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Investigation of high temperature rheological properties for attapulgite suspensions

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Understanding the high temperature rheological characteristics of attapulgite suspensions is essential for addressing issues related to smooth rock support and wellbore stabilization during deep drilling in complex formations. Rheological measurements of attapulgite suspensions were carried out at temperatures of 40 °C, 70 °C, 100 °C, 160 °C, 190 °C, and 220 °C. The viscosity values obtained were analyzed to assess slurry forming behavior, and flow curves were fitted using Bingham, Herschel-Bulkley and Casson models. Additional experiments investigated different physicochemical conditions (clay addition 2–8 wt%; shear rate $5.11s^{-1}$ to $1022s^{-1}$; aging conditions; electrolyte (NaCl) concentration 5-35%) showed that there was a significant positive correlation between clay addition and suspension viscosity, but the temperature variations complicated the rheological responses. High shear rates allowed complete dispersion of attapulgite clay to form a suspension with stable viscosity. Aging positively influenced viscosity retention at high temperatures, despite some clay agglomeration. Sodium chloride and polymers significantly affected the high temperature rheological properties of the suspensions. The Bingham model effectively described the rheological properties of the suspensions above 190 °C. While attapulgite is recognized as a salt-resistant clay, our experimental results also demonstrate its significant temperature resistance when incorporated into drilling fluids.

Keywords Attapulgite, Slurry forming performance, High temperature rheological properties, Rheological model

Abbreviations

HTHP	High temperature and high pressure
ATP	Attapulgite
T	Temperature
AV	Apparent viscosity, mPa s
η	Plastic viscosity, mPa s
τ_0	Yield stress, Pa
K	Coefficient of consistency, Pa s^n
n	Flow index, dimensionless
τ_c	Casson dynamic shear stress, Pa
η_∞	Casson ultimate viscosity, mPa s

Water-based drilling fluids typically consist of water, clay, and functional treatment agents. The main clays used are bentonite, attapuligite (ATP), and sepiolite[1–3].While these clay minerals that can disperse in water to form stable suspensions with specific viscosities, the mechanisms behind the gel structures of these suspensions differ significantly due to their unique structures, particle sizes, and shapes[4,5]. In swelling clay minerals like montmorillonite, the net negative charge from isomorphic substitution is balanced by exchangeable cations in the interlayer. The hydration of these interlayer cations causes swelling and separation of clay layers, including the movement of water molecules and the rheological properties of the swelling clays. Consequently, the swelling potential and colloidal behaviour (particle–particle interaction) in these clay minerals are determined by the layer composition, layer charge, and the nature of the exchangeable interlayer cation[6–8]. However, montmorillonite-

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based bentonite is highly sensitive to temperature and salinity due to its clay diffusion bilayer, leading to a decline in slurry-making performance at high temperatures or high salinities[9–11].

Attapulgite is an aqueous magnesium-rich aluminum silicate clay with a laminated chain transition structure, characterized by the chemical formula $[Si_8O_{20}(Mg, Al, Fe)_5(OH)_2(OH_2)_4-2H_2O]$ and crystalline, rod-like fibers[12–14]. The tiny lamellar chain-like structure contributes to the clay's fibrous shape and macroscopic appearance, with pores aligned along the fiber growth direction[15]. Compare to bentonite, attapuligte, with its fibrous structure, exhibits effective slurry forming in saline environments due to its lack of structural charges and the minimal charges generated by hydrolysis of broken bonds on its surface[16]. This lead to a reduced electrostatic repulsive force between colloidal clay particles in water, which is significantly weaker than the Van der Waals Force. Consequently, attapulgite is mainly used in brine slurry formulations[17]. When preparing an attapulgite clay suspension, it is essential to mechanically break down the fibre bundles into individual rods. This disintegration allows them to disperse in water and then overlap each other to form a three-dimensional mesh structure while binding some free water, which increases the viscosity of the suspension[18].

Several studies have explored methods to improve the slurry-forming ability of attapulgite through chemical modification, freeze-thaw treatment, ultrasonic processing, and high pressure homogenization[19–21]. These studies show that factors such as addition amount, fiber length to diameter ratio, pH, and electrolyte concentration significantly influence the rheological properties of attapulgite suspensions[22–27]. Antosik et al.[28] concluded that the viscosity response to shear flow depends on the flocculation state of the attapulgite suspension. Zhou et al.[29]. found that magnesium oxide impacted the rheological behavior of palygorskite suspension by allowing Mg^{2+} entered the channels of clay mineral particles, which lead to a shrinkage of the electrical double layer.

The rheological properties of high-temperature drilling fluids made from attapulgite have been extensively studied because of their exceptional resistance to salt and temperature[30–32]. Leroy et al.[33] analyzed the high-temperature rheological characteristics of drilling fluids formulated with bentonite and attapulgite clay. Their findings indicated that bentonite experienced a gelling issue at high temperatures, which was somewhat mitigated but not completely resolved by using a viscosity reducer. In contrast, attapulgite suspensions maintained favorable rheological properties at high temperatures[34]. However, since drilling fluids are highly customized, their rheological behavior under high temperature and high pressure (HTHP) conditions may vary based on the base slurry, additives, solid content, and other factors. Understanding the influence and mechanisms affecting the rheological properties of attapulgite clay under high temperatures is essential for developing effective, high-temperature-resistant drilling fluids.

This paper employs a HTHP rheometer to investigate the high temperature rheological characteristics of attapulgite suspension under different conditions, including clay addition, shear, aging, electrolyte, and polymer, to clarify the patterns of high temperature rheology, providing valuable theoretical insights for the development, application, and maintenance of high temperature water-based drilling fluids.

Materials and methods
Attapulgite used
Mineralogical composition
The attapulgite clay samples tested were ATP-1, ATP-2 and ATP-3, sourced from several prominent suppliers in China, including Hebei Lingshou County Shuanglong Mining Co., Ltd., Changzhou Dingbang Mineral Technology Co. Ltd., and Anhui Mingguang Guoxing Attapulgite Co., Ltd. Table 1 illustrates the mineralogical composition analyzed by X-ray diffraction (XRD). Regarding mineral composition, ATP-1 was classified as montmorillonite-attapulgite clay, ATP-2 as attapulgite clay, and ATP-3 as dolomite-attapulgite clay.

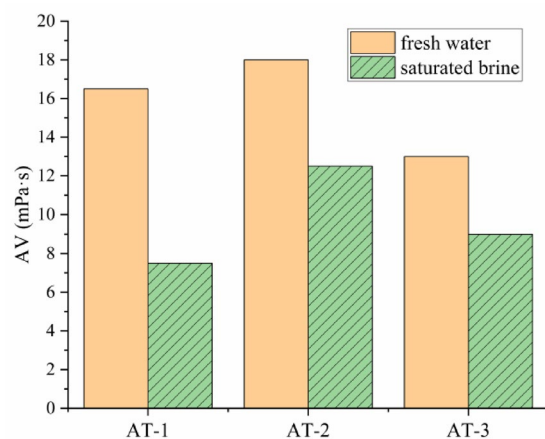*Slurry forming performance comparison*
As a clay in drilling fluid, its slurry-making performance is the most important characteristic. In the experiment, 400 mL of deionized water was used, the pH was altered with NaOH, and the ionic strength was modified with NaCl to make an aqueous solution (NaCl and NaOH, analytical grade, from Sinopharm Chemical Reagent Co. Ltd.). Gradually, 16 g of 200 mesh sieved clay was added while stirring. The mixture was then blended at a rotational speed of 12,000 r/min for 20 min at room temperature using a GJ-S high speed mixer. The apparent viscosity of the resulting suspension was determined by a ZNN-D6 six speed rotational viscometer, and the result is shown in Fig. 1.

According to the API Recommended Practice "Recommended Practice for Field Testing Water-based Drilling Fluids"[35] and GB/TT41741-2022 "Attapuligite Clay Grading Test Methods", attapuligite is assessed for its colloidal stability in saturated brine, measured by viscosity retention. This retention is calculated as the ratio of the difference in viscosity before and after treatment to the viscosity of the original slurry solution.

