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Preparation of temperature-sensitive CMC-BENTONITE-NIPAM applied to deepwater drilling fluids

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ABSTRACT

Chemically modified bentonite has greatly improved its performance due to its structural adjustability. In this study, the modification of bentonite was accomplished through the method of sodium intercalation adsorption. The temperature-sensitive modified bentonite was prepared by initially sodifying bentonite with sodium carbonate and sodium pyrophosphate, intercalating CMC into the interlayer structure of sodified bentonite, and adsorbing N-isopropyl acrylamide (NIPAM) on the surface of bentonite. Further, the deep-water bentonite drilling fluid system was prepared. The optimal sodification conditions were determined by the single-factor control variable method of expansion volume as a drug-bentonite ratio of sodium carbonate of 1:9 and an addition amount of sodium pyrophosphate of 0.5%. The ratio of sodified bentonite to CMC drug-bentonite is 30:1. The addition amount of NIPAM was determined to be 0.5 g through the orthogonal experiment method of two factors of temperature and viscosity. Meanwhile, the temperature-sensitive modification mechanism and performance changes were analyzed through microscopic characterization and performance testing. The results show that the modified bentonite can play a significant temperature regulation role within the temperature range of 60°C and above, and the prepared drilling fluid system has good rheological properties under the condition of temperature change.

Keywords: Temperature-sensitive Polymer; Rheology; Modified bentonite; Deep water drilling fluid; Microscopic characterization.

1. INTRODUCTION

Chemically modified bentonite greatly improves its performance and quality, which is due to the structural control and performance designability of the modified bentonite [1]. Bentonite is a layered structure composed of silica tetrahedron and aluminum oxide octahedron [2]. Its structural unit layers are connected by intermolecular forces, and its structure is loose [3]. Because of its unique structure, it is easy to modify and realize the composite use with different materials, so that the performance of bentonite is improved [4]. Bentonite modification methods [5] include physical modification [6] (heat treatment, mechanical grinding, etc.), chemical modification [7] (sodium modification, organic modification, composite modification, etc.) and biological modification [8] (microbial metabolites, etc.). As an important branch of chemical modification, composite modification modifies bentonite by changing the interlayer structure and increasing surface adsorption, which changes the structure and properties of bentonite. For example, Qiu ZIHAN *et al.* [9] modified bentonite by cationic polyacrylamide intercalation, showing significant adsorption and suspension properties. QI *et al.* [10] modified bentonite with CMC, and used the semi dry method to make the ion bridge and group interaction between polymer and bentonite stronger, and the modification effect is better. Zhao XIA *et al.* [11] modified bentonite with acrylic acid and other polymers, and characterized the introduced groups. The results showed that ion exchange and adsorption increased the swelling and permeability of bentonite. ZHOU *et al.* [12] modified bentonite by using nanocomposites, and the results showed that such materials greatly improved the temperature resistance of bentonite. Yan ZHICHAO *et al.* [13] used cetyltrimethylammonium bromide, sodium dodecyl sulfate and polyhydroxy iron ions to intercalate modified bentonite. Through microscopic characterization research, it was found that the interlayer structure of intercalated modified bentonite had changed, and the adsorption was good.

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With the continuous expansion of drilling field, offshore drilling has become an important part of oil and gas exploration and development. However, when the operating water depth and total well depth are constantly changing, the significant changes of temperature and pressure bring great challenges to the control of drilling fluid rheology [14]. Therefore, researchers are committed to developing drilling fluid treatment agents that can maintain stability under extreme conditions. For example, DING *et al*. [15] synthesized a new type of temperature sensitive copolymer using temperature sensitive units N-vinyl caprolactam and N, N-dimethylacrylamide as raw materials. The experimental results show that the polymer can effectively control the rheology of drilling fluid and can withstand the changes of ocean temperature. CHEN *et al*. [16] used acrylamide, N-vinyl caprolactam, divinylbenzene and sodium allyl sulfonate as raw materials to prepare temperature sensitive thickening copolymers, which were compounded with soybean gum to prepare flow pattern regulators. The experimental results show that the drilling fluid has good temperature resistance and rheology, and can meet the needs of drilling. At the same time, modified bentonite [17] is also introduced into the drilling fluid as a rheological modifier to improve its rheological properties. For example, CUI [18] modified calcium bentonite by sodium intercalation, which increased the spacing of bentonite layers and made the layers loose; compared with calcium bentonite, it has strong temperature resistance and good rheological properties.

The research group has carried out bentonite modification related experiments before. PAN *et al*. [19] grafted N-isopropylacrylamide on the surface of sodium bentonite through the dehydration condensation of silane coupling agent, which improved the rheological properties and temperature sensitivity of bentonite, but the suspension property decreased. Meanwhile, by consulting and summarizing the domestic and foreign literature on the modification of CMC and NIPAM, it can be known from the following Tables 1 and 2 that NIPAM can design smart materials with different temperature response ranges by regulating LCST through copolymer monomers, and form composite materials with inorganic materials such as nano-clay and SiO_2. CMC has excellent thickening and suspension performance, effectively prevents sedimentation, and improves the toughness and durability of cement mortar. Therefore, this study combines the suspension characteristics of CMC intercalation modification [20] and the temperature sensitive characteristics of NIPAM [21], studies and develops modified bentonite materials with improved suspension and rheological properties. At the same time, it is applied to marine drilling fluid and its performance is tested.

2. EXPERIMENTAL MATERIALS AND METHODS

2.1. Experimental medicine and instruments

Experimental medicine: Calcium bentonite (Jianping Bright Bentonite Co., Ltd.), Anhydrous sodium carbonate (Tianjin Damao Chemical Reagent Factory), Sodium pyrophosphate (Tianjin Damao Chemical Reagent Factory), Sodium carboxymethyl cellulose (Zhengzhou Xinrui Fine Chemical Co., Ltd.), N-isopropyl acrylamide (Shanghai Macklin Biochemical Technology Co., Ltd.), OCMA grade drilling fluid bentonite (Jianping Bright Bentonite Co., Ltd.), Sodium chloride (Tianjin Damao Chemical Reagent Factory), Barite powder (Hebei Huayuan Mining Co., Ltd.), Coating agent FA-36T (Renqiu High-tech Chemical Materials Co., Ltd.), polyanionic cellulose (Renqiu Jiafu Chemical Co., Ltd.), Polyacrylamide (Henan Baiyuan Environmental Protection Technology Co., Ltd.).

Experimental instruments: Digital air drying oven GZX-9023 MBE (Shanghai Boxun Industrial Co., Ltd. Medical Equipment Factory), Electronic balance CP2102 (Shanghai Aohaosi Instrument Co., Ltd.), Electronic analysis balance BSA223S (Beijing Saidolis Instrument System Co., Ltd.), Desktop high-speed centrifuge TG16-WS (Hunan Xiangyi Laboratory Instrument Development Co., Ltd.), Precision timing electric stirrer JJ-1 (Changzhou Ronghua Instrument Manufacturing Co., Ltd.), Magnetic heating stirrer 78-1 (Jintan Hengfeng Instrument Manufacturing Co., Ltd.), Frequency conversion high-speed stirrer GJD-B12K (Qingdao Hongxiang Petroleum Machinery Manufacturing Co., Ltd.), Digital six-speed rotary viscometer ZNN-D6B (Qingdao Hongxiang Petroleum Machinery Manufacturing Co., Ltd.), Constant temperature water bath filter B220).

2.2. Experimental process

(1) Sodium calcium-based bentonite [27]

Firstly, bentonite was added to distilled water to prepare a bentonite suspension with a slurry concentration of 5%. It was fully mixed with 5% sodium carbonate aqueous solution and 0.5% sodium pyrophosphate aqueous solution. The sodium bentonite suspension was obtained by magnetic stirring for 2h at a constant temperature of 30°C. The bentonite suspension was added to the centrifugal tube at 6000r/min and centrifuged for 10 minutes. After centrifugation, the lower solids were dried at 60°C for 24h to obtain sodium-modified bentonite.

Table 1: Modification methods and applications of NIPAM.

ARTICLE TITLE	MODIFICATION METHOD	JOURNAL NAME	PUBLICATION YEAR
Synthesis of modified poly (N-isopropyl acrylamide) and its temperature-sensitive characteristics [22]	NIPAM, NVP and crosslinking agent MBA were dissolved in water, nitrogen gas was passed to drive away oxygen, and then potassium persulfate and sodium bisulfite were further added and reacted in a 30°C water bath for 24 hours. After cooling, NIPAM hydrogel was obtained	Acta Agriculturae Boreali-occidentalis Sinica	2010
Preparation of thermoresponsive PVDF/SiO2-PNIPAMmixed matrix membrane for saline oil emulsion separation and its cleaning efficiency [23]	The ethanol and ammonium solutions were stirred and mixed at a constant temperature. Then, TEOS was added at 30°C and stirred for 24 hours. The ethanol mixture was dropped into the suspension and reacted for 24 hours. Then, it was heated to 80°C for 2 hours to obtain the concentration of SiO_2-MPS suspension. The suspensions of NIPAM, MBA and SiO_2-MPS particles and KPS solution were mixed to form an aqueous solution. The solution was ultrasonically treated for 15 minutes at a temperature of 70°C and the reaction was carried out and stirred for 4 hours in an argon atmosphere	Desalination	2017
Graft copolymerization of N-isopropylacrylamide and acrylic acid on bentonite colloids for in-depth fluid diversion [24]	Intercalate bentonite particles with small precursor molecules containing functional groups. And vinyl is introduced for the subsequent polymerization. Poly (NIPAM-co-AA) was grafted onto hydrophilic bentonite by the free radical polymerization method	Energy & fuels	2017
Modification of ultrafiltration membrane by thermo-responsive Bentonite-poly(N-isopropylacrylamide) nanocomposite to improve its antifouling properties [25]	Ultrasonic dispersion of nano-BNT solution for 10 minutes. Add MPS and stir at room temperature for 24 hours. The BNT-MPS produced by centrifugal dispersion and purification. The precursor solution was prepared by mixing BNT-MPS, NIPAAm, MBA, DI water and DMF. It was ultrasonically treated for 15 minutes, degapped under nitrogen bubble for about 15 minutes, stirred at 70°C and nitrogen for 24 hours, and then KPS was added to initiate the polymerization process and stirred at 70°C for 24 hours	Journal of Water Process Engineering	2020
Preparation and action mechanism of temperature sensitive N-isopropylacrylamide/nanosilica hybrid as rheological modifier for water-based drilling fluid [26]	NIPAM, RNS-D and APS were dissolved in deionized water, purged with N2 for 20 minutes, heated in a 75°C water bath and magnetically stirred for 10 hours. After the reaction was completed, they were cooled and centrifuged at room temperature, and washed three times with distilled water – ethanol to obtain gel-like samples	Journal of Petroleum Science and Engineering	2022

Table 2: Modification methods and applications of CMC.

ARTICLE TITLE	MODIFICATION METHOD	JOURNAL NAME	PUBLICATION YEAR
Preparation and sustained release properties of carboxymethyl cellulose sodium modified bentonite composite gel [27]	Urea, deionized water, bentonite and CMC were stirred into a uniform emulsion and dropped into composite hydrogel beads in Al^{3+} solution. The pellets were placed in a small bag and placed in a 25°C biochemical constant temperature incubator. Samples were taken every 24 hours in the first 7 days, and then every 72 hours. The mass concentration of urea in the samples was determined and the urea release rate was calculated	Acta Agriculturae Boreali-occidentalis Sinica	2012
Experimental study on chemical compatibility of CMC modified bentonite under the action of phenol solution [28]	CMC and distilled water were stirred in a water bath at 60°C for 30 min to make a uniform mixture of CMC-distilled water. Add bentonite and stir in 60°C constant temperature water bath for 2h; drying at 105°C, grinding and sieving	Journal of Engineering Geology	2021
Interlayer and surface characteristics of carboxymethyl cellulose and tetramethylammonium modified bentonite [29]	The water bath controls the full mixing of TMA and deionized water (DIW). Continue to add CB to stir and disperse, stir at 60°C for 6h, and wash with DIW; the product obtained by drying and grinding the mixture in the oven and screening was expressed as TMB; CMC was dispersed in DIW, and the solution was mixed with TMB or CB. Stir the mixture and grind for 6h	Construction and Building Materials	2024
A green composite of sodium carboxymethyl cellulose and amino-decorated cellulose reinforced with modified bentonite for removal of lead (II): Kinetics and isotherm studies [30]	Bentonite, distilled water and HDTMA solution were stirred at room temperature for 24 h, and the precipitate was dried, ground and sieved. The extracted cellulose was added to epichlorohydrin and anhydrous ethanol solution for magnetic stirring at 50°C for 5 h, and the epoxy-grafted cellulose EPC was obtained by filtration and washing. Continue to add $NaHCO_3$, EDA and anhydrous ethanol, stirring at 70°C for 12 h, filtering, washing and freeze-drying to obtain the product ADC. The CMC solution was dissolved and mixed with the cellulose solution at a ratio of 1:1. The modified bentonite was added to disperse and stir for 24 h. The complex containing ADC, CMC and MB was washed with distilled water and freeze-dried for 24 h to obtain CMC/ADC/MB composite adsorbent	Materials Today Communications	2024
Cadmium Removal from Aqueous Solution by Bentonite Modified with Zero-Valent Zinc Nanoparticles Stabilized with CMC [31]	Na_2ZnCl_2 solution was shaken at room temperature for 1h, and $NaBH_4$ solution was added for aging at room temperature for 23 h, and nZVZ was obtained by filtration and drying. The BT powder was added to Na_2ZnCl_2 solution and oscillated at room temperature for 1h. The mixture prepared by adding $NaBH_4$ was aged at room temperature for 23 h, and then filtered and dried to obtain BT-nZVZ CMC, Na_2ZnCl_2, deionized water and BT were mixed and stirred for 30 min, $NaBH_4$ was added dropwise, and BT-nZVZ-CMC was obtained by drying after aging for 15h	Water Conservation Science and Engineering	2025

(2) Sodium-bentonite intercalation [28]

The dried sodium-modified bentonite was ground into powder, and sodium carboxymethyl cellulose (CMC) was added for grinding for 2 h to obtain the bentonite after intercalation.

