also been investigated [22]. The compound AMS-9, which was synthesized using malic acid and tetraethylenepentamine, demonstrated remarkable effectiveness in inhibiting the expansion of bentonite hydration. The addition of this substance resulted in a notable decrease in both the swelling and dispersion of bentonite within the water-based drilling fluid with the swelling rate dropping to 57.14% at a concentration of 0.5% AMS-9. According to this study, the inhibitory mechanism of AMS-9 on bentonite is likely attributed to the process of ion exchange between ammonium and Ca^{2+}, as well as the formation of hydrogen bonds and surface modifications. Furthermore, the potential of ammonium adipate solutions (AASs) as inhibitors for the phenomenon of shale swelling has also been studied [23]. The results showed that AAS-8 exhibited significant inhibitory effects on the hydration and swelling of clay. The substance exhibited the ability to regulate alterations in particle size inside bentonite and showed compatibility with additives such as carboxymethyl cellulose (CMC) and modified starch in water-based drilling fluids.

Nonetheless, the disposal of significant quantities of amine-containing drilling fluid can have negative environmental effects, including the disruption of ecosystems and the contamination of groundwater. In addition, certain amine compounds may have adverse effects on the rheological properties of the drilling fluid, which may affect drilling performance. Proper disposal procedures and monitoring are required to ensure that the use of amine-based inhibitors does not result in environmental contamination or damage to ecosystems. In response to the environmental and toxicity issues associated with amine-based inhibitors, there has been a growing interest in researching environmentally benign and low-toxicity shale inhibition alternatives over the past few years. As prospective shale inhibitors, researchers and industry are investigating various materials, including nanomaterials, ionic liquids, natural plant extracts, and other innovative compounds. These options seek to inhibit shale effectively while minimizing toxicity and environmental impact. The ongoing research in this area reflects a broader commitment to enhancing the environmental sustainability of drilling operations and conforming to more stringent environmental protection policies.

Green shale swelling inhibitors

Graphene oxide

Graphene oxide (GO) is a notable environmentally friendly shale swelling inhibitor that has garnered prominence in recent years. Graphene oxide is an oxidation of graphene that has demonstrated potential for mitigating shale expansion while minimizing environmental impact. In shale formations, GO particles readily adsorb onto shale clay mineral surfaces due to their hydrophilic groups and large area. Once adsorbed, the graphene oxide forms extensive hydrogen bonds and van der Waals forces, adhering tightly to the shale. This also allows the graphene oxide to act as a physical barrier that obstructs nano-sized pores and interlayer spacing between clay mineral platelets. By hindering water molecule intrusion, graphene oxide mitigates the swelling and dispersion of clay components. Additionally, graphene oxide imparts hydrophobicity to the shale surface, further diminishing the affinity of clays to hydrate and swell when contacting aqueous drilling fluids. Through this multipronged mechanism of physical obstruction of nanopores, hydrogen bonding, and hydrophobic modification, graphene oxide can effectively suppress shale swelling when used as an inhibitor additive. Significant reductions in shale swelling have been observed in various studies utilizing GO as a shale inhibitor, yielding encouraging results, as shown in Figure 5. The study demonstrated the ability to plug nano-sized pores, prevent water intrusion into shale, and prevent clay mineral swelling [24]. According to the findings of his study, GO exhibited superior performance to conventional inhibitors, forming a large, uninterrupted film to protect shale and adapting to various shale pore morphologies. Based on this foundation, glucopyranose-modified graphene (Glu-Gr) as a shale swelling inhibitor has also been studied [25]. The study revealed the exceptional dispersion recovery and inhibition durability of Glu-Gr, which surpasses conventional drilling mud. The mechanism of Glu-Gr, which is characterized by scanning electron microscopy (SEM) and X-ray diffraction spectroscopy (XRD), relies on establishing hydrogen bonds, physically obstructing clay nanopores, and preventing water penetration, thereby diminishing shale swelling.

