Heliyon 9 (2023) e22990

Contents lists available at ScienceDirect

Heliyon

journal homepage: www.cell.com/heliyon

Water-based drilling fluids containing hydrophobic nanoparticles for minimizing shale hydration and formation damage

Yuexiang Li *, Changyuan Xia, Xin Liu

Faculty of Petroleum Engineering, Harbin Institute of Petroleum, Songbei District, Harbin, Heilongjiang Province, 150028, China

ARTICLE INFO

Keywords:
shale formation
Hydrophobic nano-SiO_2 dispersion
Inhibiting performance
Formation protection
Water-based drilling fluids

ABSTRACT

Wellbore instability is always inevitable in shale formation due to hydration, swelling, and dispersion of clay, especially when using water-based drilling fluids (WBDFs). To mitigate the wellbore instability of shale formation and avoid correlative detriments such as formation damage, various nano-silica particles (nano-SiO_2) were employed to plug the nano-sized pores, inhibit water invasion into shale, and prevent shale swelling. Firstly, the influence of various nano-SiO_2 on rheological and filtration properties of a set WBDF was evaluated. Then, the linear swelling test, shale recovery test, zeta potential test, imbibition test, contact angle measurement, scanning electron microscopy (SEM) observation, and computed tomography (CT) analysis were conducted to assess the characteristic of nano-SiO_2. Experimental results showed that solid phase nano-SiO_2 could dramatically increase the viscosity and yield point while liquid phase nano-SiO_2 only caused small fluctuations on these parameters. Besides, hydrophobic nano-SiO_2 displayed better filtration performance than hydrophilic nano-SiO_2. On the whole, the hydrophobic nano-SiO_2 dispersion, called as nano-2, showed the best performance in WBDFs. Furthermore, nano-2 exhibited better inhibition than hydrophilic nano-SiO_2, KCl, and polyether amine (PA). Mechanism analysis demonstrated that nano-2 could improve the hydrophobic degree of shale surface and prevent water from contacting with the shale. Meanwhile, nano-2 plugged the pores and throats in the shale. As a consequence, water in the drilling fluid was prevented from invading the shale, and the shale was inhibited. Nano-2 could form a thin barrier in the surface of shale, and mitigate the damage degree of shale cores after perforation operation. As a result, nano-2 displayed great potential to stabilize shale and protect formation in WBDFs.

1. Introduction

Wellbore instability due to shale hydration and dispersion is generally considered as an unavoidable issue, which needs a continuous effort in oil and gas drilling industry [1,2]. Generally, various inhibited drilling fluids are employed to mitigate the shale hydration and improve the stability of borehole [3,4]. Oil- and synthetic-based drilling fluids have strong inhibitive performance, but their disadvantages, such as expensive cost and pollution to environment, limit their application in a certain extent. Water-based drilling fluids (WBDFs) are cheap, have superior rate of penetration, and are environmentally friendly [5,6]. However, one of the main drawbacks for WBDFs is poor inhibition performance due to the existence of a large amount of water in the system. The penetration of water into the shale formation will cause serious clay swelling, wellbore collapse, variation in the pore size, eventually

---

* Corresponding author.
E-mail address: liyuexiang425@163.com (Y. Li).

https://doi.org/10.1016/j.heliyon.2023.e22990
Received 8 February 2023; Received in revised form 23 November 2023; Accepted 23 November 2023

leading to a decrease in permeability and formation damage [7,8]. Therefore, the formulation of high-performance WBDFs with outstanding inhibition and plugging properties has received considerable attention all the time.

WBDFs mainly consist of water, bentonite, and various additives. The use of shale inhibitors or stabilizers is the most effective method to improve the inhibition of WBDFs [9]. To develop valid inhibitive additives, obtaining insights into the mechanism of shale swelling and dispersion is important. In the terms of macroscopic mechanical theory, the primary reason for the borehole instability is the increase of pore pressure due to the penetration of filtrate into rock pores [10]. As a consequence, the original effectively binding force between mineral particles weakens, and the rock strength decreases. In the terms of microscopic view, another important reason is that the bonding force between mineral particles is destroyed by water molecules, especially the hydration, swelling and dispersion of clay [11]. Anyway, these factors that lead to the borehole instability are all generated on the premise that water from WBDFs invades the clay or shale. Over the past decades, many inhibitors or stabilizers have been employed to mitigate the shale hydration and dispersion. According to their mechanisms, these methods are usually classified into two types, chemical inhibition and physical plugging [12]. In the terms of chemical inhibition, various shale inhibitors have been developed, such as inorganic salts [13,14] (KCl, $CaCl_2$, NH_4Cl, etc), polymeric encapsulators [15,16] (Hydrolyzed polyacrylamide, HPAM, potassium polyacrylate, etc), polyglycols [17], surfactants [18], and so on. Viewing from the aspect of physical plugging, nanoparticles [19], asphaltene, silicate and aluminate compounds [20,21] and so on have been introduced into oilfield. These chemicals have been commonly selected and used according to the downhole conditions. They have exerted different performance in drilling operations. Potassium ions with appropriate ionic radius and low hydration energy is one of the most earliest used additives in WBDFs, which can suppress the swelling the clay via ion exchange with sodium [22] and have been mostly used in practice in combination with other polymers, such as HPAM. Unfortunately, a high concentration of KCl, ranging from 2 to 8%, is always required and might affect the ecosystem [23]. To deal with the adverse effect of KCl on environment, alternative cation sources acting similar excellent inhibition have been introduced to replace potassium cation. The ammonium cation possesses a similar hydration volume as the potassium cation, so it can exert function in an analogous manner [24]. These ammonium salts include monocationic, oligocationic, polycationic amines. Generally, with the same functionality, oligomeric cationic shale inhibitors perform better function than that of monocationic or polycationic shale inhibitors. Plugging performance must be also taken into account, especially in shale strata with micro-nano pores. Recent years, various nanoparticles including nano silicon, nano graphene, nano oxide, and others have attracted considerable research interests [25,26]. These nanoparticles can seal the micro pores and prevent the invasion of water, thereby improving the stability of borehole. Desired inhibition performance is always achieved by a combination of chemical inhibition and physical plugging.