(3) Bentonite adsorption

Weigh a certain amount of intercalated bentonite and added it to distilled water, add N-isopropyl acrylamide (NIPAM) and stirred for 2 h. The obtained bentonite solution was dried in a vacuum drying oven at 60°C for 24h, and the resulting bentonite product was ground into powder to obtain the final modified bentonite.

3. RESULTS AND DISCUSSION

3.1. Optimization of the synthesis index of modified bentonite

This section focuses on the amount of sodium carbonate and sodium pyrophosphate added in the process of sodium metathesis, the mass ratio of CMC to bentonite added in the intercalation process and the amount of NIPAM added in the adsorption process, and analyzes and determines the optimal synthesis conditions of modified bentonite.

3.1.1. Additive amount of sodium bentonite medicine

(1) To explore the effect of sodium carbonate addition on sodium bentonite

Due to the small radius of sodium ion (Na^+), it can penetrate into the interlayer structure of bentonite more effectively, thereby enhancing the swelling capacity and dispersion characteristics of bentonite [29]. In addition, the sodium-based bentonite exhibits superior thermal stability at high temperatures, which is essential for bentonite products applied at high temperatures. The results show that compared with the 7% slurry concentration, the crystallinity of sodium bentonite can be improved by appropriately reducing the slurry concentration, which indicates that reducing the slurry viscosity is an effective way to improve the sodium effect. However, when the slurry concentration drops to 1%, the sodium effect is weakened because the concentration of sodium carbonate decreases, resulting in a weakened driving force for Na^+ to enter the montmorillonite layer. Therefore, adjustments that are too high or too low in the slurry concentration may weaken the sodium effect of bentonite, and the choice of 5% slurry concentration proves to be the most suitable choice [30].

Pyrophosphate anion $(P2O7)^{4-}$ has strong complexation and can chemically bond with multivalent metal ions on the sur-face of montmorillonite minerals. This process effectively shields a large number of cationic active sites on the mineral surface [31]. The resulting compounds cover the mineral surface and significantly enhance its hydrophilicity. At the same time, phosphate ions will be adsorbed on the positively charged edge of montmorillonite minerals, thus forming a negative edge [32]. This change led to the comprehensive transformation of montmorillonite particles into a colloidal state with a negative electric double layer, resulting in strong mutual repulsion between the particles, and the disintegration of the original association structure, which significantly reduced the viscosity of the colloid [33].

At a concentration of 5% bentonite, its layered structure is easily permeated and disintegrated by water, so only a small amount of sodium pyrophosphate is required to achieve complete dispersion and form a tiny lattice structure [34]. However, when the concentration of sodium pyrophosphate is increased, pyrophosphate ions surround certain sheets, resulting in opposite charges on adjacent sheets and surfaces, which attract each other and restack in solution, resulting in a gradual increase in the spacing between crystal planes [35]. Considering the Zeta potential, crystal plane spacing and the size of the average particle size, it can be concluded that the optimal concentration of sodium pyrophosphate is 0.5% when the concentration of bentonite is 5%, and the stability of the solution is the best.

The addition amount of sodium carbonate was determined by the influence of the different drug bentonite ratio between calcium bentonite and sodium carbonate on the expansion capacity of wet modified bentonite. Six different ratios of sodium pyro-phosphate to bentonite were selected to test the expansion capacity. The results are shown in Figure 1. The effect of adding 0.5 g sodium pyrophosphate to the expansion capacity of sodic bentonite at all ratios is better than that without adding sodium pyrophosphate. At the same time, as shown in Figure 2, it can be concluded that adding 0.5% sodium pyrophosphate under the condition of 1:9 drug bentonite ratio can meet the standard of commercial drilling grade bentonite.

(2) To explore the effect of sodium pyrophosphate addition on sodium bentonite

Under the condition that the sodium carbonate dosage is fixed at 1:9 and the slurry concentration is 5%, the decrease of slurry viscosity can be significantly observed by adding 0.5% sodium pyrophosphate as a dispersant to the system. This phenomenon shows that the addition of dispersant is effective in reducing the viscosity

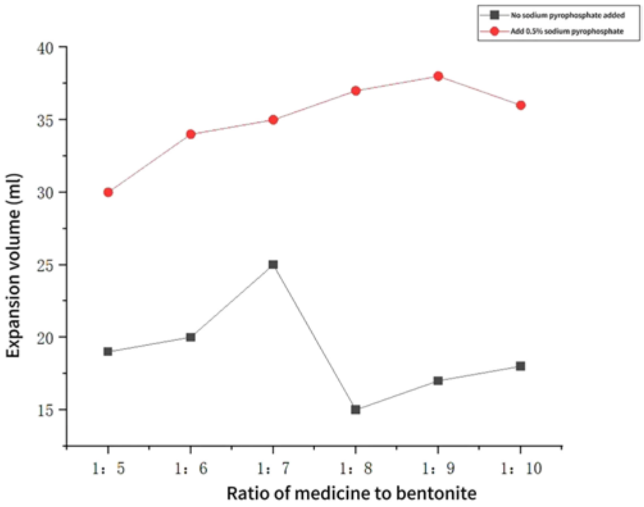


Figure 1: Effect of sodium carbonate addition on expansion capacity.

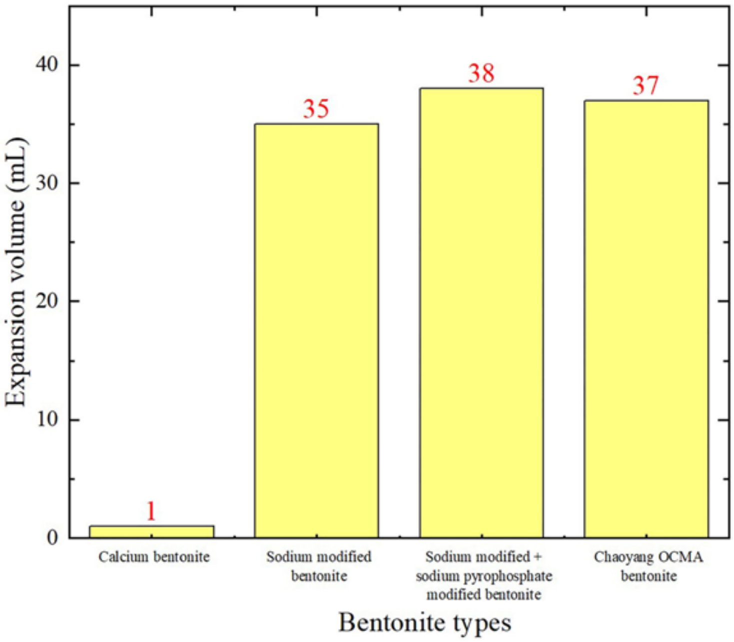


Figure 2: Expansion capacities of different bentonites.

of sodium slurry. With the addition of a dispersant, sodium pyrophosphate readily forms chemical bonds with polyvalent metal ions on the surface of montmorillonite minerals, a process that shields a large number of cationic active sites on the mineral surface [36]. Meanwhile, phosphate ions will adsorb on the positively charged side of montmorillonite minerals to form a negatively charged side. This leads to the full transformation of montmorillonite particles into a colloid with a negatively charged bilayer. This transformation leads to the disappearance of the original mutually repulsive association structure between the particles, which greatly reduces the viscosity of the slurry [37].

In order to determine the optimal amount of sodium pyrophosphate and maintain the mass fraction ratio of sodium pyro-phosphate to bentonite about 1:10, the sodium pyrophosphate addition amount of 10 different gradients in the range of 0.1–1 g was selected, and the aqueous solution of bentonite with a ratio of 1:9 to medicinal bentonite was magnetically stirred. As shown in Figure 3, with the gradual increase of sodium pyrophosphate addition, the swelling capacity of bentonite showed a trend of first increasing and then decreasing.

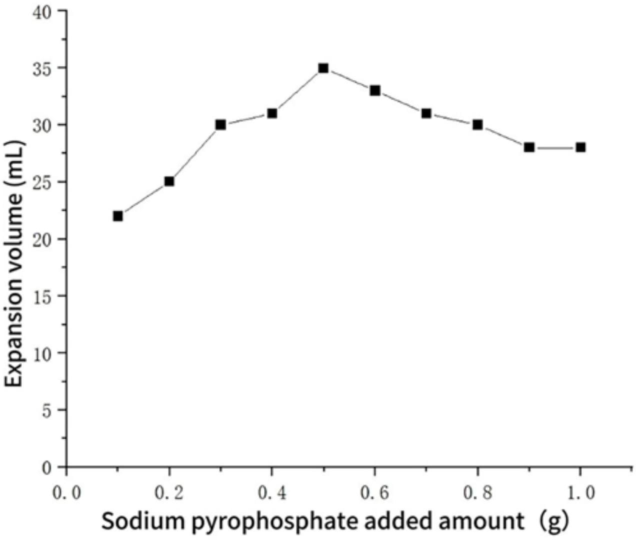


Figure 3: Effect of sodium pyrophosphate addition on expansion capacity.

Specifically, when the amount of sodium pyrophosphate is before a certain critical value, the expansion capacity will increase with the increase of the amount added. However, when the addition amount exceeds this threshold, the expansion capacity begins to gradually decrease. According to this result, it was determined that the swelling capacity of bentonite reached the maximum value when the sodium pyrophosphate addition amount was 0.5%, so 0.5g was used as the optimal sodium pyrophosphate addition amount.

3.1.2. CMC addition amount

CMC intercalation properties improve bentonite properties by embedding CMC molecules into the interlaminar structure of bentonite. This embedding increases the distance between the bentonite layers, which in turn enhances its swelling properties in water [38]. The bentonite colloidal suspension modified by CMC shows superior characteristics in terms of thixotropy and viscosity, which is of great significance for improving the rock-carrying efficiency of the drilling fluid and enhancing the stability of the borehole.

The use of grinding method to modify bentonite with CMC intercalation can not only greatly improve the physical and chemical properties of bentonite, but also effectively improve the production efficiency. In order to determine the optimal amount of drug addition, the amount of drug added was determined according to the expansion capacity obtained after intercalation modification with different ratios of sodium clay and CMC.

The effect of the ratio of sodium bentonite to CMC on the expansion capacity was used to determine the amount of CMC. Select 15:1, 20:1, 25:1, 30:1, 35:1, 40:1 six different ratios of sodium bentonite and CMC for expansion capacity test, the test results are shown in Figure 4, with the increase of CMC addition, the expansion capacity of the modified bentonite at the ratio of 30:1 appeared the highest value of expansion capacity, so the best intercalation effect can be achieved by adding drugs at the ratio of sodium bentonite to CMC of 30:1.

3.1.3. NIPAM additive amount

When the temperature of NIPAM aqueous solution rises to about 33°C, phase transition will occur, that is, at low critical solution temperature (LCST), NIPAM will change from homogeneous system to heterogeneous system. This unique property allows NIPAM to be used in a wide range of applications [39]. Especially in the field of drilling fluids, the use of temperature-sensitive polymers to modify bentonite can significantly improve the stability and plugging efficiency of drilling fluids, optimize its rheological properties, enhance lubrication properties, and strengthen anti-pollution ability. These modified bentonite materials exhibit a high degree of sensitivity to temperature changes [40].