Moreover, *Janus amphiphilic* graphene oxide (JAGO) has also been used as a high-performance and dual-functionality shale swelling inhibitor [26]. It was found that the distinctive amphiphilic structure of JAGO, obtained by dodecylamine modification, has exceptional chemical inhibition and physical plugging properties. The effectiveness of JAGO derives from its capacity to adsorb onto clay surfaces, expel water molecules, and generate hydrophobic shields. In addition, choline chloride-modified graphene (Ch-G) has also been used as an eco-friendly and effective shale inhibitor [27]. The study demonstrated the inhibition mechanism, which includes hydrogen bonds, coordination, and electrostatic interactions with clay surfaces, thereby inhibiting shale expansion. Because of graphene's high performance, it has also been employed as a fluid additive [28, 29]. The use of silica nanoparticles (SiO_2-NPs) and graphene nanoplatelets (GNPs) as additives in drilling fluids exhibited synergistic effects, improving filtration properties, enhancing thermal stability, and increasing the fluid's ability to inhibit shale-related challenges. Collectively, these studies demonstrate the transformative potential of nanomaterial-based shale inhibitors, which offer innovative and environmentally friendly methods for ensuring wellbore stability in shale formations while minimizing environmental impact. While graphene oxide offers a novel approach to inhibiting shale swelling by physically blocking water absorption and chemically interacting with clay minerals, there remain significant economic and environmental challenges to its widespread adoption in the field. Research is ongoing to overcome the cost barriers, ensure environmental safety, and maintain operational stability and compatibility within drilling fluid systems. Through innovation and rigorous testing, the goal is to optimize the use of GO in drilling operations, harnessing its unique properties to enhance wellbore stability and efficiency.

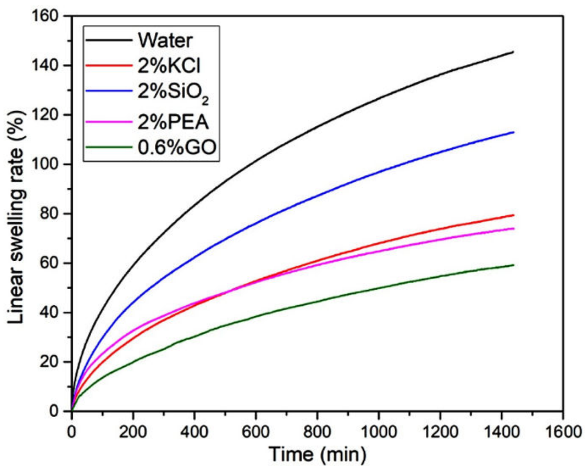

Figure 5. Linear swelling rate of Na-BT pellets in pure water, KCl, nano-SiO_2, PEA, and GO aqueous solutions [24]

Ionic liquids (ILs)

Aside from that, ionic liquids (ILs) have also emerged as an environmentally favorable option for reducing shale swelling in water-based drilling fluids. The mechanism by which ionic liquids inhibit shale swelling involves several interactions. They can replace water in the interlayer spaces of clay minerals through cation exchange, thus reducing the clay's ability to absorb water and swell. Additionally, the hygroscopic nature of ionic liquids can lower the activity of water in the drilling fluid, and their adsorption onto clay surfaces can alter the surface chemistry to further reduce swelling. In addition, ILs have garnered attention for their low toxicity and eco-friendly properties, making them a desirable option for sustainable drilling practices. Previously, the use of 1-butyl-3-methylimidazolium chloride (BMIMCl) as an inhibitor of clay expansion has been investigated [30]. It was found that BMIMCl exhibited superior inhibitory properties than the conventional stabilizer KCl, decreasing bentonite swelling rates by 19.38%. FT-IR analysis confirms that this enhanced performance is due to the unique structure of BMIMCl, which features a hydrophilic head for adsorption on bentonite surfaces, hydrogen bonding, and a hydrophobic tail to create a water-repellent shield. Besides, the use of hydrophobic ILs in conjunction with gemini surfactants to prevent clay expansion has also been studied [31]. A novel combination of hydrophobic ionic liquid (trihexyltetradecyl phosphonium bis(2,4,4-trimethyl pentyl) phosphinate) and cationic gemini surfactant (GB) enhanced inhibition efficiency.