Nano-silica (nano-SiO_2) is the most common and earliest studied nanomaterial as a shale stabilizer [27]. Generally, nano-SiO_2 can be divided into two types, hydrophilic and hydrophobic particles. To seal the nano-sized pores and throats of shales, Cai et al. [28] have tested six kinds of non-modified nano-SiO_2 by a three-step pressure penetration test. A large reduction in shale permeability was observed when using the muds to which nano-SiO_2 with a concentration of 10 wt % had been added. Higher plastic viscosity (PV) and lower yield point (YP) of the nanoparticle muds compared with base muds were also observed. They have also formulated a salt WBDF using available silica nanoparticles with high-temperature resistance for shale gas horizontal drilling [29]. A fluid-solid coupling nano-blocking model based on pore characteristics, fluid physical properties, and discrete element parameters has been established and indicated that increasing the particle size had a greater impact on plugging efficiency of vertical well pores [30]. In the multi-scale particle release mode, the particle plugging effect could be increased by more than 90 %. Furthermore, hydrophobic modification has been also conducted to improve the stabilization of nanoparticles, for example, a hydrophobic nano-silica (HNS) composited by nano-SiO_2 and stearyl trimethyl ammonium chloride [31], a multifunctional superhydrophobic nanosilica (SA) prepared using the sol-gel method between nano-SiO_2 and perfluorooctane triethoxysilane [32], a hydrophobic SiO_2 (SH–SiO_2) nanomaterial synthesized using five different silane-coupling agents [33], and so on. Generally, these modified nano-SiO_2 exert inhibition through two approaches, altering surface wettability of shale and reversing the capillary force; and plugging the shale pores effectively.

It can be seen that nano-SiO_2 particles perform satisfactory inhibition effect and is gradually playing an important role in drilling operations, especially for shales. However, many studies only focus on one kind of nano-SiO_2 and there are few studies comparing the properties of nano-SiO_2 with different characteristics, especially their influence on the performance of a set WBDF system. Moreover, the damage on formation has been also seldom investigated. In this paper, various experiments have been conducted to compare the impact of different commercial nano-SiO_2 on the rheological, filtration properties, and inhibition of WBDFs. Moreover, the formation damage has been further tested to verify their function.

Table 1

Characteristics of used nano-SiO_2 particles.

Nanoparticle	Mark	Average size	Concentration
hydrophilic liquid phase nano-SiO_2	nano-1	20 nm	30 %
hydrophobic liquid phase nano-SiO_2	nano-2	8–20 nm	55 %
hydrophobic solid phase nano-SiO_2	nano-3	20–40 nm	–
hydrophilic solid phase nano-SiO_2	nano-4	20–40 nm	–

2. Materials and methods

2.1. Materials

Sodium bentonite (Na-BT) was provided by Shandong Huawei Bentonite Co., Ltd. Attapulgite was purchased from Beijing Inokai Technology Co., LTD. Potassium chloride (KCl), sodium chloride (NaCl), and anhydrous sodium carbonate (Na_2CO_3) were obtained from Chengdu Kelong Chemical Co., Ltd. Four commercial nano-SiO_2 particles (as shown in Table 1) and polyether amine (PA) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. The shale core samples were supplied by CNPC Chuanqing Drilling Engineering Co. LTD, and their mineral compositions are shown in Table 2 and Table 3. Polyanionic cellulose (PAC-LV) and lignite resin (SPNH) were offered by Beijing Shida Bocheng Technology Co. LTD.

2.2. Methods

The flow chart of all experiments in this study is shown in Fig. 1.

2.2.1. Influence of various nano-SiO_2 on properties of WBDFs

(1) Preparation of WBDFs

Firstly, 6.0 g Na-BT, 6.0 g attapulgite, and 0.6 g Na_2CO_3 were dispersed into 300 mL deionized water and stirred at 8000 rpm for 30 min to prepare a clay suspension. Then, the suspension was allowed to stand for 24 h to fully hydrate. Secondly, while continuing to stir at 8000 rpm, a certain quality of additives was cooperated slowly with 300 mL clay suspension according to the formula (the mass/volume concentration). After each additive was added, the stirring process was continued for 20 min to ensure full solution and dispersion of the materials. Moreover, these additives would be scraped off from the sides of the cup at least twice to reduce errors. Finally, the WBDF was stirred for another 30 min to get it mixed evenly. The detailed used WBDF formula was as follows: 2 % Na-BT +2 % attapulgite +0.2 % Na_2CO_3 +0.5 % PAC-LV+ 2.0 % SPNH+ 4 % NaCl.

(2) Rheological test

Rheological properties of WBDFs containing different nano-SiO_2 were measured after hot-rolled at 120 °C for 16 h on the basis of the American Petroleum Institute (API) standards (API Recommended Practice 13B-1 Field Testing Water-based Drilling Fluids). Each WBDF was firstly stirred at 5000 r/min for 5 min to make it even. Then, a certain amount of nano-SiO_2 were added into WBDF under continuous agitation. Finally, some rheological parameters including apparent viscosity (*AV*) and yield point (*YP*) were surveyed using a ZNN-D6B rotary viscometer. The specific calculation equations are as follows:

$$AV = 0.511\times\theta_{600}, \mathrm{mPa}\cdot\mathrm{s} \tag{1}$$

$$\mathrm{YP}=\theta_{300}\text{-}0.511\times\theta_{600}, \mathrm{Pa} \tag{2}$$

where θ_{600} and θ_{300} are the readings at 600 and 300 r/min, respectively.

(3) Filtration test

Effect of adding nano-SiO_2 particles on filtration property of WBDFs after hot-rolled at 120 °C for 16 h was further measured according to the American Petroleum Institute (API) standards (API Recommended Practice 13B-1 Field Testing Water-based Drilling Fluids). Filtration tests were conducted under a 100 psi pressure by a ZNS-2A filter press. About 250 mL of the fluids was poured into a cup equipped with reinforced filter paper. The filtration volume (FL_{API}) was recorded after 30 min. Filtration volume was recorded after each test run.