However, the practical application of NIPAM modified bentonite may be limited by a variety of variables, such as the depth of modification, the length and structural characteristics of the polymer chains, and the specific operating environment [41]. Therefore, in order to obtain the best performance of modified bentonite while controlling the cost, this experimental protocol was used to evaluate the effect of NIPAM addition on the rheological properties of the solution at different temperatures.

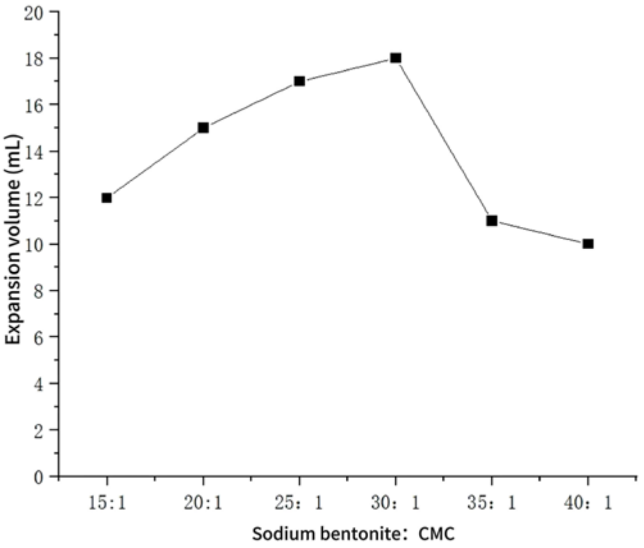


Figure 4: Effect of CMC addition on expansion capacity.

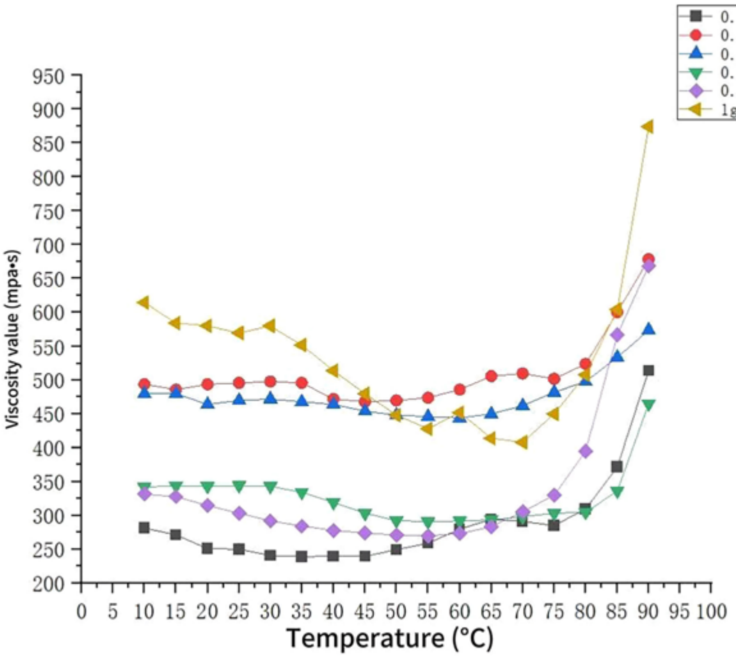


Figure 5: Effect of NIPAM addition on the rheology of the solution.

Six different amounts of NIPAM were selected and the test temperature range was set between 10°C–90°C for viscosity test. The test results are shown in Figure 5. When the addition amount of NIPAM is 0.5 g, the fluctuation range of viscosity value of modified bentonite solution with temperature is the smallest. Based on this result, it is determined that when the addition of NIPAM is 0.5 g, it can effectively control the rheology of the solution and ensure the stability of the drilling fluid under the condition of temperature change.

3.2. Performance test of modified bentonite

3.2.1. Rheological test

According to the oil and gas industry standard (GT5005-2010 Drilling Fluid Material Specification), the rheological test of modified bentonite was carried out, and the results shown in Table 3 showed that the apparent

Table 3: Bentonite viscosity determination experiment.

	AV	PV	YP	B	N
Calcium bentonite	1.5	1	0.5	0.5	0.585
Chaoyang OCMA bentonite	39	22	17	0.773	0.478
Modified bentonite	28	22	6	0.273	0.72

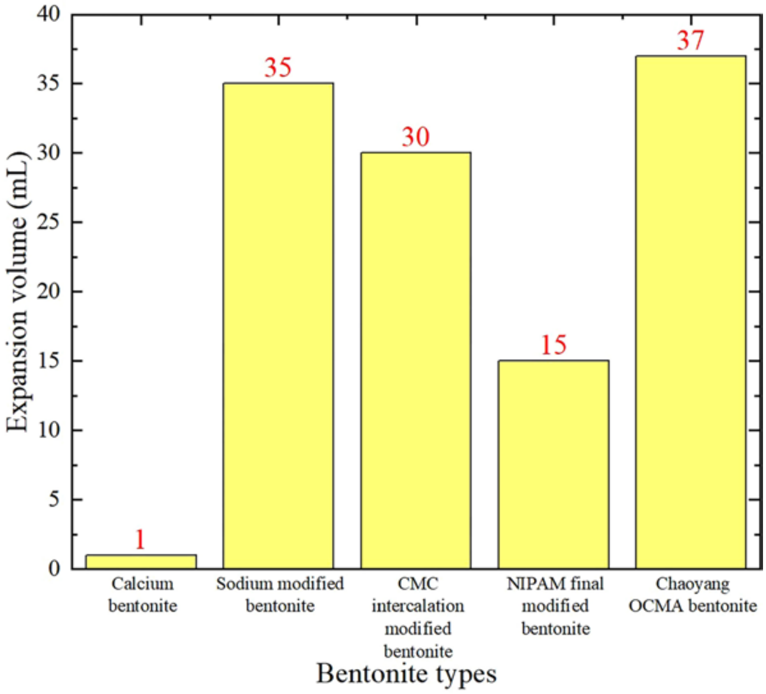


Figure 6: Expansion capacities of different bentonites.

viscosity (AV), plastic viscosity (PV), dynamic shear force (YP), dynamic plastic ratio (b) and fluidity index (n) of the four bentonite suspensions were obtained. It can be seen from the table that the rheology of calcium-based bentonite is poor, and the modified bentonite has excellent rheology, and its apparent viscosity, plastic viscosity and dynamic shear stress are far better than those of calcium-based original bentonite. Compared with the commercially available OCMA bentonite, the apparent viscosity difference is small, the plastic viscosity can reach the same level, and the dynamic plastic ratio of the modified bentonite is better than that of the commercially available drilling-grade bentonite under the condition that the fluidity index can maintain a high level.

3.2.2. Expansion capacity test

According to the expansion capacity test results shown in Figure 6, it can be observed that the modified bentonite after sodium modification, CMC addition, and grinding treatment shows excellent expansion capacity performance, and its performance index is close to the market standard of drilling grade bentonite. However, the expansion capacity of the modified bentonite decreased slightly in the end, which was attributed to the addition of macromolecular organic matter, which increased the mass of bentonite molecules and made it more prone to sedimentation.

3.2.3. Temperature sensitivity test

For drilling fluids, temperature sensitivity testing is a method to assess the variation of bentonite properties at different temperatures [42]. As the main component of drilling fluid, the temperature sensitivity test of bentonite can help to understand and predict the performance of bentonite in practical applications. The temperature-sensitive polymer NIPAM contains hydro-philic/hydrophobic groups, so the synthesized modified bentonite also has corresponding temperature-sensitive properties. Therefore, temperature sensitivity tests were carried out on bentonite, commercially available drilling-grade bentonite and modified bentonite in the range of 20°C–100°C.

As shown in Figures 7–9, the apparent viscosity, plastic viscosity and dynamic shear stress of the calcium-based native bentonite suspension decrease with the increase of temperature in the temperature range of 20°C–100°C. The apparent viscosity of Chaoyang OCMA bentonite has been increasing from 60°C to 100°C, the plastic viscosity has shown a small range of decrease in the early stage and a relatively stable state in the later stage, and the dynamic shear stress has been increasing with the increase of temperature. The apparent viscosity and plastic viscosity of modified bentonite at 60°C–100°C also showed a trend of increasing with temperature, but the fluctuation range was small compared with the range of OCMA bentonite, and its dynamic shear stress could maintain a slight fluctuation with temperature, indicating that the temperature-sensitive polymer could play a good role in the temperature range of 20°C–100°C.

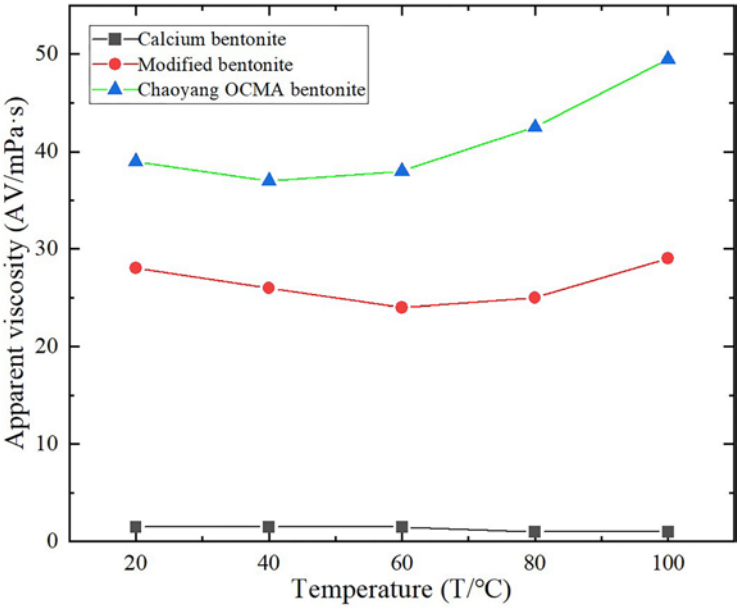


Figure 7: Apparent viscosity of different bentonite cites as a function of temperature.

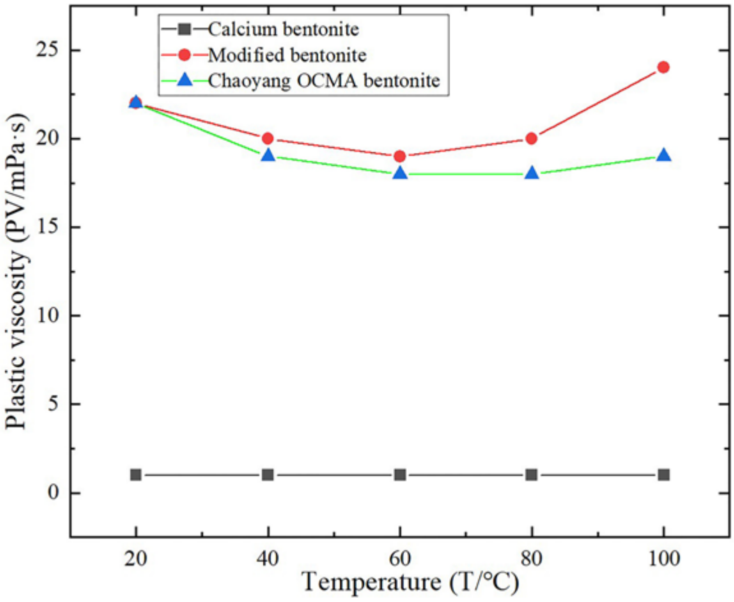


Figure 8: The plastic viscosity of different bentonite varies with temperature.

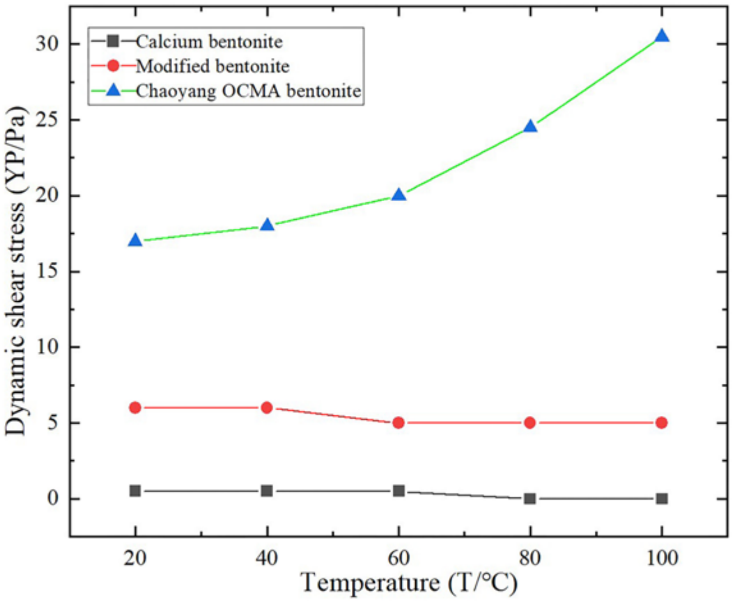


Figure 9: Dynamic shear stress of different bentonite varies with temperature.