The slurry forming behavior of the attapulgite clays in fresh water and saturated brine was significantly different. The viscosities in fresh water were generally higher than those in brine. Figure 1 shows that the viscosities of ATP-1, ATP-2 and ATP-3 in brine decreased by 54.5%, 30.5% and 30.7%, respectively, compared to

Sample	Montmorillonite	Attapulgite	Gypsum	Quartz	Feldspar	Calcite	Dolomite
ATP-1	28	41		22	5	1	3
ATP-2	18	43		20	14		5
ATP-3	6	41	5	23	10		15

Table 1. Mineral composition of attapulgite by XRD.

Fig. 1. Comparison of slurry forming properties of different attapulgite (room temperature).

(a)   6000x   (b) 10000x
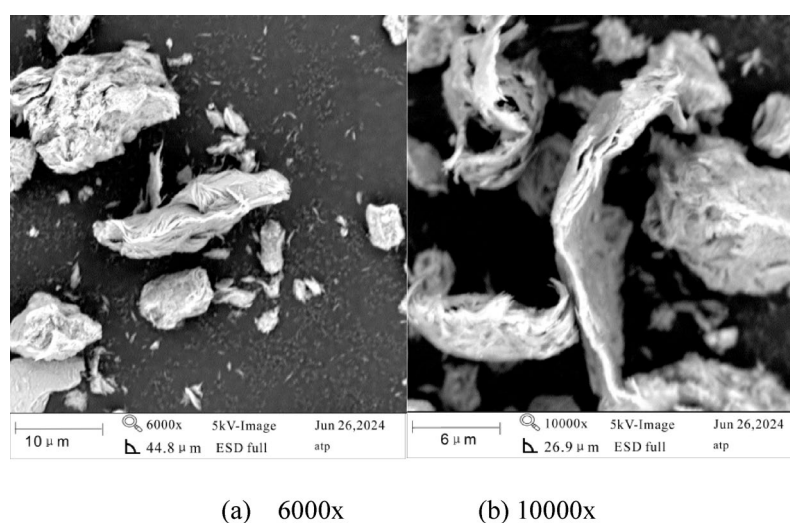
Fig. 2. Electron microscope photographs of attapulgite clay.

freshwater, which is attributed to the different salt sensitivity of the impurities within the attapuligite. Given the low viscosity values, ATP-2 was selected for further testing based on the idea that higher viscosity would be more favorable for experimental observation.

Surface morphology
A small piece of freshly flattened attapulgite clay was taken, fixed to the carrier stage with graphite conductive adhesive, sprayed with gold and examined under a scanning electron microscope, model S4800. The scanning electron microscope images of ATP-2 are shown in Fig. 2. As can be seen in Fig. 2, the morphology of the attapulgite crystals is more complex, with an overall blocky structure, obvious laminar bands on the sides, the fiber rod bundles are of different lengths and all have relatively large diameters. The attapulgite crystals are well crystallized and vary in length from a few microns to tens of microns. Although the crystals are aggregated together, the size of the aggregates is small, indicating that the aggregation force between the attapulgite is not strong.

Chemical materials and polymer
The main materials used in the test were NaCl and NaOH, analytical grade, from Sinopharm Chemical Reagent Co. Ltd.

Driscal-D, produced by Chevron Phillips Chemicals Co. Ltd, is a high temperature-resistance polymer characterized by carbon-sulfur (C-S) and/or carbon-nitrogen (C-N) single bonds in its side chain. It features functional groups such as sulfonic acid ($-SO_3H$), amide (-CONH-), and hydroxyl (-OH). The molecular structure may include a five-membered ring, although its specific chemical formula remains undisclosed, with a molecular weight of approximately $3.6*10^5$. This free-flowing white powder is recommended for ultra-deep wells with temperatures exceeding 180 °C. It effectively reduces filtration loss under high temperature and pressure

while inhibiting the hydration and dispersion of mud shale. However, the dosage must be strictly limited to less than 1.5% to avoid excessive thickening of the drilling fluid.

Experimental methods

Sample preparation
ATP suspension: The same process used in the slurry forming performance test (Sect. 2.1.2) was applied to formulate the attapulgite slurry. The addition amount of attapulgite was accurately measured based on the experimental requirements.

ATP-polymer mixture: a given mass of polymer was added to the ATP suspension and stirred at 12,000 r/min for another 20 min to set it aside.

High temperature aging test
The suspensions samples to be tested were transferred to an aging kettle, sealed and placed in an XGRL-4 A high temperature rolling heating furnace, and aged for 16 h at 70 ℃, 100 ℃, 130 ℃, 170 ℃ and 190 ℃ to simulate downhole thermal history. After cooling to room temperature, the samples to be tested were transferred to a stirring cup, and then stirred at 12 000 r/min for 20 min for preparation.

High temperature rheological property test
The basic principle of high temperature and high pressure (HTHP) rheological testing is to apply additional pressure and temperature to a fluid sample, and under constant conditions, the apparatus is driven by an electric motor to generate a shear rate on the sample, and at the same time measure the resistance of the sample to respond, namely the shear stress, and calculate the viscosity of the sample(shear stress/shear rate. The HTHP rheological tests reflect the rheological characteristics of fluids as they circulate through a borehole. Numerous previous studies have shown that pressure has little effect on the rheological properties of fluids, particularly in water-based drilling fluid systems, so the test pressure was kept constant(1000 psi) throughout the experiment.

With the Fanns 50SL HTHP rheometer, the experimental law of the rheological characteristic with variables (concentrations, temperature, salt, and polymer) of ATP was investigated. The test samples were first pre-sheared at 12,000 rpm for 20 min in a slurry cup. Subsequently, dynamic shear tests were conducted at temperatures of 40 °C, 70 °C, 100 °C, 130 °C, 160 °C, and 190 °C, with a temperature increase rate of 3–10 °C/min. Viscosity values were sequentially measured at shear rates of 1022 s^{-1}, 511 s^{-1}, 340.7 s^{-1}, 170.3 s^{-1}, 10.22 s^{-1}, and 5.11 s^{-1} during these tests. When the temperature reaches each test point, the rheometer holds that temperature for approximately 6 min to collect 1 min of viscosity data at each shear rate, with a sampling frequency of 2 s. The mean of the resulting data is taken as the shear viscosity value.

Please note that all slurries are pre-sheared for 20 min at 12,000 r/min prior to viscosity testing with the high-temperature rheometer (Fanns 50SL).

Fitting of rheological models
The shear rate-shear stress data were fitted using one dimensional linear regression and least squares methods. This paper employs three rheological models[36].

Bingham model gives two parameters: yield stress (τ_0) and plastic viscosity (η), represented by the equation $\tau = \tau_0 + \eta\dot{\gamma}$. The Herschel-Bulkley model requires three parameters: yield stress (τ_0), the consistency coefficient (K), and the flow index (n), described by the equation $\tau = \tau_0 + K\dot{\gamma}^n$. The Casson model produced two parameters: Casson dynamic shear (τ_c) and the Casson ultimate viscosity(η_∞), expressed by the equation $\tau^{1/2} = \tau_c^{1/2} + \eta_\infty^{1/2}\dot{\gamma}^{1/2}$. All models effectively characterize non-Newtonian fluids, despite varying parametric complexities.