Contact angle measurements revealed a highly hydrophobic surface and linear swelling experiments indicate that the combined solution reduces bentonite swelling. This innovative technique improves wellbore integrity in drilling applications involving high temperatures. Besides, the used of multibranched ionic liquid (Trihexyltetradecyl phosphonium bis(2,4,4-trimethyl pentyl) phosphinate, Tpb-P) in water-based drilling fluid exhibited enhanced shale recovery and reduced linear swelling compared to conventional drilling fluids [32]. Contact angle measurements confirmed decreased shale surface hydrophilicity, and Tpb-P demonstrated the potential to maintain wellbore stability under high-temperature and high-pressure conditions. The results of these experiments demonstrated that the adsorption of ILs on clay minerals is dependent on their structure and concentration, leading to intercalation between clay layers. XRD analysis revealed increased basal spacing, implying IL intercalation, which was corroborated by FT-IR spectral data. The study provides insight into the inhibitory mechanisms and adsorption behavior of ILs on clay surfaces. Due to the unique properties of ILs, they have also been proposed as completion fluids to reduce formation damage. Moreover, experiments with core-flooding on confined sandstone formations with a high clay content demonstrated that completion fluids comprised of ionic liquids effectively stabilized clays, thereby preserving in-situ permeability [32]. These results indicated that completion fluids based on ionic liquids can be used for well completion without causing formation injury. This study was supported by using tetramethylammonium chloride (TMACl) and 1-ethyl-3-methylimidazolium chloride (EMIMCl). It was found that TMACl and EMIMCl ionic liquids outperformed the conventional inhibitor potassium chloride (KCl) [33]. TMACl exhibited superior inhibition due to its more positive charge, which facilitated adsorption and decreased clay enlargement. This study emphasized the importance of cationic and anionic components in ILs for shale inhibition.

SEM images revealed fewer cavities and a smoother clay surface when ILs were added, while XRD results indicated intercalation of ILs in clay layers. The type of anion also affected rheological properties, but clay swelling was not substantially affected. In comparison to a commercial clay inhibitor, ILs exhibited superior performance with fewer adverse effects on drilling fluid properties. These studies illuminate the diversity of ionic liquids and inhibitors, shedding light on their potential to revolutionize shale inhibition strategies, assure wellbore stability, and reduce environmental impact. Nevertheless, increasing the length of the alkyl chain increased the hydrophobicity of ILs, making it more challenging for ILs to minimize layer spacing and reduce water activity as shown in Figure 6.

Deep eutectic solvents (DESs)

Building upon the promising attributes of graphene and ionic liquids as environmentally benign swelling inhibitors for shale, numerous studies explore the effectiveness of deep eutectic solvents (DES) in a similar capacity. Deep Eutectic Solvents (DESs) are a class of fluids like ionic liquids but composed of a mixture of a hydrogen bond donor and a hydrogen bond acceptor, which can form a eutectic mixture with a melting point much lower than either of the individual components. DESs interact with clay minerals via solvation and ion exchange mechanisms, thereby decreasing the tendency of shale to swell. DESs can inhibit shale swelling effectively while exhibiting low toxicity and environmental impact. Previously, the novel deep eutectic solvent CU-DES as a potential shale inhibitor was studied [34]. From the study, it was seen that CU-DES exhibits remarkable inhibitory properties, outperforming conventional inhibitors such as KCl and PDA, especially at high temperatures (160°C). CU-DES substantially reduces the swelling rate of clay samples, increases the recovery of shale cuttings after hot-rolling, and inhibits clay hydration and dispersion. Analytical techniques, such as particle size distribution measurement, Zeta potential measurement, SEM, FTIR, and XRD, demonstrated that CU-DES exerts its inhibitory effects via electrostatic attraction and hydrogen bonding with clay minerals. The findings of this study indicated that CU-DES is a prospective and cost-effective shale inhibitor for water-based drilling fluids, addressing wellbore instability issues. Recent research on DESs as shale swelling inhibitors has also been thoroughly studied [35].