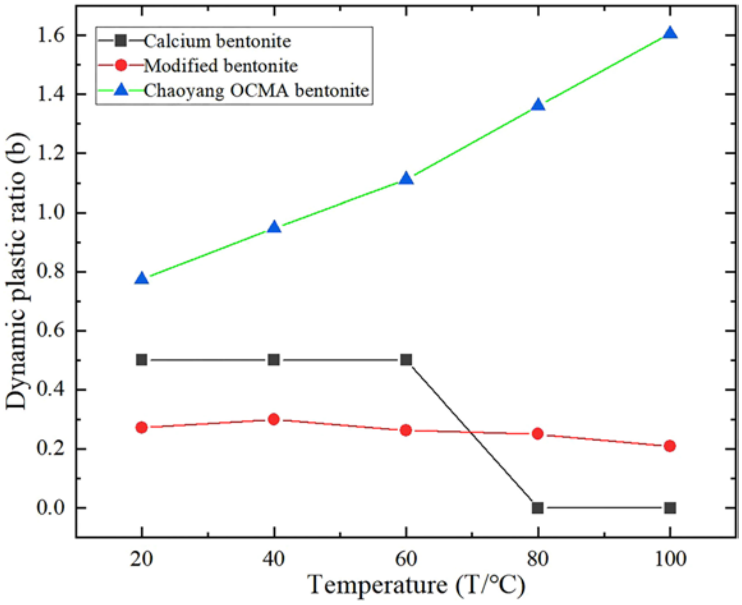


Figure 10: Variation of dynamic plastic ratio of different bentonite with temperature.

As shown in Figures 10–11, in the temperature range of 60°C–100°C, the dynamic-plastic ratio of the original bentonite suspension showed a phased downward trend, while the fluidity index showed a phased increase, which revealed the instability characteristics of the original bentonite suspension with temperature. The dynamic-plastic ratio of Chaoyang OCMA bentonite continued to increase with the increase of temperature, while the fluidity index continued to decrease. In contrast, the dynamic-plastic ratio and fluidity index of the modified bentonite suspension remained stable in the temperature range of 20°C–100°C without significant fluctuations. This comparison shows that compared to the instability exhibited by the other three bentonite suspensions, modified bentonite can demonstrate good performance stability of temperature-sensitive polymers in the temperature range of 60°C and above.

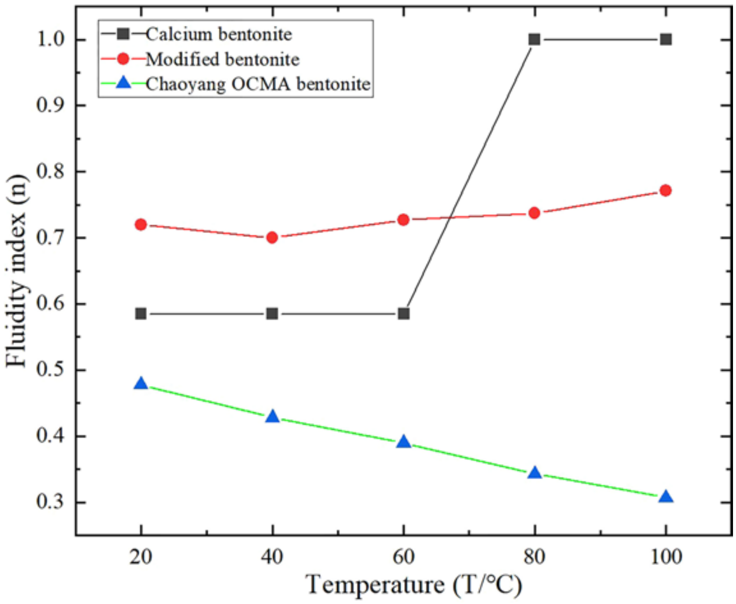


Figure 11: The fluidity index of different bentonites varies with temperature.

3.3. Microscopic characterization of modified bentonite

In order to comprehensively characterize the bentonite before and after modification [43], three analysis techniques were used: X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), and scanning electron microscopy (SEM). XRD not only enables precise phase analysis, but also accurately measures key parameters such as crystallite volume, crystallinity, and crystal orientation of materials [44]. FT-IR technology reveals the chemical composition and molecular structure characteristics of materials by analyzing the absorption bands or frequency positions of spectral bands generated by substances absorbing infrared light, which provides strong support for the determination of synthesis effects and the understanding of structural composition [45]. SEM is an observation method between transmission electron microscopy and optical microscopy, which scans the sample by focusing a high-energy electron beam, excites and collects various physical information, and then magnification and imaging processing to achieve high-definition characterization of the microscopic morphology of substances [46].

In this experiment, XRD was used to test the products of the three stages in detail, and the important parameter of D001 crystal plane spacing was calculated [47]. At the same time, FT-IR technology was used to characterize the modified bentonite, and the modification process was analyzed in depth, so as to accurately judge the synthesis effect and understand the structural composition. In addition, the microscopic morphology of the product was observed by SEM technology, which realized the clear presentation of the internal structure and external structure of bentonite, which provided an important basis for further research and application.

3.3.1. XRD characterization

XRD technology will be used to measure the microcrystal volume, crystal orientation, and crystal status of the material to determine whether the bentonite is success-fully intercalated [48]. The changes in layer spacing and diffraction Angle (2θ) of bentonite's d001 crystal plane (d001) are shown in Figure 12. It can be seen that the position of 2θ has changed and moved to a lower Angle position, that is, the position of the X-ray peak has moved forward, and the diffraction peak after intercalation has be-come more sharp. It can also be seen from the position of diffraction peaks in the figure that some characteristic peaks of bentonite disappear after CMC is combined with bentonite, which indicates that polymer CMC destroys part of the layered structure of bentonite during the process of being inserted into the bentonite layers. The intercalation process is realized under the action of internal driving force (hydrogen bond) and external driving force.

3.3.2. FT-IR test

The presence and changes of groups before and after the reaction can be judged by the characteristic absorption peaks of functional groups shown in the FT-IR spectra [49]. The following figure shows the qualitative analysis of the infrared spectra of bentonite in the modification process.

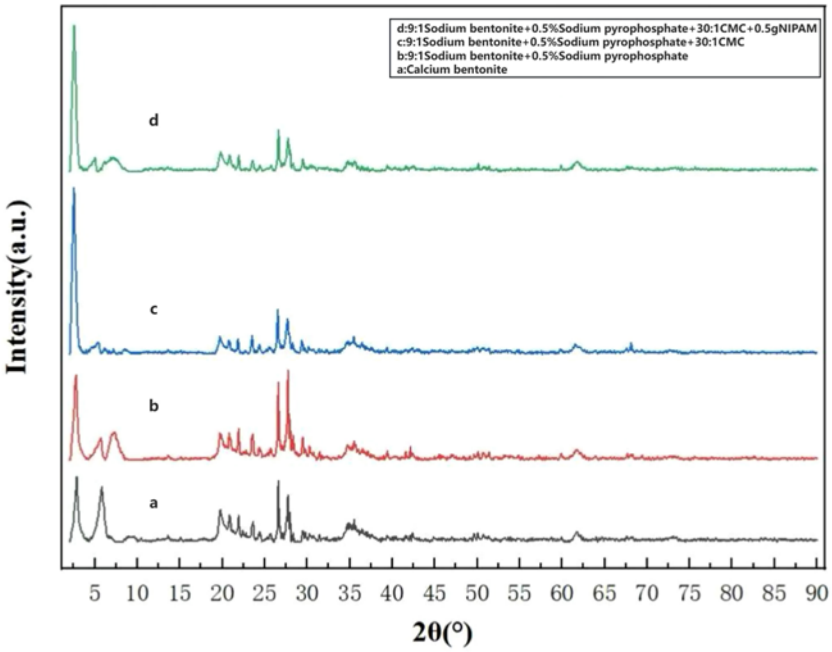


Figure 12: X-ray diffraction spectrum.

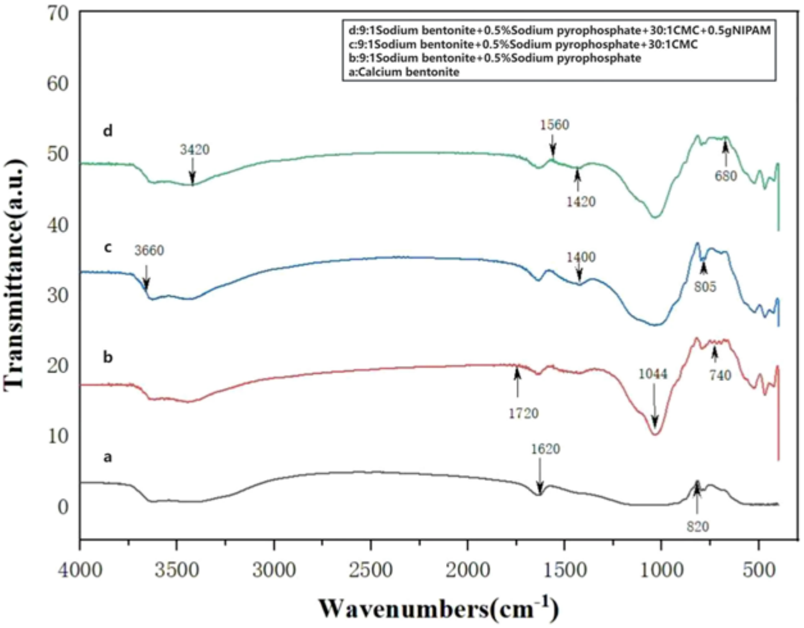


Figure 13: Fourier-infrared spectra.

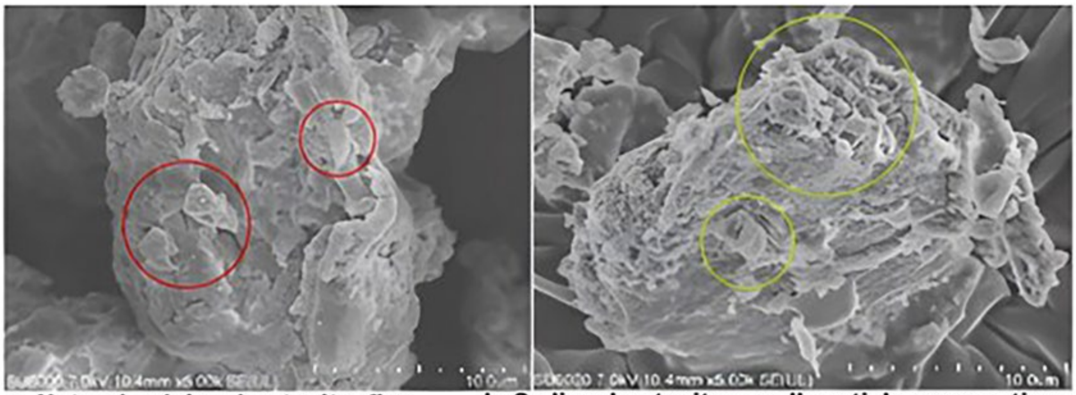
The modified bentonite was characterized by Fourier infrared spectroscopy to further judge the synthesis effect and under-stand the structure composition more accurately. As shown in Figure 13, in the infrared spectrum of the original bentonite bentonite, the area around 820 cm^{-1} is the position of the characteristic absorption peak of the Al-O bond of the octahedral structural group, and 1620 cm^{-1} is the absorption peak of the -OH bending vibration.

After iodization, the alkene C-H bending vibration at 740 cm^{-1}, the C-O bond vibration peak at 1044 cm^{-1}, and the continuous C=O vibration peak at 1720 cm^{-1} indicate that the iodization modification of the calcium-based original bentonite has been completed. After the intercalation reaction between bentonite and sodium carboxymethyl cellulose, the bending vibration at 805 cm^{-1} was enhanced. In addition, the stretching vibration absorption peak of sodium carboxymethyl cellulose appeared near 1400 cm^{-1} and the asymmetric stretching vibration peak of –CH2 appeared at 3660 cm^{-1}. It can be seen that sodium carboxymethyl cellulose has successfully entered the bentonite layer. After modification, it can be seen that the vibration peak of the continuous C-H bond at 680 cm^{-1} is significantly wider, the contraction peak of the C-N bond appears at 14200 cm^{-1}, the N-H bond on the amide absorption band is added at 1560 cm^{-1}, and the N-H bond vibration absorption peak at 3420 cm^{-1} is also significantly wider.