Results and discussions
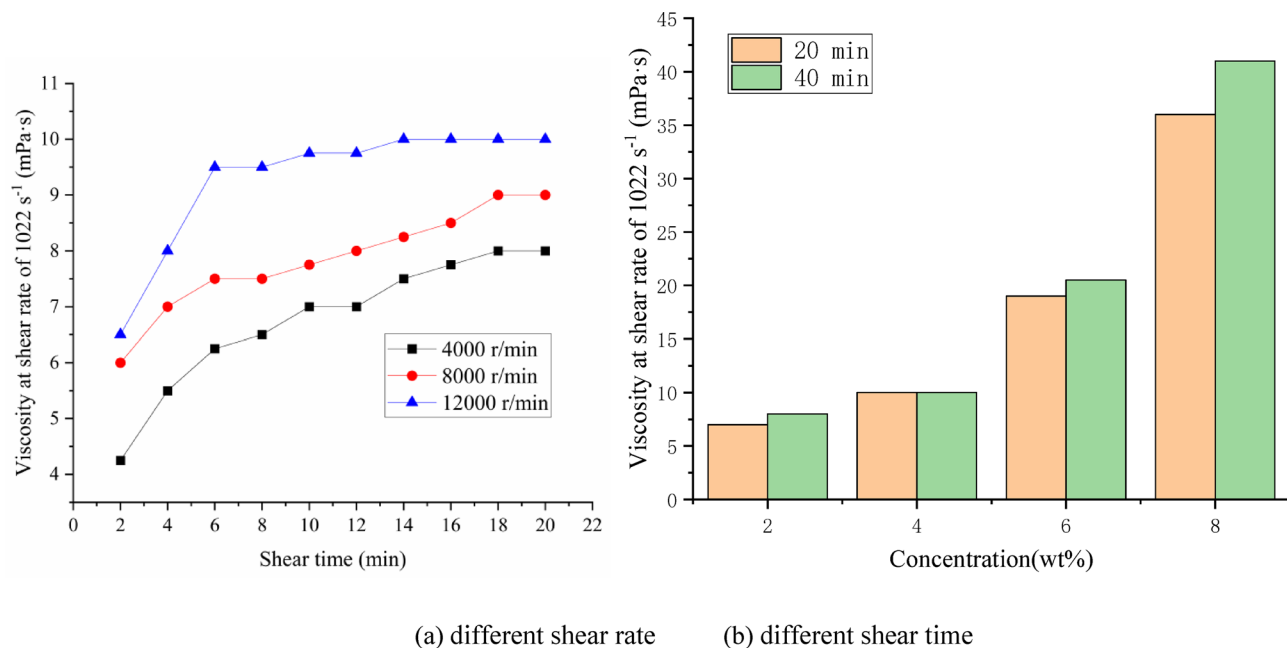### Effect of shear on the viscosity of ATP suspensions
As shear rate and shear time determine shear conditions together, the effect of these conditions on the rheological properties of ATP suspensions was examined by both factors.

Shear rate
The 4 wt% attapulgite (ATP) suspension was first sheared at 4000 r/min, 8000 r/min, and 12,000 r/min for 20 min in a high-speed mixer. The rheological properties at a high shear rate of 1022 s^{-1} were measured at room temperature using the ZNN-6D six-speed rotational viscometer, the viscosity values obtained under different shear conditions were compared, as shown in Fig. 3a.

Figure 3a shows that both shear time and shear rate have a significant effect on viscosity, with shear strength having a more pronounced effect. At a high shear rate of 12,000 r/min, the slurry formation process was essentially complete in about 6 min, resulting in a viscosity of about 20 mPa·s, whereas at 4000 r/min, the viscosity continued to increase with shear time up to 18 min, peaking at about 7.5 mPa s. This observation suggests that at low shear rates it is difficult for attapulgite to achieve complete slurry formation, even with extended shear time, whereas at high shear rates, the maximum viscosity can be achieved rapidly.

The reason for this is that under high shear, clay crystals overcome the electrostatic forces between fibers, allowing fiber bundles or laminated aggregates to separate into individual fibers. In addition, only high shear can break up tightly bonded attapulgite rod crystal bundles and disperse them effectively for slurry formation. Therefore, simply increasing the shear time cannot compensate for the low viscosity caused by insufficient shear strength.

(a) different shear rate   (b) different shear time

Fig. 3. Influence of shear conditions on viscosity of ATP suspension.

Shear time
The viscosity values obtained under different shear time were compared, illustrated in Fig. 3b. Since attapulgite can be dispersed and pulping in a high-speed shear environment, a preliminary shear treatment of 20 min at 12,000 r/min was essential.

Furthermore, the 2wt%, 4wt%, 6wt% and 8wt% ATP suspensions were sheared at 12,000 r/min for 20 min and 40 min, respectively, to assess the effect of shear time on their rheological properties. The viscosity values were measured at different shear times, with results presented in Fig. 3b.

At low concentrations (2 wt% and 4 wt% ATP), the viscosity of the suspensions did not increase when shear time was extended from 20 min to 40 min, indicating that 20 min is sufficient for adequate slurrying of attapulgite clay. However, at higher concentrations(6 wt% and 8 wt%), the viscosities showed a slight increase with longer shear times, suggesting that complete ATP dissociation becomes more challenging at these levels. To achieve fully pulping, an appropriate extension of shear time is necessary due to the increased concentration, which leads to more rod crystal bundles dissociating and a stronger reticulation structure formed by intertwining fibers. This results in a higher viscosity of the suspension.Nevertheless, at higher concentrations, once a high-viscosity slurry is formed, the mixer's capacity is limited, making it difficult to transfer the shear force from the mixing blades to the slurry's periphery. Consequently, some attapulgite clay may not fully dissociate under shear, indicating that powerful shear equipment is essential for preparing clay suspensions on-site[37,38]。.

Effect of clay addition on the high temperature rheological signature of ATP suspensions
*Room temperature rheological properties of ATP suspensions*
The ATP suspensions at concentrations of 2wt%, 4wt%, 6wt%, and 8wt% were prepared by mixing with fresh water at 12,000 r/min for 20 min. The viscosities were measured using the ZNN-6D six-speed rotational viscometer, as illustrated in Fig. 4a. These viscosity readings were then converted into shear stresses at various shear rates, resulting in the curvilinear relationship depicted in Fig. 4b.

From Fig. 4a, the viscosity values increased by 1.5, 3.75, and 8 times as the concentration increased from 2 wt% to 4 wt%, 6 wt%, and 8 wt%. The significant increase in viscosity is due to the higher attapulgite clay content. The increase in clay increases the concentration of crystalline fibre bundles within the same volume, and also increases the molecular weight of the bound water and enhances the potential for structural forces to develop though fiber entanglement, ultimately leading to an overall increase in viscosity.

The shear rate versus shear stress curves obtained (Fig. 4b) were fitted to the Bingham, Herschel-Bulkly and Casson models, as displayed in Table 2. The Power law model was excluded from fitting due to the presence of structural forces in the clay suspension, which would contradict established knowledge. For the Bingham and Casson models, the fitting results showed that the higher additions resulted in larger residuals, reflecting a decreasing trend in fit quality. In contrast, the Herschel-Bulkly model exhibited smaller residuals and the correlation coefficients above 0.995, suggesting that the ATP suspension behaves more like a Herschel-Bulkly fluid at room temperature.

Consequently, three parameters—yield stress (τ_0), coefficient of consistency (K) and flow index (n)—were analyzed to evaluate the impact of concentration on the rheological properties of the ATP suspensions at room temperature, as show in Fig. 4c. The K value characterizes the fluid's viscous resistance during flow. As clay addition increases, the number of rod-like particles in the suspension rises, forming a denser mesh structure due

(a) Viscosity   (b) shear stress versus shear rate   (c) rheological parameters of Herschel-Bulkly model
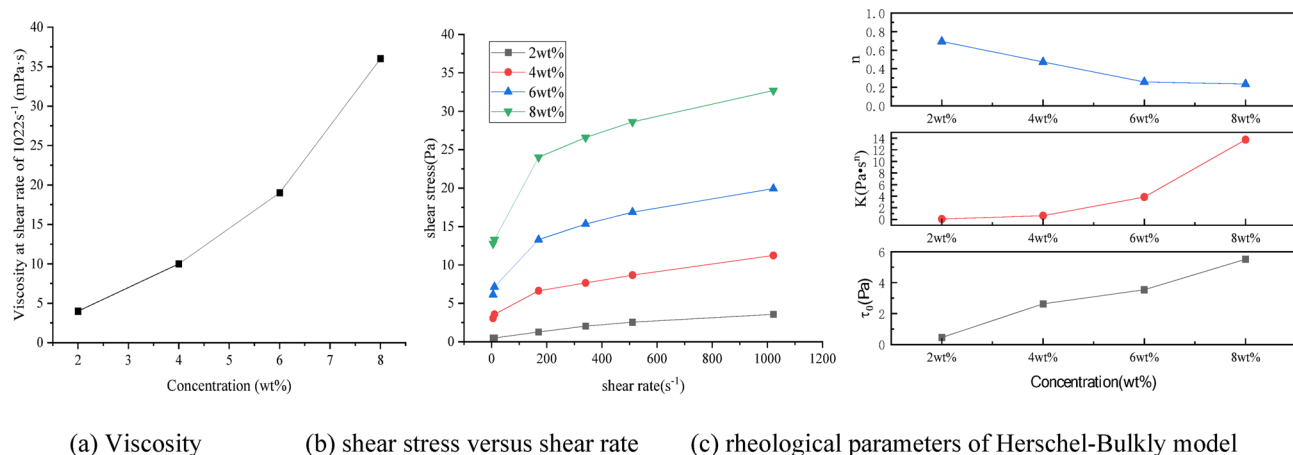
Fig. 4. Variation of rheological parameters of ATP suspension with attapulgite addition.