2.2.2. Inhibition performance of various nano-SiO_2

(1) Linear swelling test

The swelling degree of Na-BT pellet immersed in different WBDFs was determined through a NP-2S dual-channel linear swell meter

Table 2
Mineral composition of Na-BT and shale core.

mineral	quartz/%	feldspar/%	calcite/%	dolomite/%	magnesite/%	plagioclase/%	clay mineral/%
Na-BT	7.9	5.4	—*	1.2	1.3	6.9	77.3
shale	34.6	1.7	12.5	4.5	—*	6.8	39.9

Table 3
Clay mineral composition of Na-BT and shale core.

clay	smectite/%	kaolinite/%	illite/%	chlorite/%	I–S mixed layer/%
Na-BT	86	9	5	—*	—*
shale	10.5	7.2	20.8	2.0	59.5

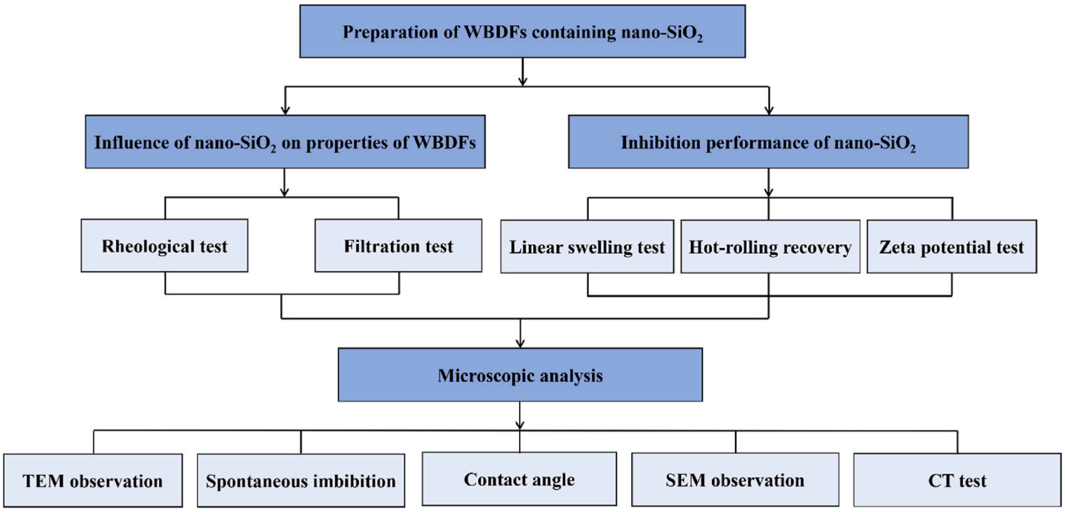

Fig. 1. The flow chart of experimental works.

referring to the Enterprise standard of China National Petroleum Corporation Limited “Evaluation procedure for the inhibition and sodium/calcium tolerance of water-based drilling fluids” (Q/SY 02408-2021). For each measurement, Na-BT (10 g) was compressed into a cylindrical device under 725 psi pressure for 10 min. Then, 20 mL of WBDF sample was added to immerse the Na-BT pellet. The swelled height of the pellet was recorded by a personal computer. The linear swelling percent is calculated by the following equation:

$$\text{Swelling perecnt} = \frac{h_t}{h_o} \times 100\% \tag{3}$$

where h_o is the original thickness of Na-BT pellet, and the h_t is the swelled height after immersing in aqueous solutions for a certain time t.

(2) Hot-rolling recovery test

The inhibition performance of WBDFs on the dispersion of shale cuttings was evaluated by hot rolling recovery test referring to above standard Q/SY 02408-2021. In this test, a total of 20 g of shale cuttings with 6–10 mesh size as well as 350 ml WBDFs were added into a jar together. The mixture was hot-rolled at 120 °C for 16 h. After cooling, the remaining cuttings were screened using a 40 mesh sieve. Then the cuttings retained on the sieve were dried at 105 °C until a constant weight. Finally, the recovery percentage was calculated by the following equation:

$$\text{Recovery} = \frac{m_1}{m_0} \times 100\% \tag{4}$$

where m_0 is the mass of shale cuttings before hot rolling and m_1 is the mass of shale cuttings after hot rolling.

(3) Zeta potential test

The stability of WBDFs was assessed by zeta potential test. The zeta potential of WBDFs was measured by a NanoBrook Omni zeta potential analyzer. The concentration of all samples was approximately 0.1 g L^{-1}.

2.2.3. Microscopic analysis

(1) Transmission electron microscopy (TEM) observation

The TEM analysis of nano-SiO_2 was performed using a F20 transmission electron microscopy. The nanoparticle suspension was diluted by deionized water and ultrasounded for 15 min. Then, a drop of the dispersion was dripped onto a carbon film supported on a copper grid and dried using an infrared lamp. After that, the samples were observed by the TEM.

(2) Spontaneous imbibition test

The spontaneous imbibition test was conducted to evaluate the mass of water that invaded into the shale cores, which will result in swelling of clay and shales. When the bottom face of shale cores touched the fluid level of samples, the spontaneous imbibition volume of water was recorded with time by a personal computer.

(3) Contact angle measurements

As mentioned above, changing surface wettability is one of the most important method to avoid adverse effects of hydrophilic characteristic of clay and water invasion [34]. Contact angle measurement is the direct method to identify the surface wettability. The hanging drop method has been used to determine the water contact angle by a JC2000C contact angle tester. Firstly, shale cores were treated with different nanoparticle dispersions using a core dynamic polluter. After cleaning the surface, shale cores modified by nanoparticles were obtained. Then, the water contact angles before and after modified with fluids containing nano-SiO_2 were tested to characterize the alteration of shale surface wettability.

(4) Scanning electron microscopy (SEM) observation

To observe the nano-SiO_2 particles, which could plug the shale pores or cracks, the microstructure of shale cores was characterized using a Quanta 200 F SEM. In detail, shale cores treated with WBDF containing nano-SiO_2 were removed from a core dynamic polluter and slowly washed with pure water to remove surface substance. Then, the cores were dried in a vacuum oven at 50 °C. Finally, the shale cores were coated with Au and measured via SEM.