3.3.3. SEM electron microscope image

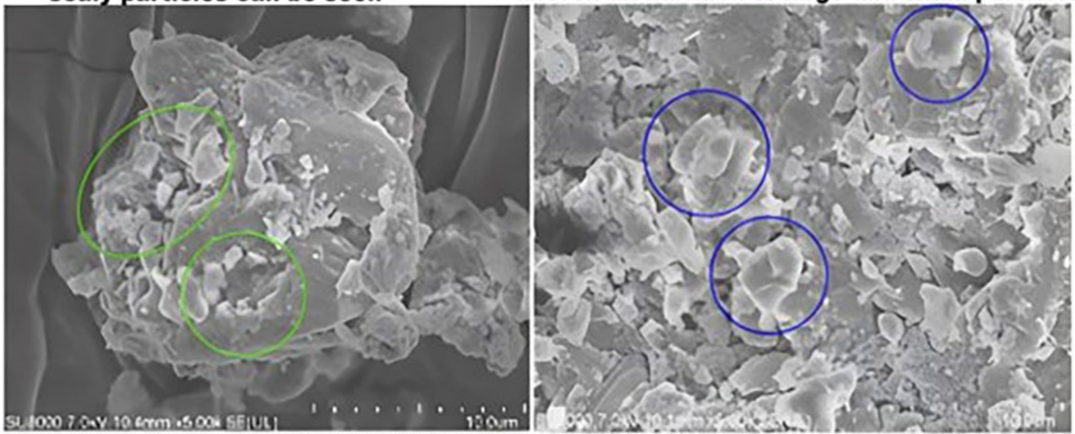
The scanning electron microscope (SEM) is a high-resolution microscope. It uses the signals generated by the interaction between the electron beam and the sample to obtain the surface morphology and composition information of the sample [50]. SEM generates high-magnification images of the surface of the sample by scanning a fine-focused electron beam on the surface of the sample and detecting the signal excited by it.

SEM electron microscopy was used to observe the microscopic morphology of modified bentonite at different stages to further verify the morphological changes generated in the modification process of bentonite. The characterization results are shown in Figure 14. It can be seen that Figure14(a) is a natural calcium bentonite, which is a clumpy aggregate composed of small-scale-like particles, and the interlamellar layer is clear. Figure14(b) is the nitrified bentonite, which is denser than the calcium-based original bentonite. The bentonite particle size is not uniform and the morphology is complete. Figure14(c) is the bentonite after CMC mechanical grinding intercalation. The surface of the bentonite becomes rough, with holes and uneven particle density, which indicates that the distance between the bentonite layers increases during intercalation, and CMC effectively enters the bentonite layers. Figure14(d) is the result of the final modified bentonite. Compared with the intercalated bentonite, more macromolecular sub-stances are attached to the surface, indicating that NIPAM is effectively adsorbed on the surface of the bentonite, thereby im-proving the temperature sensitivity of the bentonite.



a. Natural calcium-bentonite: fine, scaly particles can be seen

b. Sodium bentonite: small particle aggregation and uneven distribution of large and small particles



c.CMC intercalation modified bentonite: irregular pores appear in the particles

d.NIPAM modified bentonite: NIPAM molecule is uniforml adsorbed on the particle surface

Figure 14: SEM image (5K fold imaging).

3.4. Molecular simulation of modified bentonite

Based on the previous modification research, the microstructure characteristics of N-isopropylacrylamide (NIPAM) modified bentonite were analyzed. According to the special requirements of deepwater drilling fluid system for solid materials, sodium carbonate, sodium pyrophosphate, sodium carboxymethyl cellulose and temperature sensitive polymer NIPAM were used to modify the interlayer domain of montmorillonite in calcium bentonite. The experimental results show that the modified bentonite has excellent suspension properties, rheological properties and temperature sensitivity, especially in the high temperature and high pressure environment.

In order to reveal its micro-mechanism from the molecular level and verify the internal relationship between performance improvement and montmorillonite structure evolution, a simplified calculation model reflecting bentonite modification is con-structed in this section. The model maintains the physical and chemical properties of bentonite mineral components and organic modifiers, and accurately calculates the modification process by molecular dynamics simulation. The simulation results show that NIPAM molecular chains form an orderly arrangement with the surface of montmorillonite through hydrogen bonding, and its temperature sensitive phase transition characteristics significantly enhance the stability of the interlayer domain. It is worth noting that the predicted layer spacing change, functional group vibration mode and surface morphology characteristics are effectively verified with the experimental characterization results (XRD layer spacing analysis, FTIR characteristic peak dis-placement, SEM microscopic morphology observation).

In this section, the hydration cation exchange mechanism of montmorillonite is systematically studied. The thermodynamic and kinetic characteristics of the ion exchange process are analyzed by observing the interlayer structure evolution of Na based and CA Based Montmorillonite, combined with the interlayer cation density distribution curve. Molecular simulation technology was used to reveal the internal correlation between the relative ion concentration gradient and the material distribution between the layers of Na based and CA Based Montmorillonite, and to explain the essential differences in ion exchange capacity and selectivity. In order to further explore the micro mechanism of cation exchange, a supercell model of Ca montmorillonite was constructed. The initial cell configuration of Na montmorillonite was successfully obtained by simulating the embedding process of Na^+ in sodium carbonate and sodium pyrophosphate solution through the adsorption module. The theoretical model needs to calculate the energy minimization through the geometric optimization module to eliminate the local lattice distortion, and finally obtain the optimal interlayer configuration with thermodynamic stability. The optimization process not only verifies the observed layer spacing shrinkage phenomenon, but also provides a theoretical framework for predicting the ion ex-change performance of montmorillonite in different electrolyte systems.

As shown in Figures 15, 16, the interlayer cations are arranged in a regular manner. Before optimization, water molecules are mainly concentrated in the center of the siloxane ring. After ion exchange, the interlayer cations are still arranged in a regular manner. Compared with Ca^{2+}, Na^+ is concentrated in the interlayer area or closer to the surface of the cell, and the migration range is wide. Before cation exchange, the aqueous solution containing Na^+ was evenly arranged in the outer layer of montmorillonite cell. After cation exchange, more water molecules were adsorbed on the outer surface of the cell, and the outer solution of the cell was divided into two layers. According to the principle of charge conservation, the total charge of Ca^{2+} displaced is the same as the total charge of Na^+ exchanged into the interlayer.

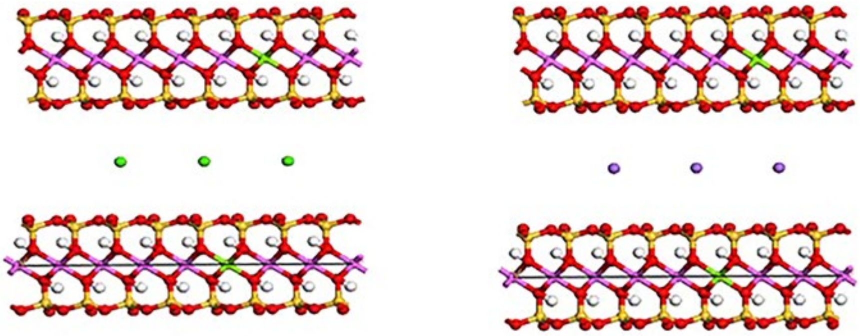


Figure 15: Montmorillonite model (calcium montmorillonite on the left and sodium montmorillonite on the right).

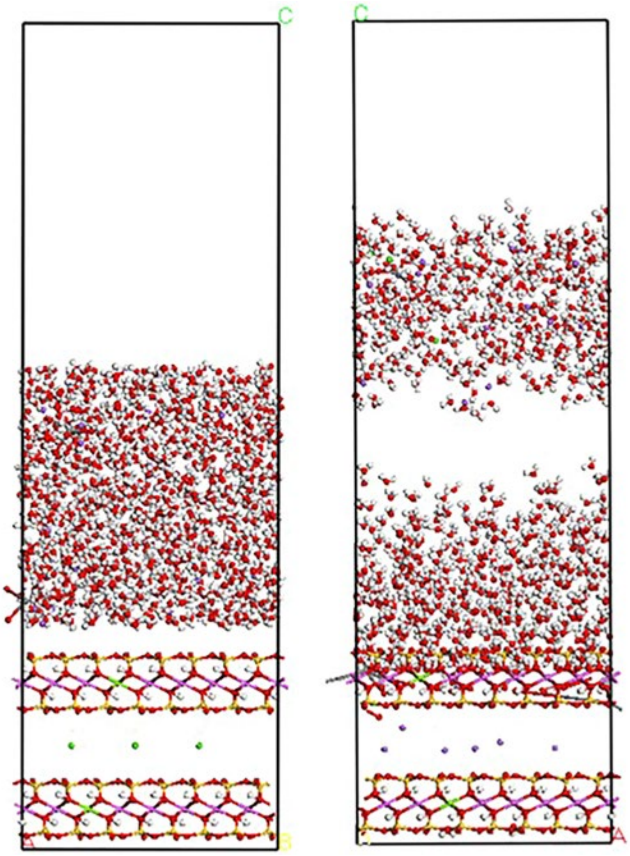


Figure 16: Conversion of calcium montmorillonite to sodium montmorillonite.

As shown in Figure 17, sodium carboxymethyl cellulose (CMC) initially presents a regular horizontal double-layer arrangement mode between montmorillonite layers, at which time Na+ ions are stably anchored in the middle of the layers. With the increase of CMC content gradient, the carboxymethyl (- CH2COO-) Group on its molecular chain replaced the original cat-ions (Na^+/Ca^{2+}) in the interlayer through ion exchange reaction, driving the flexible CMC molecular chain to penetrate into the interlayer of montmorillonite. Hydroxyl groups (-OH) in CMC chain and silicon hydroxyl groups (Si-OH) at the edge of montmorillonite laminate form a cross-scale hydrogen bond network, which significantly improves the interfacial bonding strength. The dissociated carboxylate ($-COO^-$) and the residual cations in the interlayer generate electrostatic attraction, which further promotes the deep intercalation of molecular chains. CMC molecular chains form a stable coating layer on the surface of montmorillonite through the winding adsorption composite effect, and its hydrophilic groups significantly enhance the wettability of the particle surface. Under the action of external force field, the intercalated CMC molecules have dual effects. The outer molecular chain fills the mineral pores to form a dense coating, while the inner molecular chain expands the layer spacing through electrostatic support, forming a hierarchical structure control.

As shown in Figure 18, in the initial state, NIPAM exists completely in molecular form and has no modification effect on montmorillonite, making montmorillonite suspension highly dispersed. After adsorption, two NIPAM molecules are adsorbed on the surface, and their polar head groups face the surface to form an inner layer. They are attached to the surface in a dispersed manner, and most of them are water molecules adsorbed on the surface of montmorillonite. Most NIPAM molecules are bound to the solution through the hydrophobic association between their non-polar carbon chains and some polar head groups facing the bulk solution. However, due to a large number of polar head groups in the adsorption monolayer toward the solution direction, it is not conducive to the hydrophobic modification of montmorillonite. In this case, the high stability of montmorillonite suspension is dominated by strong electrostatic repulsion between particles due to the large negative charge on the edge surface. At the interface, the polar head group of NIPAM not only interacts with the surface oxygen atom, but also interacts with water molecules by forming hydrogen bonds between the hydrogen atom of the head group and the surface oxygen atom or water oxygen atom. Water molecules

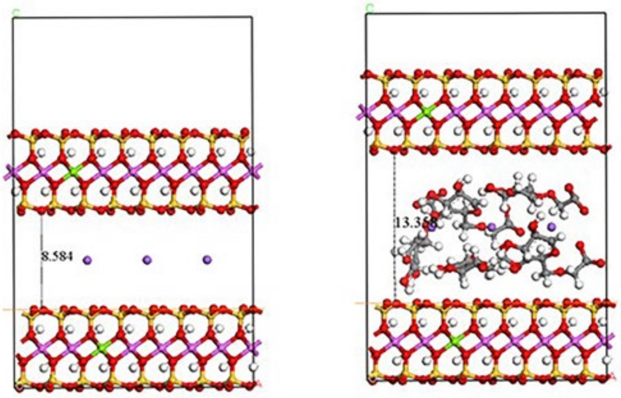


Figure 17: Layer spacing before and after CMC insertion.