Concentration	Bingham		Herschel bulkly		Casson	
	R^2	Residual sum of squares	R^2	Residual sum of squares	R^2	Residual sum of squares
2wt%	0.95497	0.33172	0.99554	0.03283	0.92761	0.41583
4wt%	0.89997	4.84078	0.99696	0.14714	0.78041	7.65306
6wt%	0.82137	26.74301	0.99979	0.0313	0.70146	35.13118
8wt%	0.78248	73.61013	0.99698	1.02117	0.69608	116.74364

Table 2. Fitting parameters of three rheological models fitted at room temperature.

to van der Waals forces, electrostatic interactions, or hydrogen bonding. This enhances the fluid's resistance to shear deformation, resulting in greater viscous resistance and an increase in the K value. This τ_0 value reflects the structural strength of the solid phase in the suspension, indicating that the attapulgite fibers have a strong ability to lap together and create a cohesive structure. Decreasing values of n (approaching 0) suggests that the fluid is deviating from Newtonian properties. At low shear rates, the mesh structure formed by the particles remains intact with a high concentration of attapulgite clay. However, at high shear rates, this structure is disrupted and aligns with the flow direction, leading to a sharp decrease in viscosity.

High temperature rheological properties of ATP suspensions
The high temperature rheological properties of the ATP suspension at concentrations of 2wt%, 4 wt%, 6 wt% and 8 wt% were tested to examine the variation in viscosity with temperature at a shear rate of 1022 s^{-1}, as illustrated in Fig. 6. All suspension were pre-sheared at 12,000 r/min for 20 min.

In Fig. 5, the viscosity of the ATP suspensions at different concentrations exhibited a decreasing trend with increasing temperature. At a constant test temperature, higher clay concentrations correlated with increased viscosity values, mirroring the behavior observed at room temperature. In particular, the absolute decreases in viscosity between adjacent temperature points was significant. Within the 160 °C range, the viscosity decreased approximately linearly, but beyond this threshold, the decrease became less pronounced at lower concentrations. Specially, at 220 °C, the viscosity reductions for 4 wt%, 6 wt% and 8 wt% ATP suspensions were 92%, 88% and 72%, respectively, when compared to the initial temperature of 40 °C.

Increasing the test temperature increases the thermal motion of the water molecules. This change reduces the intermolecular forces between water molecules, and improves the desorption between water molecules and attapulgite, contributing to an overall reduction in viscosity[39]. Other viscosity values at different shear rates with temperature exhibited similar patterns and are not repeated here.

High temperature rheological model fitting for ATP suspensions
The rheological properties of the 8 wt% ATP suspension varied significantly across the tested temperatures, as shown in Fig. 6. Within the range of 220 °C, the viscosity of the suspension generally decreased with increasing temperature, although there was a notable decline in fit quality above 160 °C. At both 190 °C and 220 °C, the viscosity also decreased with increasing temperature. Interestingly, shear stress remained relatively constant at low shear rates. To compare the rheology of ATP suspensions at different temperatures, different rheological expressions were obtained by fitting the shear rate and shear stress data at different temperature points, and the correlation coefficients for the different rheological models, as illustrated in Table 3.

As shown in Table 3, at temperatures below 160 °C, the Herschel-Bulkley model consistently achieved correlation coefficients above 0.95, demonstrating the best fit, followed by the Casson model and the Bingham model. Conversely, at temperatures above 160 °C, both the Herschel-Bulkley and Casson models experienced a
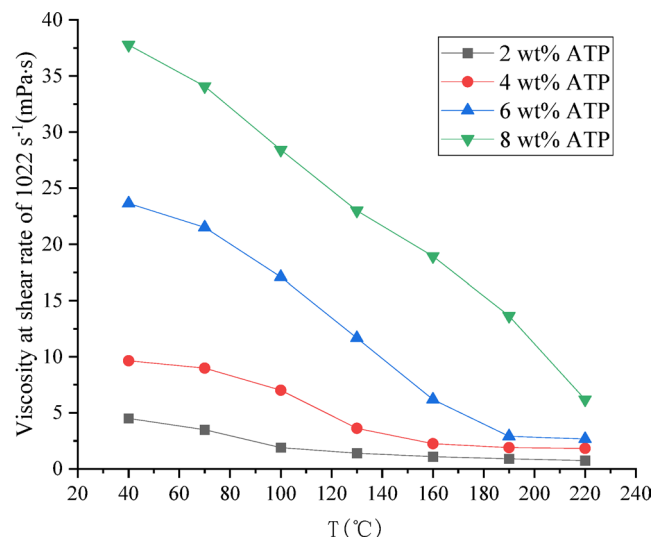
Fig. 5. Viscosity of ATP suspensions with different attapulgite additions as a function of temperature.
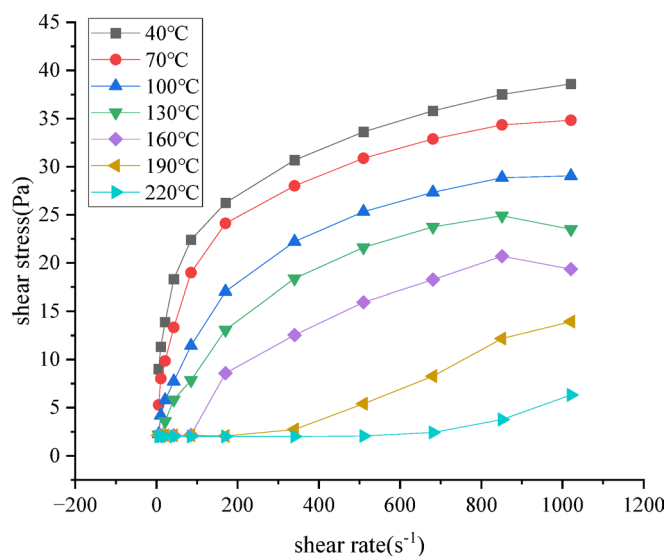
Fig. 6. Shear stress versus shear rate of 8 wt% ATP suspension at different temperatures.

significant drop in correlation coefficients, resulting in a marked decrease in fit accuracy. In this condition, the Bingham model exhibited superior fitting performance.

According to Bingham model, both plastic viscosity (η) and yield stress (τ_0) decreased with increasing temperature. When the temperature increased from 40 °C to 220 °C, the reduction rates were 85% and 91%, respectively. This indicates that high temperatures significantly affect the rheological properties of ATP suspensions.

An interesting observation during the experiment was noted at the end of the test: while cleaning the outer cylinder of the rheometer, significant changes in the properties of the ATP suspension was observed, displayed by interlayer slip during pouring. This phenomenon indicates that the unique rheological properties of attapulgite clay result in minimal changes in shear force at low shear rates at higher temperatures. The Bingham model effectively utilizes the rheological parameters at high shear rates during the fitting process, leading to a better fit. This lays the groundwork for further investigation into the high-temperature rheological properties of ATP suspensions using the parameters from the Bingham model.

Effect of aging on the high temperature rheological properties of ATP suspensions

The aging test simulates the subsurface temperature changes that occur as drilling fluid circulates through the borehole. The fluid enters from the wellhead pipe and gradually warms and undergoes a prolonged heating process. It then cools as it flows to the the surface before returning to the well. The performance evaluation after the aging test provides valuable insights into the conditions of drilling fluid in the field.