(5) CT test

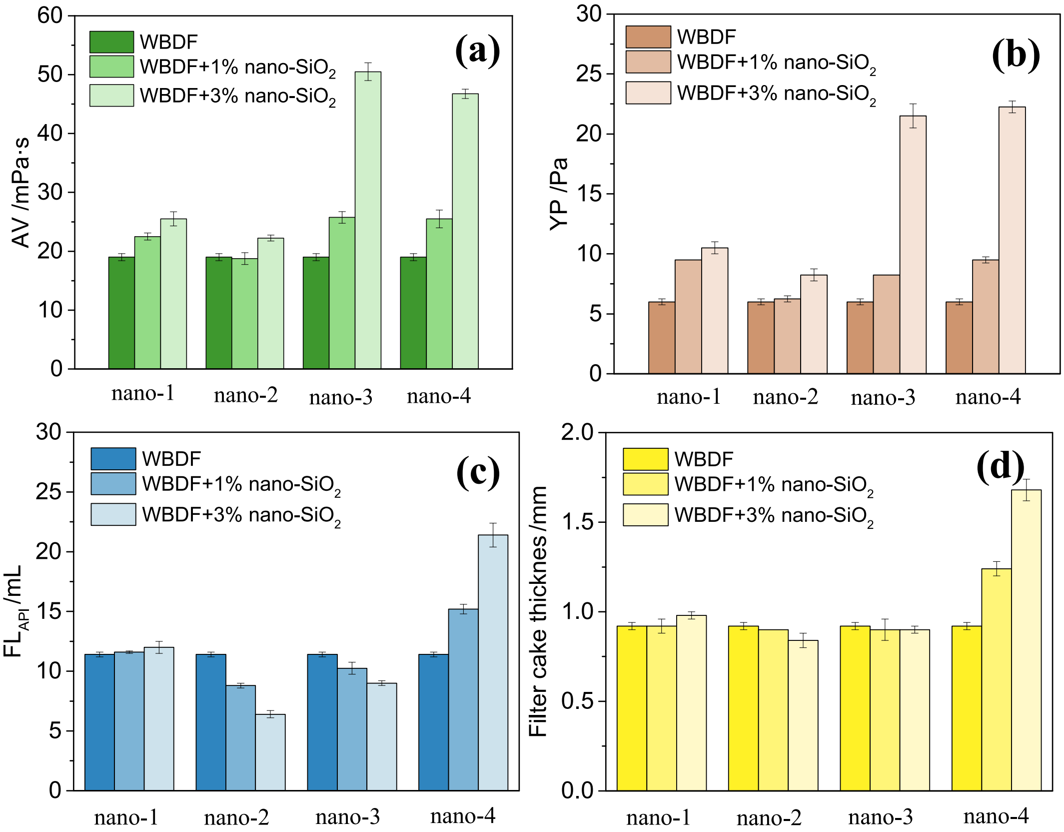

Fig. 2. The influence of different nano-SiO_2 on AV (a), YP (b), and FL_{API} (c), and filter cake thickness (d) of WBDFs.

Further, the permeability of shale cores before and after contamination was observed by the CT scanning. In comparison, the permeability of the original core was first measured. For the core after treated by WBDF containing nano-SiO_2, the face was plugged by nano-SiO_2. After cleaning, the variation of permeability was also determined.

3. Results and discussion

3.1. *Influence of nano-SiO_2 on properties of WBDFs*

As exhibited in Fig. 2, the influence degree of different nano-SiO_2 on rheological and filtration of WBDF was quite diverse. For the AV and YP (Fig. 2a and b), which were calculated according to equations (1) and (2), it could be seen that these parameter values always increased with the enhancement of nano-SiO_2 concentration. However, the AV and YP sharply increased after the addition of solid phase nano-SiO_2 (nano-3 and nano-4), especially at high concentrations, while that slightly gained by the cooperation of nano-SiO_2 dispersion (nano-1 and nano-2). It was referred that solid phase nano-SiO_2 particles were more difficult to distribute evenly in the drilling fluid, compared with nano-SiO_2 dispersion. They might form aggregation with clay and polymer, which offered more friction and grid structure [25,35], no matter what kind of solid phase nano-SiO_2 was used. For the FL_{API} (Fig. 2c), hydrophobic nano-SiO_2 including liquid phase nano-2 and solid phase nano-3 could decrease the fluid loss, and nano-2 performed better filtration property. On the contrary, hydrophilic nano-SiO_2 was inoperative in improving the filtration performance. In detail, the fluid loss volume haven't varied with the addition of liquid phase nano-1, while that dramatically grew after cooperated with solid phase nano-4, which might attribute to the agglomeration of solid nanoparticles forming more pores and flow channels and the wastage of the other polymer additives by the adsorption of hydrophilic solid phase nano-4 [36]. The results of filter cake thickness tests also performed a similar rule to that of filtration experiments (Fig. 2d). Furthermore, it could also prove that hydrophobic modification improved the filtration property. Overall, hydrophobic nanoparticles, especially the liquid phase nano-2, have better properties in WBDFs due to its stable dispersion, hydrophobic surface, and plugging performance.

3.2. *Inhibition performance of WBDFs containing nano-SiO_2*

Based on above analysis, hydrophobic nano-SiO_2 dispersion, nano-2 particles, has the optimal performance. Its inhibitive property was further investigated and compared with other additives.

The swelling percent of all Na-BT pellets (obtained through equation (3)) increased with increasing immersing time and the swelling rate gradually decreased with increasing immersing time during the first 24 h (Fig. 3). All WBDFs containing diverse additives displayed a positive influence on reducing the swelling degree of Na-BT. In detail, WBDFs containing 3 % KCl, 3 % nano-1, and 3 % nano-2 decreased the swelling percent to 31.4 %, 40.6 %, and 25.3 %, respectively, compared to that of 47.75 % in pure WBDFs without inhibitors (Fig. 3b). Their inhibition at 3.0 % concentration was in an ascending order of nano-1 < KCl < PA < nano-2. Nano-2 revealed the best inhibition performance. The inhibition effect of nano-SiO_2 was enhanced by the hydrophobic modification, which was also in accordance with filtration results, showing that nano-2 had superior plugging effects to help preventing water penetration.

Moreover, the influence of concentration of nano-2 on the linear swelling degree of Na-BT was also conducted. Fig. 3a indicated that increasing the concentration of nano-2 was beneficial for improving the inhibition effect. By comparing the performance difference between nano-1 and nano-2, it could be understood that hydrophobic characteristic played a primary role in exerting their inhibition.

To assess the inhibitive performance of a drilling fluid in controlling the dispersion of drilled cuttings transported from downhole to the surface, shale recovery tests were organized and the results were calculated by equation (4). The inhibitive performance of nano-2

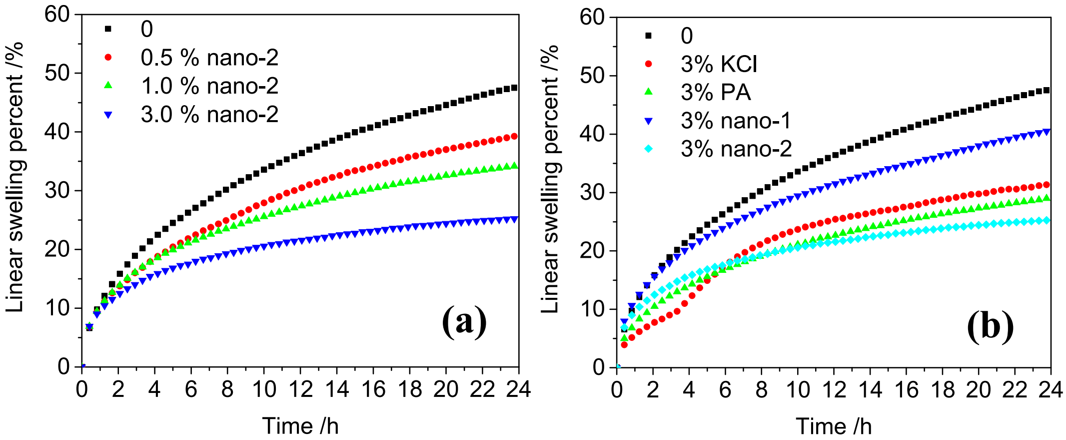

Fig. 3. Linear swelling percent of Na-BT in WBDFs containing various inhibitors: (a) 0 %, 0.5 % nano-2, 1.0 % nano-2, and 3.0 % nano-2; (b) 0 %, 3 % KCl, 3 % PA, 3 % nano-1, and 3 % nano-2.