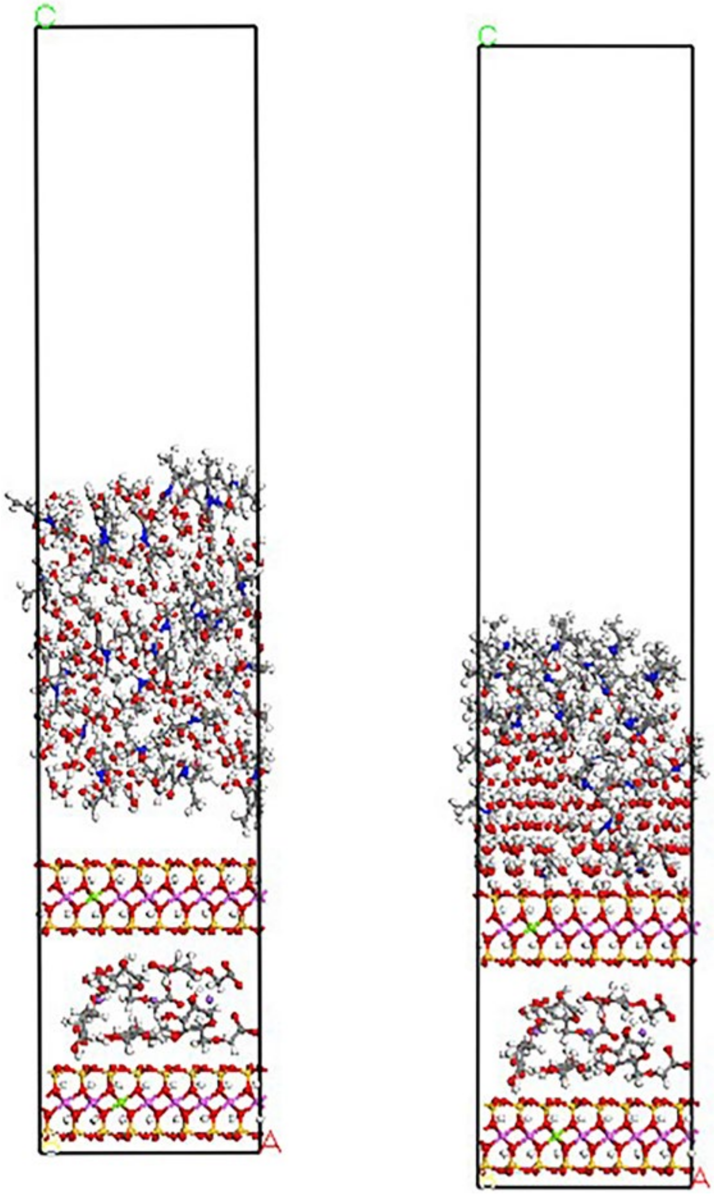


Figure 18: Structure diagram of montmorillonite before and after NIPAM adsorption.

and NIPAM have competitive adsorption on the surface. The hydrogen bond between polar head groups and water molecules causes NIPAM to be inclined rather than perpendicular to the surface. However, NIPAM itself is neutral and non charged, so its adsorption is mainly achieved through non charged interaction. Therefore, large volume NIPAM clusters adhere to the surface and are obviously exposed to solvents. The charge neutral NIPAM molecule interacts with the surface of montmorillonite through the hydrogen bond between the hydroxyl group of water molecule and amide.

4. PREPARATION AND EVALUATION OF DRILLING FLUID FORMULATION

In the drilling process, the performance of drilling fluid is directly related to the safety, efficiency and cost control of the operation. In order to enhance the stability, lubricity, and ability of drilling fluids to carry chips, various additives are widely used in the formulation of drilling fluids [51]. Oilfields with complex geological conditions (such as high temperature, high salt, high pressure, etc.) need to choose additives with better chemical stability and stronger adaptability. At the same time, some additives are not effective when used alone, but can significantly improve the performance of drilling fluids when combined with other additives [52]. Therefore, when selecting additives, it is necessary to consider the effect of their compounding with other additives.

4.1. Preparation of drilling fluid formula

Through the determination of the concentration of the base slurry of the drilling fluid and the optimization and analysis of the types and dosages of additives, the preparation method of "350 ml distilled water+6% modified bentonite+94% additives" was finally determined. The additives include 0.05% barite, 0.2% sodium chloride, 0.4% polyacrylamide, 0.4% FA-36T and 0.4% polyanionic cellulose, which will be used in the formulation of deepwater drilling fluid system performance evaluation.

4.2. Drilling fluid performance test

4.2.1. Rheological test

The rheology of drilling fluid has a critical impact on the safety of drilling operations. The rheology of drilling fluid affects its rock-carrying capacity, that is, its ability to carry cuttings from the bottom of the hole to the surface [53]. If the rheological proper-ties of the drilling fluid are insufficient, cuttings may be deposited in the hole, increasing the risk of sticking during drilling. In addition, the rheological properties of the drilling fluid also affect the stability of the wellbore [54]. Appropriate viscosity and shear force help to form a protective film on the wellbore, reduce the formation of fluid entry into the wellbore, and avoid wellbore collapse. Good rheology can ensure the stability of drilling fluid in downhole high-temperature and high-pressure environments, and avoid downhole accidents caused by poor rheology, such as wellbore instability and complex conditions.

Table 4 shows the rheological test results of drilling fluid prepared with different bentonites of the same formulation. The main reference indexes are apparent viscosity (AV), plastic viscosity (PV), dynamic shear stress (YP), dynamic plastic ratio (b), and fluidity index (n).

With the same drilling fluid formula, the viscosity of Chaoyang OCMA bentonite is too high, the dynamic shear stress and dynamic plasticity ratio are high, and the flow coefficient is too small. This will lead to increased tripping circulation pressure consumption and pressure fluctuation, which is prone to risks during drilling. Although the dynamic plastic ratio and fluidity index of the calcium based original bentonite drilling fluid and the calcium based original bentonite drilling fluid added with NIPAM meet the drilling requirements, it has the disadvantages of too low viscosity and slightly insufficient dynamic shear stress. The low viscosity drilling fluid has low flow resistance in the annulus, which leads to the failure of the drilling fluid to effectively suspend rock cuttings and affects the carrying capacity of the drilling fluid; The drilling fluid with NIPAM as an additive can meet the viscosity requirements, but the dynamic shear stress, dynamic plastic ratio and fluidity index are poor, which is prone to the risk similar to OCMA bentonite drilling fluid in the drilling process; The modified bentonite drilling fluid can meet the requirements of practical drilling application in rheological test, and its performance is relatively excellent.

4.2.2. Temperature sensitivity test

Due to the particularity of the deepwater environment, the rheological properties of drilling fluid under variable temperature conditions are very important for the smooth drilling operation [55]. The rheological properties of deepwater drilling fluids change under temperature conditions, which may affect the rock-carrying capacity of drilling fluids, the cooling effect, and the service life of the bit [56]. To meet the rheological regulation requirements of deepwater water-based drilling fluids, bentonite modified by temperature-sensitive polymer NIPAM was developed as a solid phase additive for drilling fluids. To test the temperature-sensitive properties of the

Table 4: Rheological determination experiments of drilling fluids.

	AV	PV	YP	B	N
Calcium bentonite drilling fluid	27.5	19	8.5	0.447	0.611
Chaoyang OCMA bentonite drilling fluid	82.5	43	39.5	0.919	0.435
Modified bentonite drilling fluid	43	30	13	0.433	0.619
NIPAM drilling fluid was added to the calcium bentonite	49.5	14	5.5	0.393	0.642
NIPAM drilling fluid is added independently	59	31	28	0.903	0.44

Table 5: Variation of apparent viscosity of different drilling fluids with temperature.

TEMPERATURE	CALCIUM BENTONITE DRILLING FLUID	MODIFIED BENTONITE DRILLING FLUID	CALCIUM BENTONITE+ NIPAM DRILLING FLUID	MODIFIED BENTONITE+ NIPAM DRILLING FLUID	CHAOYANG OCMA BENTONITE DRILLING FLUID
25°C	27.5	43	19.5	59	82.5
35°C	22	41	18	51	80.5
45°C	19	40	16.5	47.5	79
55°C	18	40	14	44.5	81.5
65°C	16.5	42	12	42	87
75°C	14	42.5	10.5	45	93.5
85°C	14	40.5	9.5	50.5	98
95°C	11.5	41	8	58	103.5

modified bentonite drilling fluids, eight temperature gradients ranging from 25°C to 95°C were selected to evaluate the rheological properties of five drilling fluids at different temperatures.

As shown in Tables 5, 6, the viscosity of Calcium bentonite drilling fluid and Calcium bentonite drilling fluid added with NIPAM decreased with the increase of temperature until the viscosity was almost zero, indicating that the solid components in the drilling fluid were precipitated, indicating that these drilling fluid systems were extremely unstable under temperature changes.

In contrast, Chaoyang OCMA bentonite drilling fluid shows the phenomenon of temperature rise and thickening, but the plastic viscosity changes significantly, fluctuates violently and has no fixed law. This may be due to the different reactions of the additives added to the drilling grade bentonite under specific temperature conditions, resulting in a large difference in the state of the drilling fluid at different temperatures. While the drilling fluid with NIPAM as additive has certain fluctuations in the range of 45°C–75°C, it can better control the viscosity of the drilling fluid in general. This indicates that NIPAM has good temperature sensitivity in solution system. However, compared with modified bentonite drilling fluid, the viscosity of NIPAM additive changes more violently. In contrast, the viscosity curve of the modified bentonite drilling fluid is smoother, which shows that the ability of NIPAM modified bentonite in controlling the temperature of drilling fluid is better than that of NIPAM as a drilling fluid additive directly.

As shown in Table 7, the dynamic shear stresses of Calcium bentonite drilling fluid and its modified system with N-isopropyl acrylamide (NIPAM) addition both show a linear decreasing trend with the increase of temperature, and have a positive correlation with the change of viscosity. This phenomenon can be explained by the enhanced thermal motion of bentonite particles: An increase in temperature leads to a weakening of the interlayer hydration of bentonite, a reduction in the degree of particle aggregation, and a decrease in the internal frictional resistance of the fluid, thereby simultaneously causing the synchronous attenuation of viscosity and dynamic shear stress. The dynamic shear stress of Chaoyang OCMA bentonite shows an abnormal exponential increase with the rise of temperature. This is because it contains a relatively high proportion of montmorillo-niteillite mixed-layer minerals. At high temperatures, interlayer cation desorption and lattice expansion occur, resulting in the formation of a rigid network structure within the fluid.

Table 6: Variation of plastic viscosity of different drilling fluids with temperature.

TEMPERATURE	CALCIUM BENTONITE DRILLING FLUID	MODIFIED BENTONITE DRILLING FLUID	CALCIUM BENTONITE+ NIPAM DRILLING FLUID	MODIFIED BENTONITE+ NIPAM DRILLING FLUID	CHAOYANG OCMA BENTONITE DRILLING FLUID
25°C	19	30	14	31	43
35°C	16	28	13	27	38
45°C	14	29	13	26	30
55°C	13	28	11	22	30
65°C	13	30	10	22	41
75°C	11	29	9	26	39
85°C	11	28	8	29	29
95°C	9	28	7	35	38

Table 7: Variation of dynamic shear stress of different drilling fluids with temperature.

TEMPERATURE	CALCIUM BENTONITE DRILLING FLUID	MODIFIED BENTONITE DRILLING FLUID	CALCIUM BENTONITE+ NIPAM DRILLING FLUID	MODIFIED BENTONITE+ NIPAM DRILLING FLUID	CHAOYANG OCMA BENTONITE DRILLING FLUID
25°C	8.5	13	5.5	28	39.5
35°C	6	13	5	24	42.5
45°C	5	11	3.5	21.5	49
55°C	5	12	3	22.5	51.5
65°C	3.5	12	2	20	46
75°C	3	13.5	1.5	19	54.5
85°C	3	12.5	1.5	21.5	69
95°C	2.5	13	1	23	65.5

The drilling fluid system with NIPAM added all shows a reduced fluctuation amplitude of shear stress when the temperature changes. This is due to the temperature sensitivity of NIPAM molecules: At low temperatures, the NIPAM molecular chains are in an extended state and bridge bentonite particles through hydrogen bonds to form a reversible cross-linked network. When the temperature rises above its low critical dissolution temperature, the molecular chains contract into a hydrophobic spherical structure, and some crosslinking points break, but the remaining physical entanglements can still maintain the relative stability of the fluid structure. Therefore, the NIPAM modification technology significantly improves the thermal stability of the drilling fluid, featuring both low shear rate and high viscosity as well as high shear rate and low viscosity, and can better meet the requirements of safe and efficient drilling under complex geological conditions.

The results show that the dynamic plastic ratio of native bentonite drilling fluid and native bentonite drilling fluid added with NIPAM decreases continuously with the increase of temperature as shown in Table 8. The dynamic plastic ratio of Chaoyang OCMA bentonite drilling fluid increases with the increase of temperature, which is far beyond the level required for practical application. In particular, the dynamic plastic ratio of Chaoyang OCMA bentonite drilling fluid showed a sharp fluctuation similar to the viscosity in the temperature range of 35°C–65°C, which further confirmed that Chaoyang OCMA bentonite, as a solid component of drilling fluid, may react with its internal additives in this temperature range. However, when the temperature reaches 85°C, the dynamic plastic ratio of the two OCMA drilling fluids decreases sharply, which is likely because the internal structure of bentonite has been damaged. On the other hand, the two drilling fluid systems with NIPAM

Table 8: Variation of dynamic plastic ratio of different drilling fluids with temperature.