T (°C)	Bingham				Herschel-Bulkly					Casson			
	η (mPa·s)	τ_0 (Pa)	R^2	Residual sum of squares	K (Pa·s^n)	n	τ (Pa)	R^2	Residual sum of squares	η (mPa·s)	τ_c (Pa)	R^2	Residual sum of squares
40	27.4	15.5	0.8723	206.82147	0.97	0.53	7.2	0.9628	9.33458	12.2	9.9	0.9491	8178.51331
70	27.0	12.6	0.8471	247.53562	1.26	0.50	3.1	0.9574	27.18482	15.1	6.7	0.9292	6520.02309
100	25.2	8.0	0.8736	162.46167	1.07	0.50	0.2	0.9700	20.61301	17.9	3.1	0.9353	4095.88007
130	21.2	6.2	0.8676	125.86944	0.7	0.53	0.21	0.9648	26.20979	16.0	2.1	0.9289	2830.23777
160	17.3	4.2	0.9346	52.178	0.54	0.52	0.62	0.9923	24.00973	11.6	1.75	0.9694	1644.40777
190	11.3	1.1	0.9507	14.39877	0.01	0.83	1.98	0.4597	2.89653	4.6	0.98	0.8834	473.99269
220	4.0	1.37	0.8674	6.40601	0.02	0.44	1.93	0.0769	0.01947	0.8	1.38	0.6671	92.25302

Table 3. Correlation parameters of three rheological models fitted at different temperatures.

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(a) Test temperature: 40°C   (b) Test temperature: 220°C
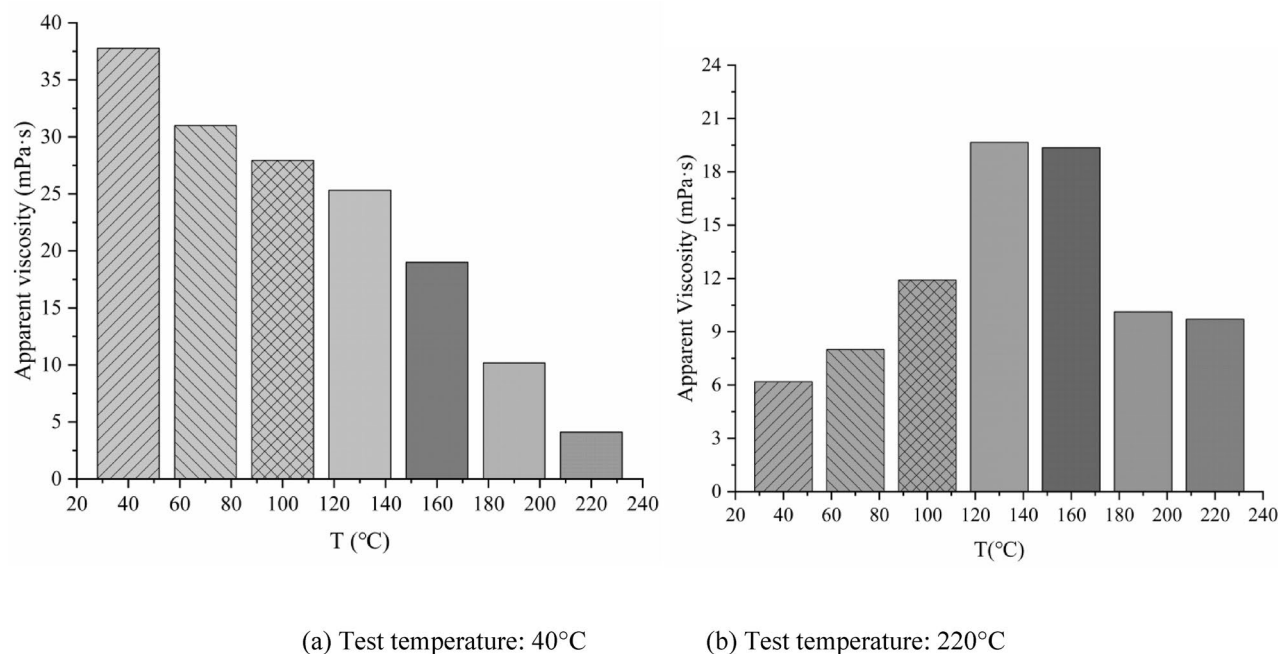
Fig. 7. Viscosity of ATP suspensions after aging at different temperatures.

T (℃)	η (mPa·s)	τ_0 (Pa)	R^2	$\Delta \eta$	$\Delta \tau_0$
40	11.6	0.68	0.9528	-	-
100	13.2	4.0	0.9095	13.8%	488.2%
130	13.7	5.5	0.8664	18.1%	708.8%
160	17.6	4.5	0.8758	51.7%	561.7%
190	16.1	2.5	0.9669	38.8%	267.6%

Table 4. Effect of aging temperature on rheological parameters of the Bingham model.

The 8 wt% ATP suspensions samples were aged for 16 h at temperatures of 100 °C, 130 °C, 160 °C, 190 °C and 220 °C. And then, the aged suspensions were pre-sheared for 20 min at 12,000 r/min then subjected to the HTHP rheological test to obtain the viscosity value at 40 °C and 220 °C as shown in Fig. 7. Thermal stability was assessed by comparing the changes in rheological properties before and after aging.

The results show that when the aged ATP suspensions were subjected to the HTHP rheological test, the viscosity values at 40 °C decreased compared to the pre-aging, and this decrease in viscosity became more pronounced at higher hot rolling temperatures. In contrast, at the HTHP rheological test temperature of 220 °C, a significantly different behavior was observed compared to 40 °C. Figure 7b illustrates an increase in the viscosity of the aged ATP suspensions compared to the suspensions before aging, for the suspensions aged at 160–190 °C, the viscosity peaked at 220 °C of the HTHP rheological test.

This phenomenon suggests that it is misleading to claim that the viscosity of the aged clay suspension is significantly reduced based solely on room temperature viscosity measurements before and after aging. In fact, the viscosity of the aged clay suspension at higher temperatures shows an increase compared to that before aging. This implies that the temperature aging has a beneficial effect on the viscosity retention of attapulgite clay at high temperatures, but the mechanism behind this beneficial effect remains unclear. At present, it can only be assumed that high temperature aging process affects the internal structure of the attapulgite clay, and this experimental phenomenon warrants careful consideration in the formulation of high temperature drilling fluids at temperatures above 220℃.

The rheological parameters of ATP suspensions aged at different temperatures were fitted, specifically at 190 °C (as data at 220 °C was poorly fitted), using the Bingham model, as shown in the Table 4. The results revealed that the plastic viscosity of the ATP suspension increased by 13.8–51.7%, while the dynamic shear force rose significantly by 267.6–708.8%. This suggests that aging positively influences the viscosity retention of the ATP suspension at high temperatures, particularly regarding dynamic shear.

Effect of NaCl on the high temperature rheological properties of ATP suspensions

400 mL of saline solution containing NaCl were prepared with concentrations of 5 wt%, 15 wt% and 35 wt%, respectively, and 32 g of attapulgite powder was slowly added to the saline while stirring at 12,000 r/min for

20 min. Subsequently, them were placed into the Fanns 50SL HTHP rheometer to test their rheological properties at different temperatures, and the results are shown in the Fig. 8.

The Fig. 8 showed that at 40 ℃, the shear stress of the ATP suspension in a brine environment at high shear rates was lower than that in freshwater. As salt content increased, shear stress decreased at the same shear rate. At 70 ℃, the rheological curves of the brine and freshwater suspensions intersected. At high shear rates, the shear stress of the brine was lower, while at low shear rates, it was higher. As temperature increased, the intersection point of the curves shifted to the right. Between 100 and 130 ℃, the shear stress of the ATP suspension with 5 wt% NaCl at high shear rates was similar to that of the freshwater suspension. Above 130 ℃, the shear stress of some brine suspensions surpassed that of the freshwater slurry, with a more significant difference at low shear rates.