at different concentrations was firstly considered. Fig. 4a demonstrated that the remaining shale in pure WBDF accounted for only 59 % depending on the sample components after hot rolling at 120 °C for 16 h. From the addition of 0.5–3 % nano-2, larger shale recovery compared to that in pure WBDFs without nano-SiO_2 was obtained, proving the inhibition of nano-2 on shale dispersion. What's more, at a same concentration of 3 %, WBDF containing nano-2 had the higher recovery value than those WBDFs containing KCl or nano-1, and a similar recovery level with WBDF containing PA (Fig. 4b). This result was consistent with that of linear swelling experiments. It could be concluded that among diversified nano-SiO_2 particles, nano-2 had the most potential to inhibit shale and reduce formation damage due to hydration.

Inhibitors, depending on the type, structure, molecular mass, and functionalities, might change the electrokinetic potential of WBDFs. To further investigate the inhibitive performance of nano-SiO_2, electrokinetic potential was also measured (Table 4). WBDFs were negatively charged and could form stable dispersed suspension owing to repulsive forces. The zeta potential of pure set WBDF in our study was −73.2 mV, showing considerable stability. After adding KCl and PA, the zeta potential was reduced to −70.3 mV and −68.5 mV, suggesting suppressed double electrical layer and stability reduction in a certain degree. In comparison, nano-1 and nano-2 decreased the zeta potential to −72.0 mV and −70.8 mV, displaying less effect on the zeta potential of WBDFs. Based on these results, it was speculated that the inhibition effect of nano-2 was mainly through plugging and hydrophobic action, rather than electrostatic action.

3.3. Microstructure analysis

3.3.1. TEM of nano-2

In order to explore the action of nano-2 in WBDFs, microstructure of nano-2 was observed through TEM. As displayed in Fig. 5, nano-2 particles exhibited small size and the diameter was approximately 10 nm–20 nm. This condition was beneficial for the absorption on Na-BT or shale surface. These nanoparticles were connected to each other but did not aggregate. Besides, they had irregular shape and performed flat circle structure, which might be advantageous to plugging.

3.3.2. Spontaneous imbibition test

Spontaneous imbibition has been usually used to measure the volume of water that invades the sensitive core pores, which is the direct reason for clay hydration, swelling and dispersion [33]. In general, the less water that invaded into pores of shale, the less likely that wellbore instability would occur. Fig. 6 shows that approximately 4.15 g of water invaded the core after 180 min when it was in pure water. After the water was replaced by nano-2 with a concentration of 0.5 %, 1.0 %, and 3.0 %, the invaded water volume sharply decreased to 3.85, 3.57, and 2.62 g, respectively. Obviously, the addition of nano-2 showed effective performance on preventing water imbibing into shale cores. It was proposed that nano-2 could adsorb on the surface of cores and plug the nanopores of cores. Meanwhile, they altered the core inner surface from hydrophilic to hydrophobic. Finally, the addition of nano-2 prevented water invasion into the core pores and reduced the possibility of shale swelling.

3.3.3. Wettability of shale cores

To further prove the wettability modification of shale caused by nano-2, the contact angles of shale surface after treated by nano-2 were measured, and the results are shown in Fig. 7. The initial core sample was hydrophilic and the water contact angle on the edge of the core sample was 36°, displaying a typical hydrophilic behavior. Obviously, nano-2, as a hydrophobic nanofluid, gradually increased the water contact angle on the surface of cores. After adding 3 % nano-2, the contact angle was increased to 67°. A stronger hydrophilic surface predicted less water contacting with shale core. This result confirmed the analysis in spontaneous imbibition test, and proved that the hydration and swelling of clay minerals could be mitigated through the wettability alteration.

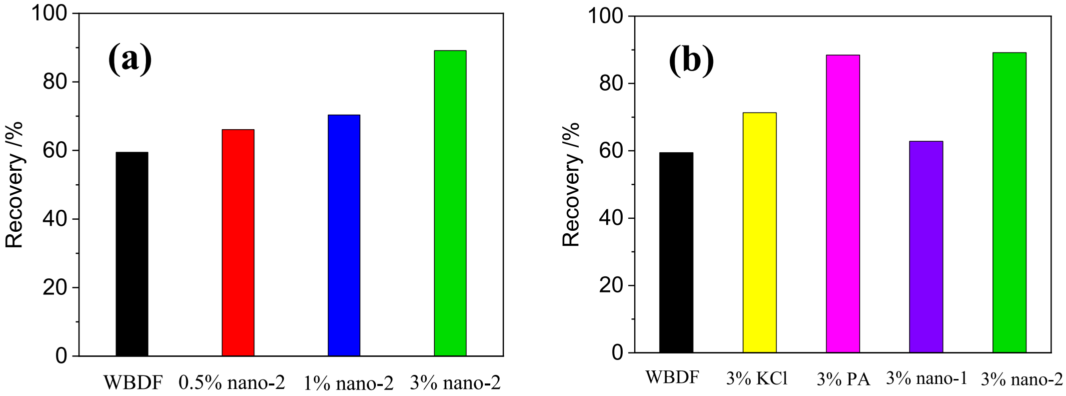

Fig. 4. Shale recovery of WBDFs containing various inhibitors: (a) 0 %, 0.5 % nano-2, 1.0 % nano-2, and 3.0 % nano-2; (b) 0 %, 3 % KCl, 3 % PA, 3 % nano-1, and 3 % nano-2.

Table 4
The zeta potential of WBDFs containing various inhibitors.