TEMPERATURE	CALCIUM BENTONITE DRILLING FLUID	MODIFIED BENTONITE DRILLING FLUID	CALCIUM BENTONITE+ NIPAM DRILLING FLUID	MODIFIED BENTONITE+ NIPAM DRILLING FLUID	CHAOYANG OCMA BENTONITE DRILLING FLUID
25°C	0.447	0.433	0.393	0.903	0.919
35°C	0.375	0.464	0.385	0.889	1.118
45°C	0.357	0.379	0.269	0.827	1.633
55°C	0.385	0.429	0.273	1.022	1.717
65°C	0.269	0.4	0.2	0.909	1.122
75°C	0.273	0.466	0.167	0.731	1.397
85°C	0.273	0.446	0.188	0.741	2.379
95°C	0.278	0.464	0.143	0.657	1.724

Table 9: Variation of fluidity index of native bentonite drilling fluid with temperature.

TEMPERATURE	CALCIUM BENTONITE DRILLING FLUID	MODIFIED BENTONITE DRILLING FLUID	CALCIUM BENTONITE+ NIPAM DRILLING FLUID	MODIFIED BENTONITE+ NIPAM DRILLING FLUID	CHAOYANG OCMA BENTONITE DRILLING FLUID
25°C	0.611	0.619	0.642	0.44	0.436
35°C	0.652	0.603	0.646	0.444	0.388
45°C	0.663	0.65	0.722	0.461	0.338
55°C	0.646	0.622	0.72	0.41	0.293
65°C	0.722	0.637	0.778	0.438	0.387
75°C	0.72	0.602	0.807	0.492	0.337
85°C	0.72	0.612	0.789	0.488	0.231
95°C	0.716	0.603	0.83	0.518	0.293

showed a relatively gentle change trend when the temperature changed. However, it is worth noting that the overall dynamic plastic ratio of drilling fluid with NIPAM as an additive shows a high value.

As shown in Table 9, with the increase of temperature, the fluidity coefficient of native bentonite drilling fluid and native bentonite drilling fluid added with NIPAM increases continuously, especially after 65°C, their fluidity coefficient increases significantly, showing strong shear thickening characteristics. This property may increase the viscosity of the drilling fluid at the water hole of the bit, thereby increasing the risk of swabbing during tripping.

In contrast, the fluidity index of Chaoyang OCMA bentonite decreases with the increase of temperature. Within the temperature range of 35°C–65°C, the dynamic plastic ratio of the drilling fluid shows a sharp fluctuation opposite to the viscosity, which further confirms that Chaoyang OCMA bentonite is adversely affected by temperature within this temperature range. When the temperature reaches 85°C, the fluidity index of the drilling fluid first decreases sharply and then increases, which once again proves that the internal structure of bentonite has been seriously damaged. On the other hand, the two kinds of drilling fluid systems added with NIPAM show a relatively gentle change trend when the temperature changes. However, it is worth noting that at the termination temperature, the fluidity index of the drilling fluid with NIPAM as an additive increases compared with the initial state, indicating that NIPAM as a drilling fluid additive can increase the viscosity of the drilling fluid.

Table 10: Drilling fluid thixotropy determination experiments.

	25	**35**	**45**	**55**	**65**	**75**	**85**	**95**
Calcium bentonite drilling fluid	0	0	0	0	0	0	0	0
Chaoyang OCMA bentonite drilling fluid	6	10	12	12	15	12	12	14
Modified bentonite drilling fluid	–15	–12	–9	–2	1	2	0	0
NIPAM drilling fluid was added to the calcium bentonite	1	0	0	0	0	0	0	0
NIPAM drilling fluid is added independently	–6	–6	–8	–11	–14	–19	–16	–14

4.2.3. Thixotropy test

Thixotropy of drilling fluid is the property that it becomes thin after being stirred and dense after standing. Specifically, the shear force of drilling fluid will gradually increase with the increase of standing time after mixing. Thixotropy is a key property of viscous non newtonian fluids. From the perspective of colloidal chemistry, it reflects the reversible conversion ability of fluids between gel state and sol state.

At present, the main method to evaluate the thixotropy of drilling fluid is the static shear force method. The thixotropy of the drilling fluid was evaluated by measuring the difference in shear stress when the drilling fluid was stirred at a high speed of 600r/min in a rotary viscometer for 10 minutes.

As shown in Table 10, it can be observed that both the calcium-based original bentonite drilling fluid and the original bentonite drilling fluid with NIPAM show good thixotropy. It can also quickly return to the initial state. At the same time, this characteristic does not change significantly with the increase of temperature. In contrast, Chaoyang OCMA bentonite has the worst thixotropy performance, and the static shear difference of Chaoyang OCMA bentonite increases with the increase of temperature. Although the initial thixotropy of modified bentonite drilling fluid is poor, with the change of temperature, its thixotropy gradually tends to be stable, showing a stable trend. Although the initial thixotropy of drilling fluid prepared with NIPAM as an additive is good, its thixotropy gradually becomes worse with the increase of temperature. Therefore, after comparing the other five drilling fluids, it can be found that the modified bentonite drilling fluid has a good adjustment ability under the condition of temperature change, and can effectively adjust the rheology of the drilling fluid. This enables it to give full play to its temperature-sensitive adjustment ability and maintain excellent thixotropy when encountering ambient temperature changes, which is conducive to the suspension of drilling cuttings.

Thixotropy is essentially the characteristic of the internal structure of drilling fluid changing with shear stress, and its core lies in the reversible microstructure reconstruction ability. The increase in temperature enhances the molecular thermal motion, weakens the van der Waals forces and hydration between the layers of bentonite, and makes the spatial network structure formed by the drilling fluid under static conditions more vulnerable to damage, which is manifested as a reduction in the area of the thixotropic ring. For drilling fluids with added NIPAM, the increase in temperature will trigger the phase transition of polymer molecules, change their adsorpt-bridging effect with bentonite particles, and thereby affect the thixotropic recovery rate and amplitude. Adding NIPAM can smooth out the change of thixotropy with temperature and enhance the thixotropic strength as a whole. Thixotropy is the dynamic response of drilling fluid to temperature changes, and temperature sensitivity quantifies the intensity of this response. Therefore, the two form a closed-loop regulation through microstructure reconstruction and macroscopic rheological parameters, which better explains the temperature response mechanism of NIPAM.

5. CONCLUSIONS

In this study, CMC was intercalated into calcium bentonite, and then N-isopropylacrylamide (NIPAM) was grafted on the surface of calcium bentonite. The rheological properties, expansion capacity and temperature sensitivity of CMC-B-NIPAM suspension were analyzed, and the temperature sensitive modification mechanism of bentonite was given through microscopic characterization:

(1) The preparation conditions of CMC-B-NIPAM were optimized. Through the experimental results, the optimal synthesis conditions of CMC-B were determined as follows: the ratio of sodium carbonate to calcium bentonite was 1:9; The addition of sodium pyrophosphate was 0.5%; The ratio of sodium bentonite to CMC was 30:1, and the amount of NIPAM was 0.5 g.

(2) Characterization of CMC-B-NIPAM. After the characterization of CMC-B-NIPAM by XRD, the results showed that the layer spacing of bentonite increased by 0.3324 nm compared with that before intercalation. The results show that CMC successfully destroys the original layer structure of bentonite, realizes intercalation into the bentonite layer, and effectively expands the layer spacing. At the same time, NIPAM was combined with the surface of CMC-B-NIPAM through coupling, to complete the temperature-sensitive modification of CMC-B-NIPAM. In addition, the presence of chemical bonds such as -CH(CH3)2, N-H, and C-N was detected by Fourier transform infrared spectroscopy (FT-IR) analysis, which further confirmed that the structure of CMC-B-NIPAM met the design requirements.

(3) The rheological properties, temperature sensitivity and thixotropy of the modified bentonite CMC-B-NIPAM were tested. The results show that NIPAM-B can respond to temperature changes and has good rheological and temperature sensitive viscosity increasing properties.

(4) The formulation of “400 ml distilled water+4% CMC-B-NIPAM+1.5%NaCl+0.3% barite +1.5%PAC+2% polyacrylamide” was finally determined through the optimization of base slurry concentration, inorganic salts, weighting materials, fluid loss reduction agents and anti-slumping agents. The formulation is simple and easy to operate and can be used in Marine strati-graphic environments.

(5) Performance evaluation of temperature-sensitive modified Marine drilling fluid system. A drilling fluid system with temperature-sensitive viscosity enhancement properties was evaluated for offshore drilling operations. The system shows good temperature-sensitive response-ability and effectively overcomes the defect of viscosity reduction of traditional drilling fluid during the heating process. This process ensures that the rheological properties of the drilling fluid can be restored to the expected state and that the flow pattern stability of the drilling fluid system is maintained.

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7. BIBLIOGRAPHY

[1] ZHANG, P., “Research on modification methods and applications of bentonite”, *Science and Technology Innovation and Application*, v. 21, pp. 29, 2013. doi: http://doi.org/10.19981/j.cn23-1581/g3.2013.21.025.

[2] SU, C.Z., “Research on modification and hygroscopic properties of bentonite”, *China Non-metallic Minerals Industry Guide*, 2023, v. 3, pp. 55–57+60.

[3] YU, Y.Y., JING Q.S., YU X.H., *et al*., “Study on preparation of drilling mud additve by upgrading low--grade bentonite”, *Mineral Protection and Utilization*, v. 42, n. 4, pp. 60–67. doi: http://doi.org/10.13779/j.cnki.issn1001-0076.2022.04.007.

[4] YANG, K., LI, Z., “Montmorillonite swell structure characteristics analysis”, *Journal of Silicate Bulletin*, v. 29, n. 5, pp. 1154–1158. doi: http://doi.org/10.16552/j.cnki.issn1001-1625.2010.05.012.

[5] PAN, Y., ZHANG, X., JI, C., *et al*., “Modification method of high-efficiency organic bentonite for drilling fluids: a review”, *Molecules (Basel, Switzerland)*, v. 28, n. 23, pp. 7866, 2023. doi: http://doi.org/10.3390/molecules28237866. PubMed PMID: 38067595.

[6] BARAKAN, S., AGHAZADEH, V., “Separation and characterisation of montmorillonite from a low-grade natural bentonite: using a non-destructive method”, *Micro & Nano Letters*, v. 14, n. 6, pp. 688–693, 2019. doi: http://doi.org/10.1049/mnl.2018.5364.

[7] YU, C., LIAO, R., CAI, X., *et al*., “Sodium polyacrylate modification method to improve the permeant performance of bentonite in chemical resistance”, *Journal of Cleaner Production*, v. 213, pp. 242–250, 2019. doi: http://doi.org/10.1016/j.jclepro.2018.12.179.

[8] ALI, I., AHMAD, M., LASHARI, N., “Improving the performance of bentonite-free water-based mud with lignin-based biopolymer”, *Petroleum Science and Technology*, v. 43, n. 8, pp. 831–843, 2025. doi: http://doi.org/10.1080/10916466.2024.2326648.

[9] ZIHAN, Q., KUANGWU, Q., XIAODONG, G., “Preparation and properties of cationic polyacrylamide intercalated modified bentonite”, *Yunnan Chemical Industry*, v. 45, n. 10, pp. 52–54, 2018. doi: http://doi.org/10.3969/j.issn.1004-275X.2018.10.019.

[10] QI, C., BING, C., LEI, L., *et al*., "Effects of synthetic processes on the swelling capacity and modification mechanism of CMC-modified bentonite composites", *Applied Clay Science*, v. 241, pp. 107005, 2023. doi: http://doi.org/10.1016/j.clay.2023.107005.

[11] XIA, Z., XIANG, F., ZHI, W., *et al*., "Composite-polymer modified bentonite enhances anti-seepage and barrier performance under high-concentration heavy-metal solution", *Journal of Cleaner Production*, v. 376, pp. 134253, 2022. doi: http://doi.org/10.1016/j.jclepro.2022.134253.

[12] ZHOU, P., LI, M., WU, Y.P., "Research progress of polymer/bentonite nanocomposites", *Journal of Functional Materials*, v. 53, n. 7, pp. 7058–7068, 2022. doi: http://doi.org/10.3969/j.issn.1001-9731.2022.07.007.

[13] YAN, Z.C., WANG, H.L., SUN D.S., *et al*., "Microstructure and adsorption mechanism of sodium bentonite intercalation modification", *Chinese Journal of Environmental Engineering*, v. 10, n. 9, pp. 4879–4886, 2016. doi: http://doi.org/10.12030/j.cjee.201504207.