Overall, the effect of NaCl concentration on the shear stress of the ATP suspension exhibited an increasing trend followed by a decrease, peaking at approximately 5 wt%. For shear stress at a high shear rate, an increase in temperature leads to a gradual decrease in the difference in shear stresses between the freshwater and brine slurries. When the temperature exceeded 130℃, the shear stress of the brine slurry surpassed that of the

(d) 130℃   (e) 160℃   (f) 190℃

(g) 220℃
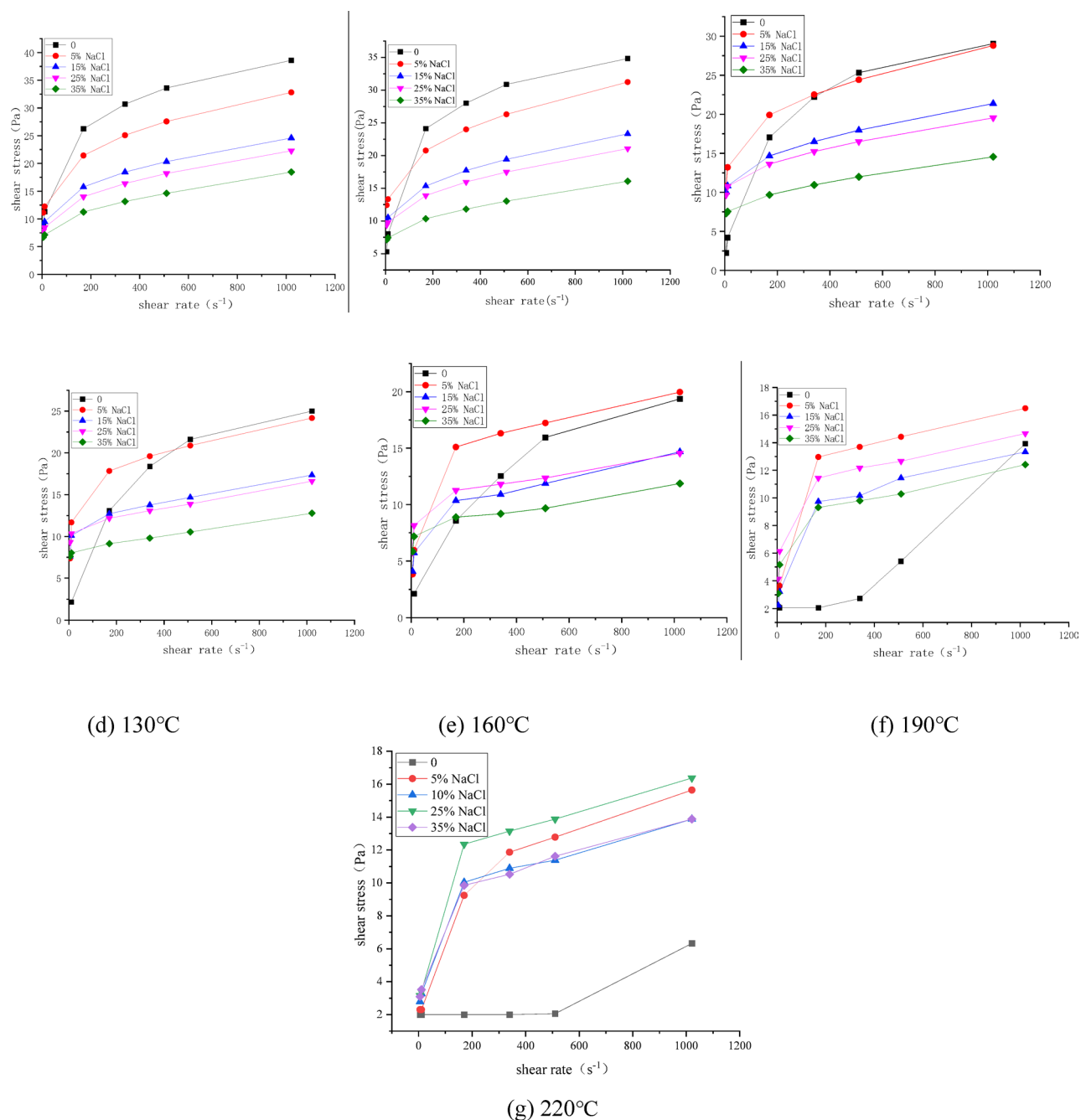
Fig. 8. Rheological diagrams of 8wt%ATP suspensions with different NaCl concentration.

T (℃)	Fresh water			5% NaCl		
	η (mPa·s)	τ_0 (Pa)	R^2	η (mPa·s)	τ_0 (Pa)	R^2
40	27.4	15.5	0.8723	20.5	14.7	0.9207
70	27.0	12.6	0.8471	17.9	15.2	0.9339
100	25.2	8.0	0.8736	16.2	14.4	0.9169
130	21.2	6.2	0.8676	13.9	12.1	0.8629
160	17.3	4,2	0.9346	14.1	8.2	0.8304
190	11.3	1.1	0.9507	12.0	6.6	0.8116
220	4.0	1.37	0.8674	12.8	4.6	0.8888

Table 5. Rheological parameters of freshwater versus saline ATP suspensions.

(a) 1022 s⁻¹   (b) 511 s⁻¹
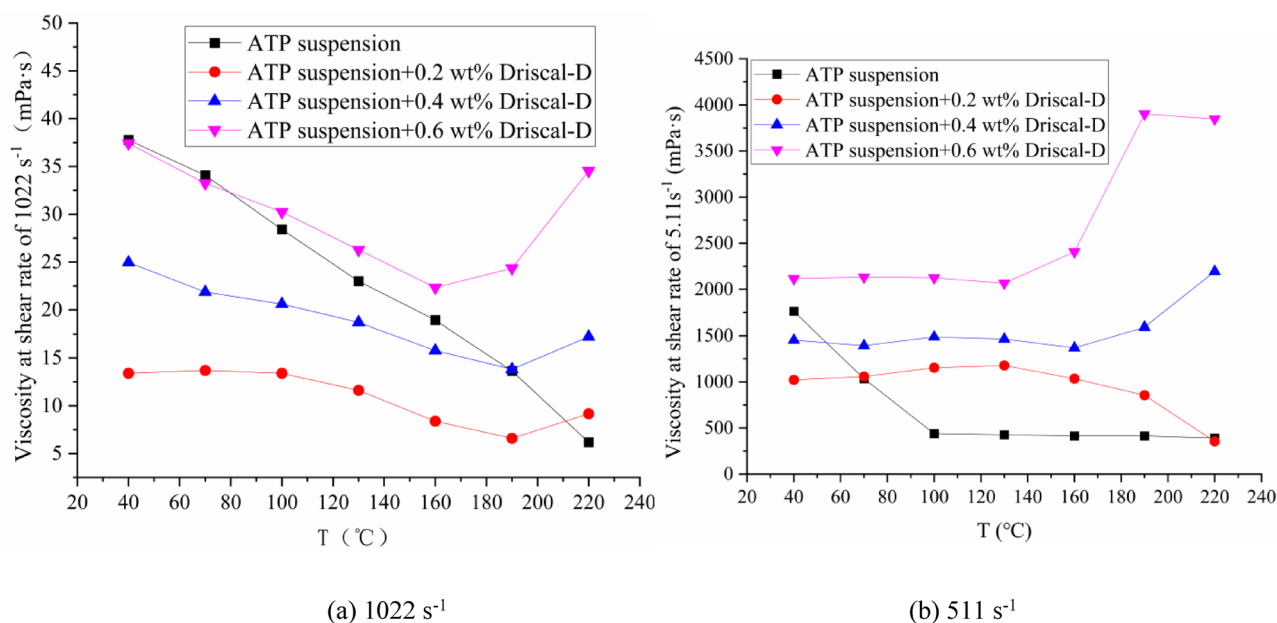
Fig. 9. Effect of polymer on the viscosity of ATP suspensions.

freshwater slurry, and this difference became more pronounced with an increase in temperature. For low shear rates, the shear stress of the freshwater slurry was lower than that of the brine slurry at temperatures above 70 ℃, with this disparity becoming more obvious as temperature increased. This highlights the significant impact of salt on the high-temperature rheology of clay, particularly its viscosity at low shear rates. The presence of salt slows the increase in viscosity with temperature and enhances the stability of clay viscosity at high temperatures.

To further clarify the specific influence of NaCl on the high temperature rheological parameters of the ATP suspensions, a comparison was made between the ATP suspension before and after the addition of 5 wt% NaCl at different temperatures, as shown in Table 5. The results show that as the test temperature increased, the rheological parameters of the ATP suspension exhibited a decreasing trend, with the saline environment showing a slower rate of decrease. Specifically, the η values of the freshwater suspension were higher than those of the brine at temperatures below 190 ℃, while at 190 ℃, the two were relatively similar. However, at 220 ℃, the η value in the freshwater decreased to about 30% of the brine's. Throughout the test temperature range of 220 ℃, the τ_0 values of the brine suspension consistently maintained higher compared to the freshwater suspension, in particular, reaching approximately 3.35 times higher at 220 ℃.