Sample	Zeta potential/mV
Pure WBDF	−73.2
WBDF+3%KCl	−70.3
WBDF+3 % PA	−68.5
WBDF+3 % nano-1	−72.0
WBDF+3 % nano-2	−70.8

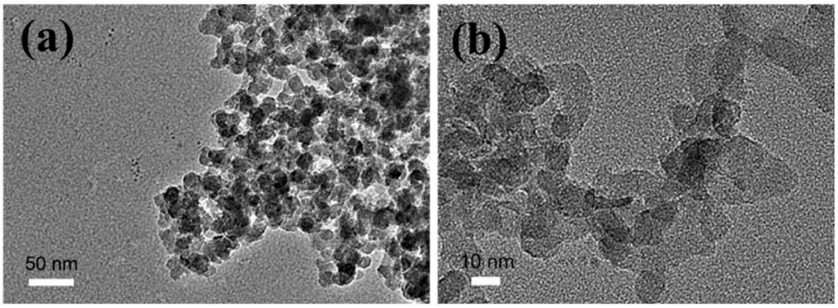

Fig. 5. TEM images of nano-2 (a, b).

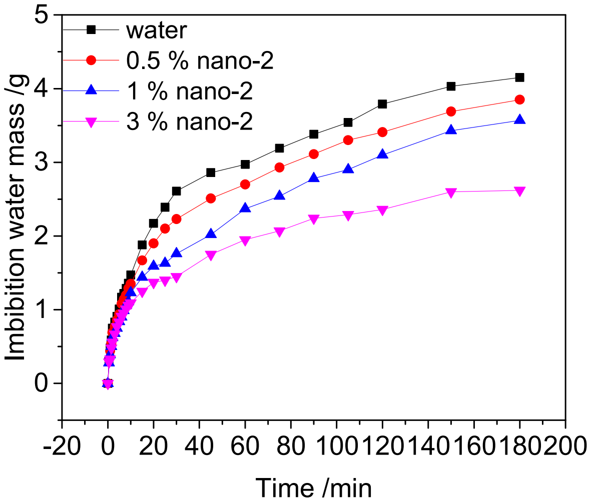

Fig. 6. Imbibition of water mass into cores as a function of time for nano-2.

3.3.4. *SEM of shale cores*

As nanoparticles, another considerable effect is the plugging effect that is verified to be in favor of plugging shale pores. Under positive differential pressure between the drilling fluid (high) and formation (low), nanoparticles are pushed close to the wellbore wall and block the shale pores. Fig. 8a shows the initial microstructure of shale surface, presenting some porous structure. After being plugging by 3 % nano-2, a more smooth and seamless surface like a plugging film was observed (Fig. 8b), which could be beneficial to reducing water invasion into the formation.

3.3.5. *Shale CT analysis*

Based on above results, it was clear that nano-2 could prevent the invasion of water by plugging and wettability modification, thereby inhibiting the hydration, swelling, and dispersion of clay and shales. However, for the shale formation, nanoparticles might cause formation damage due to the blocking of pores or throats in the oil and gas formation away from wellbore wall. Considering this potential hazard, the permeability of shale cores was tested by CT. As displayed in Fig. 9a, original shale core was not plugged and there were many pores and throats (light colored part, the pore connection part). After treated by nano-2, it could be obviously found that the colour of the edge of core became darker (Fig. 9b), indicating that the edge part of the core was sealed and the porosity of the core reduced. In addition, from Fig. 9b, it could be perceived that the plugging effect only occurred at the edge of core, and the porosity

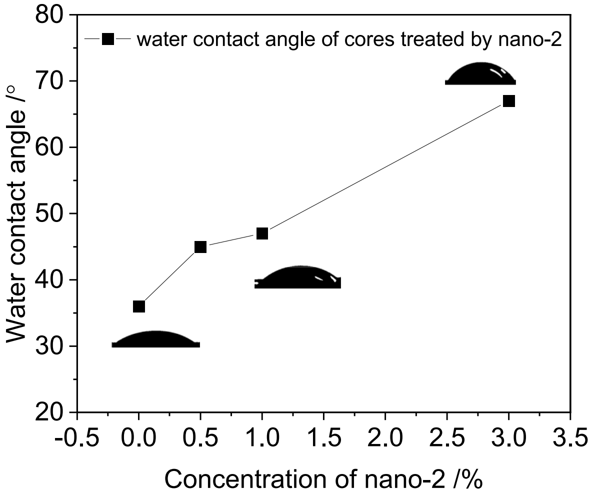

Fig. 7. Water contact angle on cores treated by nano-2 with different concentrations.

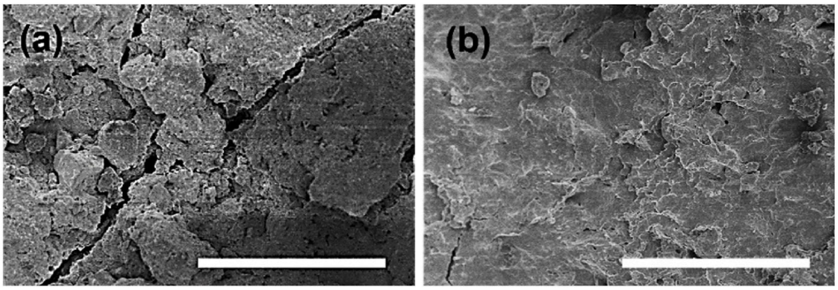

Fig. 8. SEM images of the shale surface before (a) and after (b) treated by nano-2. The legend is 20 μm.

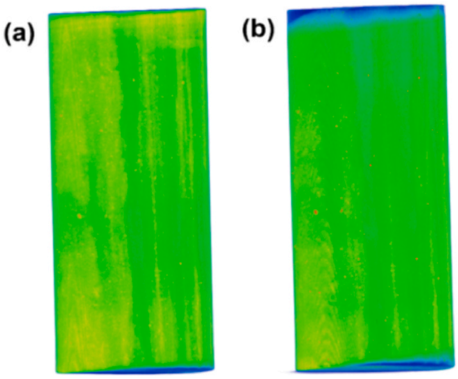

Fig. 9. CT images of the shale cores before (a) and after (b) treated by nano-2.

in the middle of the core was almost unaffected. Thus, the permeability of core would recover after cutting off the short edge part of the core, which was similar with the perforation process during the completion operation. So nano-2 was advantageous for reducing formation damage.