[14] LI, H.K., LUO, J.S., GENG, T., *et al*., "Advances in deepwater drilling fluid technology at home and abroad", *Drilling Fluid & Completion Fluid*, v. 32, n. 6, pp. 85–88+109, 2015. doi: http://doi.org/10.3696/j.issn.1001-5620.2015.06.022.

[15] DING, T., WANG, R., XU, J., *et al*., "Synthesis and application of a temperature sensitive poly(N-vinylcaprolactam-co-N,N-diethyl acrylamide) for low-temperature rheology control of water-based drilling fluid", *Colloids and Surfaces. A, Physicochemical and Engineering Aspects*, v. 644, pp. 128855, 2022. doi: http://doi.org/10.1016/j.colsurfa.2022.128855.

[16] CHEN, L., YOU, F.C., ZHOU S.S., *et al*., "Preparation and performance evaluation of drilling fluid for deepwater constant rheological solid-free reservoir", *Oilfield Chemistry*, v. 40, n. 1, pp. 1–6, 2023. doi: http://doi.org/10.19346/j.cnki.1000-4092.2023.01.001.

[17] CHEN, L., GUO, Z.X., SUN, K., *et al*., "Research on deepwater drilling technology in marine", *Natural Gas Technology*, v. 3, n. 6, pp. 37–39+79, 2009.

[18] CUI, M.L., "Development and performance study of organic bentonite for high-temperature resistant white oil-based drilling fluid", *Guangzhou Huagong*, v. 42, n. 6, pp. 70–72, 2014.

[19] PAN, Y., XU, M., ZHAN, Q., *et al*., "Preparation and properties of N-isopropylacrylamide-based intelligent bentonite", *Fine Chemicals*, v. 38, n. 10, pp. 2057–2063+2071, 2021. doi: http://doi.org/10.13550/j.jxhg.20210608.

[20] XIAO, C.L., FAN R.D., YANG A.W., "Experimental study on chemical compatibility of CMC modified bentonite under the action of phenol solution", *Journal of Engineering Geology*, v. 29, n. 5, pp. 1286–1294, 2021. doi: http://doi.org/10.13544/j.cnki.jeg.2021-0392.

[21] DONG, Q.J., DING H., HOU Y.M., *et al*., " Synthesis and properties of polyn-isopropylacrylamide copolymers containing pyrene group in side chain", *Journal of Fine Chemical Industry*, v. 11, pp. 2273–2279, 2020. doi: http://doi.org/10.13550/j.jxhg.20200513.

[22] LIN, T., LING, W., XIAO, Y., *et al*., "Poly(N-isopropylacrylamide)-based smart hydrogels: Design, properties and applications", *Progress in Materials Science*, v. 115, pp. 100702, 2021. doi: http://doi.org/10.1016/j.pmatsci.2020.100702.

[23] NGANG, H.P., AHMAD, A.L., LOW, S.C., *et al*., "Preparation of thermoresponsive PVDF/SiO2-PNIPAM mixed matrix membrane for saline oil emulsion separation and its cleaning efficiency", *Desalination*, v. 408, pp. 1–12, 2017. doi: http://doi.org/10.1016/j.desal.2017.01.005.

[24] AHMED, A.A., SAAID, I.M., AKHIR, N A M., "Graft copolymerization of N-Isopropylacrylamide and acrylic acid on bentonite colloids for in-depth fluid diversion", *Energy & Fuels*, v. 31, n. 4, pp. 3537–3545, 2017. doi: http://doi.org/10.1021/acs.energyfuels.6b02507.

[25] YAGHOUBI, Z., BASIRI-PARSA, J., "Modification of ultrafiltration membrane by thermo-responsive Bentonite-poly(N-isopropylacrylamide) nanocomposite to improve its antifouling properties", *Journal of Water Process Engineering*, v. 34, pp. 101067, 2020. doi: http://doi.org/10.1016/j.jwpe.2019.101067.

[26] CHENG, L., YANG, G., ZHANG, S., *et al*., "Preparation and action mechanism of temperature sensitive N-Isopropylacrylamide/nanosilica hybrid as rheological modifier for water-based drilling fluid", *SSRN Electronic Journal*, v. 219, pp. 111096, 2022. doi: http://doi.org/10.1016/j.petrol.2022.111096.

[27] YAN, B.Y., "Research on the sodification process of natural montmorillonite", *Quality & Market*, n. 15, pp. 83–85, 2020.

[28] WANG, X., ZHANG, Z., XIE, H., "Preparation, characterization and intercalation mechanism of bentonite modified with different organic ammonium", *Chemical Engineering Science*, v. 301, pp. 120758, 2025. doi: http://doi.org/10.1016/j.ces.2024.120758.

[29] HU, J.L., FU, F., TAO, S.X., *et al*., "Characterization of sodified and organically modified bentonite and research on drilling fluid performance// Exploration Engineering Professional Committee of the Geological Society of China,". In: *Proceedings of the 16th National Academic Exchange Conference on Prospecting Engineering (Geotechnical Drilling and Excavation Engineering) Technology College of Engineering and Technology*, China University of Geosciences (Beijing) Beijing Institute of Prospecting Engineering, pp. 297–302, 2011.

[30] MIAO, Y.H., ZHAO, Y.L., CHEN, L.C., et al., "Study on the sodium process of calcium-based bentonite and its effect on the viscosity of slurry", *Chinese Journal of Ceramics*, v. 41, n. 10, pp. 3525–3532, 2022. doi: http://doi.org/10.16552/j.cnki.issn1001-1625.2022.10.014.

[31] QIAN Y., JI J., WANG F., *et al*., "Effect of sodium pyrophosphate on the dispersion of modified bentonite", *Coating & Coatings*, v. 40, n. 10, pp. 8–11+14, 2010.

[32] LEIVA, W., AYALA, L., ROBLES, P., *et al*., "Sodium acid pyrophosphate as a rheological modifier of clay-based tailings in saline water", *Applied Clay Science*, v. 253, pp. 107352, 2024. doi: http://doi.org/10.1016/j.clay.2024.107352.

[33] YOON, J., MOHTAR, E.C., "Dynamic rheological properties of sodium pyrophosphate-modified bentonite suspensions for liquefaction mitigation", *Clays and Clay Minerals*, v. 61, n. 4, pp. 319–327, 2013. doi: http://doi.org/10.1346/CCMN.2013.0610411.

[34] MONTORO, M.A., FRANCISCA, F.M., "Effect of ion type and concentration on rheological properties of natural sodium bentonite dispersions at low shear rates", *Applied Clay Science*, v. 178, pp. 105132, 2018. doi: http://doi.org/10.1016/j.clay.2019.105132.

[35] QIU, J., CUI, X.Q., LV, X.J., *et al*., "Determination of charge of montmorillonite layer", *Mining Letters*, n. 06, pp. 6–9, 2005.

[36] YANG, C.H., LI, Z., YANG K., "Study on sodium modification and microstructure change of Ca-MMT", *Journal of Nonmetallic Minerals*, v. 34, n. 3, pp. 19–21+44. 2011.

[37] SUMAN, K., MITTAL, M., JOSHI, Y.M., "Effect of sodium pyrophosphate and understanding microstructure of aqueous LAPONITE® dispersion using dissolution study", *Journal of Physics: Condensed Matter*, v. 32, n. 22, pp. 224002. doi: http://doi.org/10.1088/1361-648X/ab724d.

[38] LIU, Q.F., WANG, D., GUO, P., *et al*., "Preparation and structural characterization of quaternary ammonium-kaolinite intercalation complexes", *Journal of the Chinese Ceramic Society*, v. 43, n. 2, pp. 222–230, 2015. doi: http://doi.org/10.14062/j.issn.0454-5648.2015.02.14.

[39] NONG, W.W., *Study on surface modification of bentonite with coupling agent*, Nanning: Guangxi University, 2007.

[40] XIE, B.Q., TAO, H.Z., ZHANG, J., *et al*., "Regulation of comb-type temperature-sensitive polymers on high-temperature rheology of solid-free water-based drilling fluids", *Acta Petrolei Sinica*, v. 45, n. 2, pp. 427–436, 2024. doi: http://doi.org/10.7623/syxb202402008.

[41] LIPING, C., GUANGBIN, Y., SHENGMAO, Z., *et al*., "Preparation and action mechanism of temperature sensitive N-isopropylacrylamide/nanosilica hybrid as rheological modifier for water-based drilling fluid", *Journal of Petroleum Science Engineering*, v. 219, pp. 111096, 2022. doi: http://doi.org/10.1016/j.petrol.2022.111096.

[42] DING, T., WANG, R., XU, J., *et al*., "Synthesis and application of a temperature sensitive poly(N-vinylcaprolactam-co-N,N-diethyl acrylamide) for low-temperature rheology control of water-based drilling fluid", *Colloids and Surfaces. A, Physicochemical and Engineering Aspects*, v. 644, pp. 128855, 2022. doi: https://doi.org/10.1016/j.colsurfa.2022.128855.

[43] HUANG, W., *Preparation and characterization of modified bentonite and its application*, Xiangtan, Xiangtan University, 2017.

[44] XIE, W.N., NIE, J.X., ZOU, X.J., *et al*., "Preparation and characterization of modified bentonite composite new particles", *Chinese Journal of Ceramics*, v. 35, n. 9, pp. 2990–2994, 2016. doi: http://doi.org/10.16552/j.cnki.issn1001-1625.2016.09.052.

[45] ZHANG, Y.M., REN, J.M., LIU, G.Y., *et al*., "Preparation and characterization of modified bentonite", *Journal of Chongqing Technology and Business University*, v. 26, n. 3, pp. 286–290, 2009.

[46] SUN, Y., LI, X., REN, Z., "Preparation, characterization and adsorption properties of composite modified bentonite", *Journal of Lanzhou Jiaotong University*, v. 34, n. 3, pp. 175–180, 2015. doi: http://doi.org/10.3969/j.issn.1001-4373.2015.03.033.

[47] CHENG, W.Y., *Study on preparation of modified bentonite and adsorption properties of heavy metals*, Shandong, Shandong University of Science and Technology, 2018. doi: http://doi.org/10.27275/d.cnki.gsdku.2018.000173.

[48] MAHDI, E.A., ABBAS, K.K., ALJUMAILY, M.M., *et al*., "Preparation, characterization and applications of polyethersulfone/bentonite clay composite for protein removal", *Desalination and Water Treatment*, v. 320, pp. 100653, 2024. doi: http://doi.org/10.1016/j.dwt.2024.100653.

[49] AWINASH, K., PRADIP, L., "Fourier transform infrared spectroscopic, X-Ray fluorescence and X-Ray diffraction characterization of sodium bentonite clay and kaolin clay, potentials as a catalyst for plastic waste valorization", *Current Organocatalysis*, 2019. In press. doi: http://doi.org/10.2174/2213337206666191018104929.

[50] WANG, X., ZHANG, Z., XIE, H., "Preparation, characterization and intercalation mechanism of bentonite modified with different organic ammonium", *Chemical Engineering Science*, v. 301, pp. 120758, 2025. http://doi.org/10.1016/j.ces.2024.120758.

[51] LI, Y.J., WU, Z.M., XU, Y.L., *et al*., "Construction and performance evaluation of 220°C resistant deepwater high-density drilling fluid system", *Chemical and Biological Engineering*, v. 37, n. 7, pp. 42–46, 2020. doi: http://doi.org/10.3969/j.issn.1672-5425.2020.07.009.

[52] YAO, Q., *Research on deepwater high-temperature and high-pressure constant rheological water-based drilling fluid system*, Hubei, Yangtze University, 2020. doi: http://doi.org/10.26981/d.cnki.gjhsc.2020.000113.

[53] THAKUR, K.N., DHASMANA, P., KANDWAL, R., *et al*., "Experimental investigation of ionic liquid as an additive in enhancing the rheological and filtration properties of water-based drilling fluid", *Materials Today: Proceedings*, v. 99, pp. 99119–99125, 2024. doi: http://doi.org/10.1016/j.matpr.2023.05.524.

[54] FAN, L.C., SUN, M.J., "Research and application of strong inhibition sealing and anti-collapse drilling fluid", *Inner Mongolia Petrochemical Industry*, v. 48, n. 9, pp. 12–16, 2022.

[55] YANG, S., ZHAN, Q., PAN, Y., *et al*., "Research progress on low-temperature rheology of high-performance ocean deepwater drilling fluids: an overview", *Journal of Petroleum Science Engineering*, v. 218, pp. 110978, 2022. doi: http://doi.org/10.1016/j.petrol.2022.110978.

[56] HU, Y.L., WANG, J., YAN, Z., *et al*., Research progress on drilling fluids for marine deepwater drilling. *Off-shore Oil*, v. 4, pp. 83–86, 2004.

DATA AVAILABILITY

Data sharing is not applicable to this article as no new data were created or analyzed in this study.