Effect of polymer on the high-temperature rheological properties of ATP suspension
Figure 9 illustrates how viscosity changes in ATP suspensions at high ($1022 s^{-1}$) and low($5.11 s^{-1}$) shear rates with different polymer additions.All the blend were pre-sheared for 20 min at 12,000 r/min.

After adding the polymer, the overall viscosity initially decreased and then increased with increasing temperature (Fig. 9). At a high shear rate of $1022 \, s^{-1}$, the viscosity dropped with polymer addition within a specific temperature range, although it remained lower than that of the slurry without polymer. Once the temperature reached certain thresholds–around 210 °C, 190 °C, and 90 °C for three different polymer concentrations–the viscosity of the polymer-added samples exceeded that of the blank samples. This indicates that while the polymer initially reduces the slurry viscosity, it ultimately slows the decrease in viscosity as temperature increases. A

T(℃)	η (mPa·s)	τ_0 (Pa)	R^2	S_{total}^2	$S_{residual}^2$
40	17.4	8.96	0.9758	225.8	11.31
70	14.7	8.31	0.9780	160.5	7.28
100	13.1	8.40	0.9857	127.9	3.7
130	11.1	8.39	0.9815	92.7	3.5
160	8.9	7.30	0.9959	58.9	0.48
190	5.7	8.3	0.9924	24.4	0.37
220	6.3	11.6	0.9781	29.6	1.3

Table 6. Fitting of rheological parameters at different temperatures of 8wt%ATP + 0.4 wt%Driscal-D.

similar trend was observed at a low shear rate of 5.11 s^{-1}, with critical temperatures for the 0.2 wt% and 0.4 wt% polymer concentrations at approximately 50 °C and 70 °C, respectively. Beyond these points, the viscosity of the polymer-containing slurry surpassed that of the blank sample, and for the 0.6 wt% concentration, the viscosity remained higher than that of the blank throughout the test.

The total viscosity of the ATP suspension is mainly influenced by the structural forces between the rod crystal bundles. When a small amount of polymer is added, it forms an adsorption layer around these bundles, thickening the hydration film and enhancing their negative charge[40]. This weakens the interaction between the rod crystal bundles, resulting in a decrease in viscosity. Conversely, adding more polymer increases the viscosity of the liquid phase of the suspension by enhancing the entanglement and interaction among the polymer chains, resulting in an overall increase in slurry viscosity. Thus, the impact of polymer addition on the viscosity of the ATP suspensions can be described as a "sensitization"effect.

The shear rate-shear force of the 8 wt% ATP suspension containing 0.4wt% Driscal-D at different temperatures was analyzed using the Bingham model, with results presented in Table 6. The results indicate that plastic viscosity(η) and dynamic shear force(τ_0) initially decrease and then increase with increasing temperature. This suggests that the polymer effectively enhances the viscosity retention of the ATP slurry at high temperatures, creating favorable conditions for formulating attapulgite-based high temperature drilling fluids.

Conclusions

1. At a shear rate of 1022 s^{-1}, the viscosities of ATP suspensions with different clay additions decreased as the test temperature increased. The Casson and Herschel-Bulkley models more accurately described the rheological properties of ATP suspensions, with correlation coefficients of at least 0.95 across a temperature range of 160 °C. However, the Bingham model is more appropriate for the entire temperature range.
2. When tested for high temperature rheology, the viscosity of aged attapulgite suspension exhibited significant variations with temperature. At 40 °C, the viscosity values fell below those observed before hot rolling. However, at 220 °C, the viscosity of the aged ATP suspensions was lower than that of the pre-rolled samples. This indicates that concluding that the viscosity of aged clay suspensions is significantly lower based solely on low-temperature comparisons can be misleading. Therefore, the impact of proper aging on the high-temperature rheological properties of ATP suspensions must be considered when formulating drilling fluids for temperatures above 220 °C.
3. Compared to fresh water, the sensitivity of the viscosity of the ATP suspension to temperature changes decreased in a saline environment. With salt concentration concentration increased, the high temperature viscosity of ATP suspension showed a significant decline, but the viscosity began to rebound at 190 °C and 160 °C, respectively, with a marked increase occurring after 190 °C. The introduction of NaCl (5 wt%) proves effective in maintaining the viscosity of the ATP suspension at high temperatures, even in saturated brine solutions, above 190℃.
4. After adding the polymer, the viscosity of ATP suspensions initially decreased and then increased with rising temperature, at both high and low shear rates. This behavior is primarily due to the interaction between the polymer and the textured clay. Thus, the impact of the polymer on the high-temperature rheology of ATP suspensions should be important.

Data availability

All data can be requested from the corresponding author.

References

1. Zhang, J. R., Xu, M. D., Christidis, G. E. & Zhou, C. H. Clay minerals in drilling fluids: functions and challenges. *Clay Min.* **55**(1), 1–11. https://doi.org/10.1180/clm.2020.10 (2020).
2. Muhammed, N. S., Olayiwola, T. & Elkatatny, S. A review on clay chemistry, characterization and shale inhibitors for water-based drilling fluids. *J. Petrol. Sci. Eng.* **206**, 109043. https://doi.org/10.1016/j.petrol.2021.109043 (2021).
3. Osgouei, A. G., Ettehadi, A. & Ozyurtkan, M. H. Customization of sepiolite based drilling fluids at high temperatures. In *48th U.S. Rock Mechanics/Geomechanics Symposium, Minneapolis, Minnesota*, (2014).