3.3.6. Mechanism analysis of nano-2

Based above experiments, the hydrophobic nanofluids, nano-2, displayed satisfactory inhibitive and formation protection performance. Nano-2 particles show small spheroidicity. These nanoparticles can be evenly dispersed in the drilling fluid without excessive influence on the viscosity or shear force of the drilling fluid. They can adsorb onto Na-BT or shale and the adsorbed nano-SiO_2 particles onto Na-BT and shale surface enhance the surface hydrophobic characteristic, which can prevent water from contacting with clay. Meanwhile, in the drilling fluid system, nano-SiO_2 can perform as a plugging additive and decrease the fluid loss. Therefore, the pores or throats in shale are sealed and water from the drilling fluid is prevented from invading the shale. Therefore, hydration, swelling, and dispersion are inhibited to ensure wellbore stability. Moreover, though nano-SiO_2 can plug the pores of shale, they only form a thin barrier in the surface of shale and cause less adverse influence on the variation of permeability of the shale core. Finally, nano-2 shows excellent performance on inhibiting shale and reducing formation damage.

4. Conclusions

Various nano-SiO_2 particles have been utilized to prepare WBDFs. The influence of nano-SiO_2 on the properties of WBDFs was investigated and the mechanisms of nano-SiO_2 in inhibition and formation protection were analyzed. The following conclusions are drawn accordingly from the research work.

(1) For different nano-SiO_2 particles, solid phase nano-SiO_2 can dramatically increase the viscosity and yield point while liquid phase nano-SiO_2 will only cause small fluctuations on that. Besides, hydrophilic nano-SiO_2 will increase the fluid loss of WBDFs and hydrophobic nano-SiO_2 can decrease the fluid loss. On the whole, the hydrophobic nano-SiO_2 dispersion, called as nano-2, shows the best comprehensive performance in WBDFs.
(2) Nano-2 exhibits better inhibition compared to nano-1, KCl, and PA in WBDFs. In comparison with pure WBDF, WBDFs containing 3 % nano-2 can reduce the swelling percent of Na-BT from 47.75 % to 25.3 % and increase the shale recovery from 59 % to 89 %, respectively.
(3) Nano-2 can improve the hydrophobic characteristic of shale surface and prevent water from contacting with the clay and shale. Meanwhile, nano-2 can also exert plugging effect and seal the pores or throats in shale. Finally, the invasion of water into shales from WBDFs is prevented, thereby inhibiting the hydration, swelling, and dispersion of clay and shales.
(4) Nano-2 particles only form a thin barrier in the surface of shale. They will not cause adverse influence on the variation of permeability of the shale core after perforation operation. Thus, nano-2 can minimize the formation damage.

Funding

This work was financially supported by the Research Project of Natural Science.
Foundation of Heilongjiang Province (LH2021D013).

Ethics approval

Not applicable.

Data availability statement

Data will be made available on request.

CRediT authorship contribution statement

Yuexiang Li: Writing – original draft. **Changyuan Xia:** Investigation. **Xin Liu:** Investigation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

[1] E. van Oort, On the physical and chemical stability of shales, J. Petrol. Sci. Eng. 38 (2003) 213–235, https://doi.org/10.1016/S0920-4105(03)00034-2.
[2] R.L. Anderson, I. Ratcliffe, H.C. Greenwell, P.A. Williams, S. Cliffe, P.V. Coveney, Clay swelling — a challenge in the oilfield, Earth Sci. Rev. 98 (2010) 201–216, https://doi.org/10.1016/j.earscirev.2009.11.003.
[3] A. Al-Ansari, K. Yadav, Saudi Aramco, D. Anderson, R. Leaper, W. Dye, N. Hansen, SPE/IADC Middle East drilling Technology Conference & exhibition, in: Diverse Application of Unique High-Performance Water-Based-Mud Technology in the Middle East, 2005, https://doi.org/10.2118/97314-MS. SPE/IADC 97314.
[4] M. Attia, W. Elsorafy, S. D'Angelo, New Engineered Approach to Replace Oil-Based Drilling Fluids with High Performance Water-Based Drilling Fluids in Mediterranean Sea, North Africa Technical Conference & Exhibition, 2010, https://doi.org/10.2118/127826-MS. SPE 127826.
[5] R. Caenn, G. Chillingar, Drilling fluids: state of the art, J. Pet. Sci. Eng. 14 (1996) 221–230, https://doi.org/10.1016/0920-4105(95)00051-8.
[6] M.-C. Li, Q. Wu, K. Song, S. Lee, C. Jin, S. Ren, T. Lei, Soy protein isolate as fluid loss additive in bentonite–water-based drilling fluids, ACS Appl. Mater. Interfaces 7 (2015) 24799–24809, https://doi.org/10.1021/acsami.5b07883.
[7] Q. Lyu, P.G. Ranjith, X. Long, Y. Kang, M. Huang, A review of shale swelling by water adsorption, J. Nat. Gas Sci. Eng. 27 (2015) 1421–1431, https://doi.org/10.1016/j.jngse.2015.10.004.
[8] G.W.-D. Zhou Z, B. Kadatz, S. Cameron, Effect of clay swelling on reservoir quality, J. Can. Pet. Technol. 35 (1996) 18–23, https://doi.org/10.2118/96-07-02.

[9] R. Gholami, H. Elochukwu, N. Fakhari, M. Sarmadivaleh, A review on borehole instability in active shale formations: interactions, mechanisms and inhibitors, Earth Sci. Rev. 177 (2018) 2–13, https://doi.org/10.1016/j.earscirev.2017.11.002.

[10] M. Lal, Shale Stability: Drilling Fluid Interaction and Shale Strength, SPE Latin American and Caribbean Petroleum Engineering Conference, Caracas, Venezuela, 1999, https://doi.org/10.2118/1199-0030-jpt.

[11] N.S. Muhammed, T. Olayiwola, S. Elkatatny, A review on clay chemistry, characterization and shale inhibitors for water-based drilling fluids, J. Petrol. Sci. Eng. 206 (2021), 109043, https://doi.org/10.1016/j.petrol.2021.109043.

[12] H. Zhong, Z. Qiu, D. Sun, D. Zhang, W. Huang, Inhibitive properties comparison of different polyetheramines in water-based drilling fluid, J. Nat. Gas Sci. Eng. 26 (2015) 99–107, https://doi.org/10.1016/j.jngse.2015.05.029.

[13] R.T. Ewy, Shale swelling/shrinkage and water content change due to imposed suction and due to direct brine contact, Acta Geotechnica 9 (2014) 869–886, https://doi.org/10.1007/s11440-013-0297-5.

[14] T.M. Al-Bazali, The consequences of using concentrated salt solutions for mitigating wellbore instability in shales, J. Petrol. Sci. Eng. 80 (2011) 94–101, https://doi.org/10.1016/j.petrol.2011.10.005.