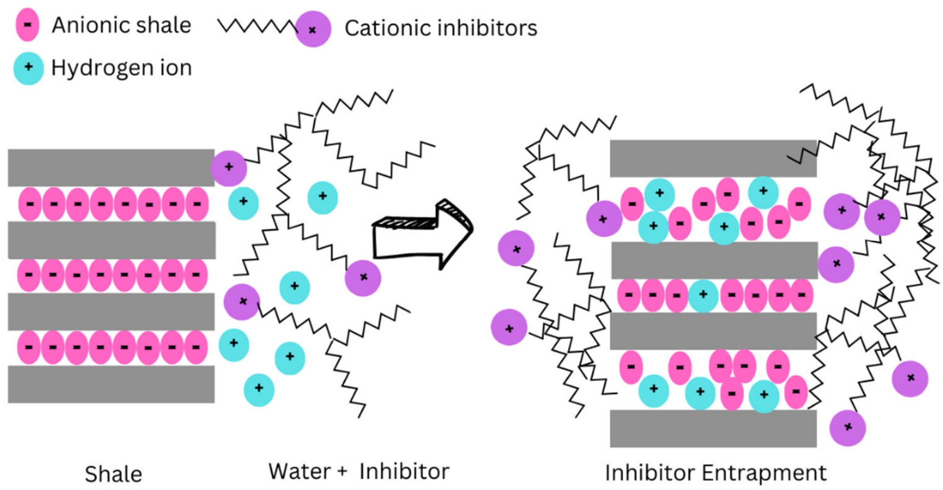

Figure 6. Inhibitor entrapment due to the length of the alkyl chain

Even at low concentrations, DESs exhibit extraordinary inhibitory performance, effectively reducing shale swelling. This study emphasizes the electrostatic attraction, hydrogen bonding mechanisms, and charge neutralization of clay surfaces. It highlighted the significance of comprehending DES-clay interactions for effective shale stabilization. As a drilling fluid adjuvant, a Natural Deep Eutectic Solvent (NADES) based on Epsom salt and glycerine was also introduced [36]. The results indicated that NADES significantly enhances the properties of drilling fluids. NADES reduces mudcake thickness by 26% and filtrate volume by 30.1% at a concentration of 1%. It inhibited the shale swelling by an impressive 49.14% due to hydrogen bonding and clay structure modification. The results of this study suggest that NADES could replace conventional inhibitors that are toxic and non-biodegradable. An extensive study using calcium chloride with NADES as a versatile drilling mud additive has also been done [37]. It was found that NADES improved mud rheology and inhibited hydrate formation by up to 80%, according to the findings. Moreover, it inhibited shale swelling by a remarkable 62.8% and enabled an 84.1% enhancement in shale recovery. These results are supported by surface tension, d-spacing, zeta potential, and FESEM analyses. This paper suggests that NADES is an environmentally favorable alternative to conventional additives, effectively addressing drilling operations' cost, biodegradability, and environmental impact issues. In comparison to conventional inhibitors, the results consistently demonstrate DES' superior inhibitory properties, cost-effectiveness, and environmental advantages. These results contribute to the advancement of environmentally sustainable drilling practices and highlight the need for additional research and optimization to realize their maximum potential in the industry.