4. Heller, H. & Keren, R. Rheology of Na-rich montmorillonite suspension as affected by electrolyte concentration and shear rate. *Clays Clay Min.* **49**(4), 286–291. https://doi.org/10.1346/CCMN.2001.0490402 (2001).
5. Paineau, E., Michot, L. J., Bihannic, I. & Baravian, C. Aqueous suspensions of natural swelling clay minerals. 2. Rheological characterization. *Langmuir* **27**(12), 7806–7819. https://doi.org/10.1021/la2001267 (2011).
6. Christidis, G. E., Blum, A. E. & Eberl, D. D. Influence of layer charge and charge distribution of smectites on the flow behaviour and swelling of bentonites. *Appl. Clay Sci.* **34**(1–4), 125–138. https://doi.org/10.1016/j.clay.2006.05.008 (2006).
7. Cinar, M., Can, M. F., Sabah, E., Karaguezel, C. & Celik, M. S. Rheological properties of sepiolite ground in acid and alkaline media. *Appl. Clay Sci.* **42**(3–4), 422–426. https://doi.org/10.1016/j.clay.2008.04.010 (2009).
8. Thomas, C. S., Sridhar, K. & Rustum, R. Gelling properties of sepiolite versus montmorillonite. *Appl. Clay Sci.* **3**(2), 165–176. https://doi.org/10.1016/0169-1317(88)90016-6 (1988).
9. Galindo, K. A., Zha, W. B., Zhou, H. & Jay, P. D. High temperature, high performance water-based drilling fluid for extreme high temperature wells. In *SPE International Symposium on Oilfield Chemistry, The Woodlands, Texas, USA* https://doi.org/10.2118/173773-MS (2015).
10. Li, J. B., Ma, H. Y., Yan, Y. G., Zhang, J. & Li, Z. Molecular insights into the aggregation mechanism of montmorillonite colloid due to calcium contamination: A molecular dynamics simulation study. *Appl. Clay Sci.* **247**, 107191. https://doi.org/10.1016/j.clay.2023.107191 (2024).
11. Zhong, H. Y. et al. Hydrothermal synthesis of bentonite carbon composites for ultra-high temperature filtration control in water-based drilling fluid. *Appl. Clay Sci.* **230**, 106699. https://doi.org/10.1016/j.clay.2022.106699 (2022).
12. Song, Y. Y., Lei, X. P., Liu, J., Guan, X. L. & Yuan, H. D. Preparation and properties of superhydrophobic surface with titanium dioxide and attapulgite. *J. Chin. Ceramic Soc.* **49**(10), 2242–2250. https://doi.org/10.14062/j.issn.0454-5648.20210174 (2021).
13. Allawi, A. H., Mohammed, M. Y., Ayrim, N. B., Alheety, M. A. & Mahmood, A. R. Synthesis of attapulgite-MnO$_2$ nanocomposite from manganese complex by ultrasound for hydrogen storage. *J. Indian Chem. Soc.* **99**, 100596. https://doi.org/10.1016/j.jics.2022.100596 (2022).
14. Suliman, N. M. & Al-Zubaidi, N. S. Improve rheological properties of Palygorskite water-based drilling fluid by caustic soda and soda Ash. *J. Eng.* **26**(6), 1–17. https://doi.org/10.31026/j.eng.2020.06.01 (2020).
15. Malata, G. & Tkaczewska, E. Application of thermal methods in the studies of potential pozzolanic reactivity of attapulgite and sepiolite. *J. Therm. Anal. Calorim.* **148**, 7611–7622. https://doi.org/10.1007/s10973-023-12257-3 (2023).
16. Christidis, G. E., Katsiki, P., Pratikakis, A. & Kacandes, G. Rheological properties of palygorskite—smectite suspensions from the Ventzia basin, W. Macedonia, Greece. *Bull. Geol. Soc. Greece.* **43**, 2562–2569. https://doi.org/10.12681/bgsg.11663 (2011).
17. Viana, A. C. et al. Release of aggregation pheromone rhynchophorol from clay minerals montmorillonite and kaolinite. *J. Therm. Anal. Calorim.* **147**, 4995–5007. https://doi.org/10.1007/s10973-021-10932-x (2021).
18. Li, D. H., Cheng, J. W. & Guo, L. C. Rheological properties of aqueous attapulgite suspensions & its industrial significance. *Non-Metallic Mines.* **3**, 8–10. https://doi.org/10.3969/j.issn.1000-8098.2005.03.003 (2005).
19. Ma, G. et al. Effectiveness and potential mechanism of hydrothermal modification of attapulgite for cadmium passivation in soil. *Inter J. Environ. Sci. Technol.* **21**, 2953–2964. https://doi.org/10.1007/s13762-023-05124-z (2024).
20. Chen, J., Jin, Y. L. & Wu, J. Super-dispersion technology of palygorskite ore based on freeze-thaw processes. *J. China U Min. Technol.* **39**, 134–138 (2010).
21. Xu, J., Wang, W. & Wang, A. Superior dispersion properties of palygorskite in dimethyl sulfoxide via high-pressure homogenization process. *Appl. Clay Sci.* **86**, 174–178. https://doi.org/10.1016/j.clay.2013.10.006 (2013).
22. Mohamed, E., Ren, J., Tao, L. & Mala, A. Effectiveness of attapulgite modified by chlorides on speciation and environmental risk of heavy metals in soil. *Inter J. Environ. Sci. Technol.* **21**, 6713–6732. https://doi.org/10.1007/s13762-023-05423-5 (2024).
23. Zhu, X. M., Wu, X. M., Zheng, W. L., Mulati, D. N. & Jiang, Z. W. Factors affecting high temperature rheological properties of polymers used in drilling fluid. *Bull. Geol. Sci. Technol.* **40**(1), 200–208 https://doi.org/10.19509/j.cnki.dzkq.2021.0115 (2021).
24. Amighi, M. R. & Shahbazi, K. The best common ways to manage barite sag in HPHT and deviated operations with a case study in the Iran oil industry. *Petrol. Sci. Technol.* **29**, 1864–1872. https://doi.org/10.1080/10916461003662992 (2021).
25. Neaman, A. & Singer, A. Rheological properties of aqueous suspensions of palygorskite. *Soil. Sci. Soc. Am. J.* **64**(1), 427–436. https://doi.org/10.2136/sssaj2000.641427x (2000).
26. Al-Futaisi, A., Jamrah, A. & Al-Hanai, R. Aspects of cationic dye molecule adsorption to palygorskite. *Desalination* **214**, 327–342. https://doi.org/10.1016/j.desal.2006.10.024 (2007).
27. Neaman, A. & Singer, A. Possible use of the sacalum (Yucatan) palygorskite as drilling muds. *Appl. Clay Sci.* **25**(1–2), 121–124 (2004).
28. Antosik, A. K., Makuch, E. & Gziut, K. Influence of modified attapulgite on silicone pressure-sensitive adhesives properties. *J. Polym. Res.* **29**, 135. https://doi.org/10.1007/s10965-022-02981-z (2022).
29. Zhou, F. et al. Enhanced viscosity of aqueous palygorskite suspensions through physical and chemical processing. *Adv. Mater. Sci. Eng.* https://doi.org/10.1155/2015/941580 (2015).
30. Viseras, C., Meeten, G. H. & Lopez-Galindo, A. Pharmaceutical grade phyllosilicate dispersions: the influence of shear history on Floc structure. *International J. Pharmaceutics.* **182**(1), 7–20 (1999).
31. Huang, Y. M., Zheng, W. L., Zhang, D. Y. & Xi, Y. W. A modified Herschel–Bulkley model for rheological properties with temperature response characteristics of poly-sulfonated drilling fluid. *Energy Sources Part. A.* **42**, 1464–1475. https://doi.org/10.1080/15567036.2019.1604861 (2019).
32. Zuo, C. W. et al. The Preparation integrated suspension liquid system with high-temperature and shear-resistance by anhydrous pre-mixing with novel titanium crosslinking agent. *J. Polym. Res.* **31**, 134. https://doi.org/10.1007/s10965-024-03971-z (2024).
33. Leroy, L., Guven, N. & McGrew, G. T. Investigation of high temperature fluid loss control agents in geothermal drilling fluids. In *SPE-10736-MS, SPE California Regional Meeting, San Francisco, California* https://doi.org/10.2118/10736-MS (1982).
34. Farid, E., Kamoun, E. A., Taha, T. H., Dissouky, A. E. & Khalil, T. E. PVA/CMC/attapulgite clay composite hydrogel membranes for biomedical applications: factors affecting hydrogel membranes crosslinking and bio-evaluation tests. *J. Polym. Environ.* **30**, 4675–4468. https://doi.org/10.1007/s10924-022-02538-7 (2022).
35. API Recommended Practice13B-1, Third & Edition December ANSI/API 13B-1/ISO10414-1, 7–8 (2003).
36. Wang, F. H. et al. High temperature and high pressure rheological properties of high-density water-based drilling fluids for deep wells. *Petrol. Sci.* **9**, 354–362. https://doi.org/10.1007/s12182-012-0219-4 (2012).
37. Viseras, C., Meeten, G. H. & Lopez, G. A. Pharmaceutical grade phyllosilicate dispersions: the influence of shear history on Floc structure. *Int. J. Pharm.* **182**(1), 7–20 (1999).
38. Zhou, F. S., Li, T. Q., Yan, Y. H., Cao, C. & Lin, L. Y. Enhanced viscosity of aqueous palygorskite suspensions through physical and chemical processing. *Adv. Mater. Sci. Eng.* **2015**, 1–7. https://doi.org/10.1155/2015/941580 (2015).
39. Pillon, L. Z. Effect of clays and adsorbents on the nitrogen content and the stability of jet fuels. *Petrol. Sci. Technol.* **19**(7–8), 961–970. https://doi.org/10.1080/10916460008949850 (2001).
40. Zuo, C. W. et al. The preparation integrated suspension liquid system with high-temperature and shear-resistance by anhydrous pre-mixing with novel titanium crosslinking agent. *J. Polym. Res.* **31**, 134. https://doi.org/10.1007/s10965-024-03971-z (2024).

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Author contributions

Wenlong Zheng: Conceptualization, Resources, Funding acquisition, Writing—original draft, Writing—review and editing; Suzhou Wang: Data curation, Formal Analysis, Writing—review and editing; Lingguo Bai: Data curation, Formal Analysis, Methodology, Writing—original draft; Chiheng Yang: Data curation, Formal Analysis, Investigation, Writing—review and editing.

Declarations

Competing interests

The authors declare no competing interests.

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