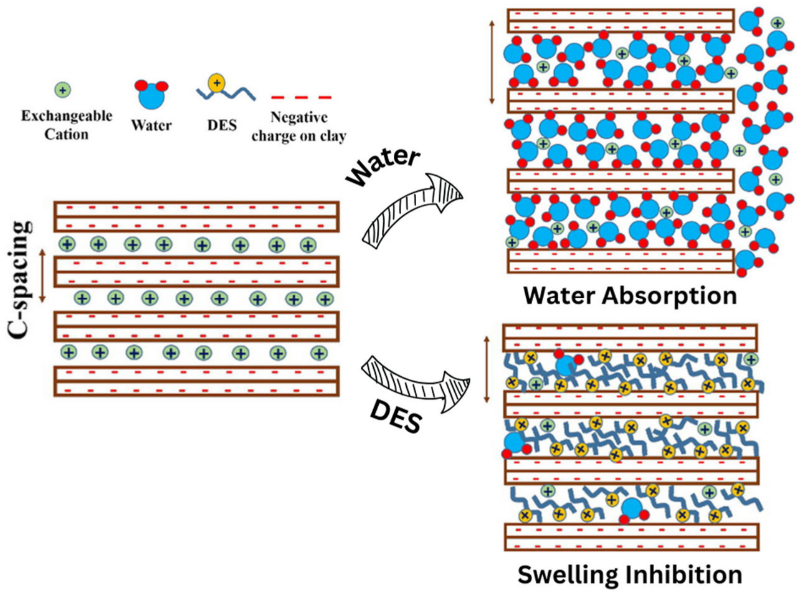

Figure 7. Shale swelling inhibition mechanism by using DES inhibitor [38]

Nanoparticles and nanocomposites

Similarly, numerous researchers have also conducted extensive studies on nanomaterials such as nanoparticles and nanocomposites. Nanoparticles and nanocomposites frequently perform their functions by adhering to clay surfaces and preventing water absorption. Figure 8 shows the surface of the shale sample using SEM. Their effectiveness in inhibiting shale swelling has been demonstrated, and their low environmental impact is encouraging. A novel method for enhancing the effectiveness of water-based drilling muds through the utilization of nanocomposites consisting of single-walled carbon nanotubes (SWCNTs) and polyvinylpyrrolidone (PVP) has been proposed [39]. The findings of their research demonstrated that the presence of 5-SWCNTs/PVP in the drilling fluid resulted in greater control of fluid loss and effectively reduced shale swelling. The combination of single-walled carbon nanotubes (SWCNTs) with polyvinylpyrrolidone (PVP) resulted in enhanced shale stability through the establishment of a protective barrier that effectively hindered the penetration of water. Additionally, the synergistic effect of ZnO nanoparticles and polymer additives in drilling fluids has also been investigated [40]. This study provided important insights into how the combination of these additives improves rheological properties, filtration control, and shale stability. The results indicated that this synergistic strategy significantly reduces shale swelling and enhances drilling fluid performance. Alternatively, the addition of two-dimensional nanoparticles, such as graphene and nanosheets, to water-based drilling fluids demonstrated that these nanomaterials significantly improve the rheological, viscoelastic, and filtration properties of drilling fluids while contributing to the stability of the wellbore [41]. In a recent study, the researchers examined the role of different nanoparticles in completion fluids [42]. The study specifically focused on the dual impact of these nanoparticles, which included both enhancing well stimulation and inhibiting clay swelling damage. The results of the study revealed that specific nanoparticles, specifically those possessing positive charges, could significantly enhance the mobility of crude oil and inhibit the swelling of clay. The study highlighted the importance of both the chemical composition and dosage of nanoparticles. Nevertheless, the necessity for further investigation to assess a broader range of nanoparticle categories and their performance in dynamic reservoir circumstances must be emphasized [43]. The study suggested delving deeper into the interactions between various nanoparticles and polymers to optimize their formulations for particular downhole conditions. Therefore, to fully exploit the benefits of nanoparticles in drilling fluids, future research should strive to bridge the gap between laboratory experiments and actual drilling operations.

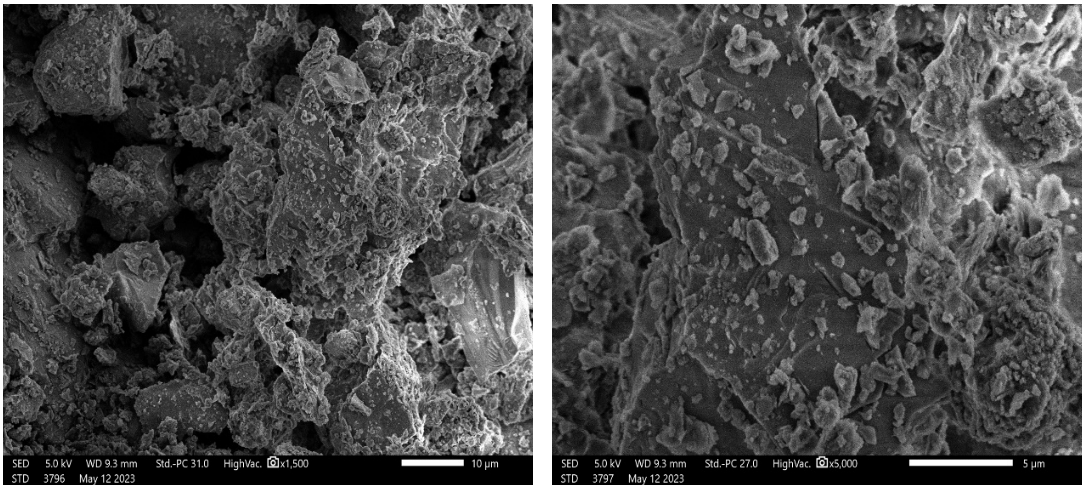

Figure 8. SEM images of the surface of shale taken at (a) 1500x resolution and (b) 5000x resolution

Biosurfactants

As eco-friendly shale inhibitors, biomolecules and biosurfactants derived from natural sources such as plants and microorganisms have been explored. Previously, a biodegradable and environmentally benign shale inhibitor based on chitosan-grafted l-arginine (CA) for shale formation was synthesized and used as a shale swelling inhibitor [44]. The results demonstrated that the inhibition of CA was superior to that of KCl, HPA, and SIAT, and that it can recover more than 90% of hot-rolled shale at 150 °C, indicating that CA has greater temperature resistance and prolonged durability. It was found that the positively charged CA effectively adhered to the surfaces of both MMT and shale, achieving multiple beneficial effects. It neutralized the negative charge associated with MMT, compacted the diffused electric double layer, and simultaneously enhanced the contact angle of both MMT and shale surfaces. This dual action resulted in an increased hydrophobicity of MMT and shale, effectively impeding their hydration enlargement and dispersion. Furthermore, compatibility experiments revealed that CA displayed compatibility with widely used treatment agents, demonstrating no impact on the rheology of water-based drilling fluids, and contributing to reduced fluid loss due to degradation.

Moreover, a fascinating investigation into the potential use of green and biodegradable surfactants, namely *Flaxseed Protein* (FP) and *Flaxseed Mucilage* (FM), as shale inhibitors in water-based drilling fluids has also been presented [45]. This research showed that these surfactants have the potential to reduce clay swelling and enhance drilling efficacy. The compatibility of these surfactants with salt (KCl) and their survivability under varying temperature conditions qualify them for further study. Nevertheless, the study suggests that future research should concentrate on optimizing the extraction methods to increase the yield and functionality of these surfactants, paving the way for more environmentally friendly drilling fluid additives. In addition, field-scale testing and compatibility evaluations with other drilling fluid components would shed light on the practical implementation of these surfactants in real-world drilling operations. Similarly, the feasibility of using Korean Red Ginseng root extract, rich in non-ionic surfactants, as a clay swelling inhibitor in water-based drilling muds has also been widely studied [46]. The research emphasized several distinctive properties of mud systems prepared with biosurfactants, including a low rheological profile, good sedimentation, and high recovery of shale cuttings. These characteristics demonstrated the efficacy of the biosurfactant in inhibiting clay swelling. The study also examined the mechanisms underlying this inhibition, proposing that the biosurfactant produces a hydrophobic layer on clay surfaces, thereby decreasing water absorption and clay swelling. Optimizing the performance of the biosurfactant and investigating its potential as an environmentally friendly drilling fluid additive could be the focus of future research. Future research could entail scaling up the use of plant or food waste extract biosurfactants to assess their performance under field conditions. For practical applications, investigating its long-term stability and potential interactions with other drilling fluid additives would also be essential. Additionally, investigating cost-effective methods for obtaining the biosurfactant on a larger scale would make its industrial application more feasible.

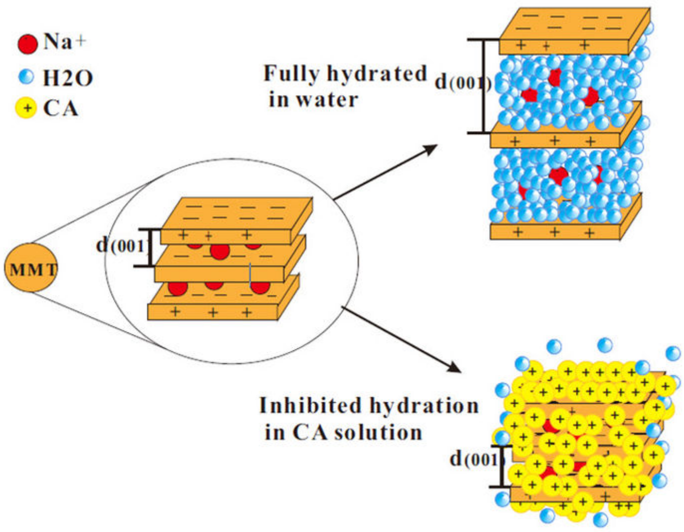

Figure 9. Inhibition mechanism of CA on shale surface [45]

Conclusion

In summary, the transition from conventional shale swelling inhibitors to environmentally friendly alternatives represent a significant paradigm shift within the drilling industry, highlighting the industry's commitment to conservation and environmental sustainability. Shale swelling, a common issue in drilling operations, is increasingly being handled using environmentally friendly inhibitors, which are replacing conventional options such as potassium chloride (KCl). The study has examined a range of environmentally friendly inhibitors, such as graphene oxide, ionic liquids, deep eutectic solvents, nanoparticles, nanocomposites, and biosurfactants. Graphene oxide, with its high surface area and functional groups, can interact with clay particles in shale to prevent water uptake. Ionic liquids and deep eutectic solvents (DESs) offer tunable properties that can be designed to reduce water activity and clay swelling without the environmental harm associated with inorganic salts like KCl. Nanoparticles and nanocomposites act at the nanoscale to block the pathways for water molecules or alter the surface chemistry of the clay minerals, preventing them from swelling. Biosurfactants, derived from biological processes, offer a biodegradable and less toxic alternative to traditional surfactants.

The transition to these greener inhibitors is not without challenges. There are concerns about cost, effectiveness under a range of geological conditions, potential health impacts, and long-term environmental effects. However, through ongoing research and development, improvements in these inhibitors are being made. Innovations in material science, chemistry, and engineering are leading to more effective and environmentally sustainable drilling practices. The use of environmentally friendly shale swelling inhibitors is a testament to the drilling industry's commitment to reducing its environmental footprint while still meeting global energy demand. By investing in these technologies, industry not only adheres to stricter environmental regulations but also contributes to the broader goal of sustainable development. Attention may also turn to the life cycle analysis of these inhibitors to ensure their sustainability from production to disposal. Additionally, the integration of digital technologies like AI and machine learning could revolutionize the selection and application of swelling inhibitors by optimizing their performance in real time and predicting their behavior under various geological conditions. Furthermore, collaborative efforts between industry, academia, and regulatory bodies will likely be pivotal in establishing standardized protocols for the assessment and implementation of these green inhibitors.

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