[15] RF Scheuerman Rk Clark, H. Rath, Polyacrylamide/potassium-chloride mud for drilling water-sensitive shales, J. Petrol. Technol. 28 (1976) 719–727, https://doi.org/10.2118/5514-pa.

[16] X.Z. Guancheng Jiang, Tengfei Dong, Yang Xuan, Le Wang, Qihui Jiang, A new inhibitor of P(AM-DMDAAC)/PVA intermacromolecular complex for shale in drilling fluids, J. Appl. Polym. Sci., 135: 1-8. DOI: 10.1002/app.45584.

[17] S. Liu, X. Mo, C. Zhang, D. Sun, C. Mu, Swelling inhibition by polyglycols in montmorillonite dispersions, J. Dispersion Sci. Technol. 25 (2004) 63–66, https://doi.org/10.1081/dis-120027669.

[18] N.S. Muhammed, T. Olayiwola, S. Elkatatny, B. Haq, S. Patil, Insights into the application of surfactants and nanomaterials as shale inhibitors for water-based drilling fluid: a review, J. Nat. Gas Sci. Eng. 92 (2021), 103987, https://doi.org/10.1016/j.jngse.2021.103987.

[19] K. Wang, G. Jiang, X. Li, P.F. Luckham, Study of graphene oxide to stabilize shale in water-based drilling fluids, Colloids Surf. A Physicochem. Eng. Asp. 606 (2020), 125457, https://doi.org/10.1016/j.colsurfa.2020.125457.

[20] Z. Wei, S. Zhu, C. Li, A novel aluminum-based shale inhibitor and its wellbore stabilization effect, Alex. Eng. J. 60 (2021) 5463–5471, https://doi.org/10.1016/j.aej.2021.04.009.

[21] J. Guo, J. Yan, W. Fan, H. Zhang, Applications of strongly inhibitive silicate-based drilling fluids in troublesome shale formations in Sudan, J. Petrol. Sci. Eng. 50 (2006) 195–203, https://doi.org/10.1016/j.petrol.2005.12.006.

[22] L. Yang, G. Jiang, Y. Shi, X. Yang, Application of ionic liquid and polymeric ionic liquid as shale hydration inhibitors, Energy & Fuels 31 (2017) 4308–4317, https://doi.org/10.1021/acs.energyfuels.7b00272.

[23] J.L. Suter, P.V. Coveney, R.L. Anderson, H.C. Greenwell, S. Cliffe, Rule based design of clay-swelling inhibitors, Energy Environ. Sci. 4 (2011) 4572–4586, https://doi.org/10.1039/c1ee01280k.

[24] A.D. Patel, Design and Development of Quaternary Amine Compounds: Shale Inhibition with Improved Environmental Profile, SPE International Symposium on Oilfield Chemistry, 2009, https://doi.org/10.2118/121737-ms. SPE 121737.

[25] A.E. Bayat, R. Shams, Appraising the impacts of SiO2, ZnO and TiO2 nanoparticles on rheological properties and shale inhibition of water-based drilling muds, Colloids Surf. A Physicochem. Eng. Asp. 581 (2019), 123792, https://doi.org/10.1016/j.colsurfa.2019.123792.

[26] A.I. Jose Aramendiz, Silica and Graphene Oxide Nanoparticle Formulation to Improve Thermal Stability and Inhibition Capabilities of Water-Based Drilling Fluid Applied to Woodford Shale, SPE International Conference on Oilfield Chemistry, SPE-193567-MS, 2019, https://doi.org/10.2118/193567-PA.

[27] B.R.R. Peter, J. Boul, Matt Hillfiger, T. Pete O' Connell, Carl Thaemlitz, Functionalized Nanosilicas as Shale Inhibitors in Water-Based Drilling Fluids, the Offshore Technology Conference, OTC-26902-MS, 2016, https://doi.org/10.2118/185950-PA.

[28] M.E.C.J. Cai, M.M. Sharma, Jim Friedheim, Decreasing water invasion into atoka shale using nonmodified silica nanoparticles, SPE Drill. Complet. 27 (2012) 103–112, https://doi.org/10.2118/146979-PA.

[29] X. Yang, Z. Shang, H. Liu, J. Cai, G. Jiang, Environmental-friendly salt water mud with nano-SiO2 in horizontal drilling for shale gas, J. Petrol. Sci. Eng. 156 (2017) 408–418, https://doi.org/10.1016/j.petrol.2017.06.022.

[30] X. Yang, J. Cai, G. Jiang, Y. Zhang, Y. Shi, S. Chen, Y. Yue, Z. Wei, D. Yin, H. Li, Modeling of nanoparticle fluid microscopic plugging effect on horizontal and vertical wellbore of shale gas, Energy 239 (2022), 122130, https://doi.org/10.1016/j.energy.2021.122130.

[31] X. Huang, J. Sun, H. Li, R. Wang, K. Lv, H. Li, Fabrication of a hydrophobic hierarchical surface on shale using modified nano-SiO2 for strengthening the wellbore wall in drilling engineering, Engineering 11 (2022) 101–110, https://doi.org/10.1016/j.eng.2021.05.021.

[32] Y. Geng, J. Sun, S. Xie, X. Huang, R. Wang, J. Wang, Q. Wang, Novel use of a superhydrophobic nanosilica performing wettability alteration and plugging in water-based drilling fluids for wellbore strengthening, Energy & Fuels 36 (2022) 6144–6158, https://doi.org/10.1021/acs.energyfuels.2c00760.

[33] X. Ni, G. Jiang, Y. Li, L. Yang, W. Li, K. Wang, Z. Deng, Synthesis of superhydrophobic nanofluids as shale inhibitor and study of the inhibition mechanism, Appl. Surf. Sci. 484 (2019) 957–965, https://doi.org/10.1016/j.apsusc.2019.04.167.

[34] Y. Yue, S. Chen, Z. Wang, X. Yang, Y. Peng, J. Cai, H.A. Nasr-El-Din, Improving wellbore stability of shale by adjusting its wettability, J. Petrol. Sci. Eng. 161 (2018) 692–702, https://doi.org/10.1016/j.petrol.2017.12.023.

[35] M. Al-Yasiri, A. Awad, S. Pervaiz, D. Wen, Influence of silica nanoparticles on the functionality of water-based drilling fluids, J. Petrol. Sci. Eng. 179 (2019) 504–512, https://doi.org/10.1016/j.petrol.2019.04.081.

[36] M.A. Abbas, A. Zamir, K.A. Elraies, S.M. Mahmood, N. Aslfattahi, R. Saidur, M. Ahmad, M.H. Rasool, Characterization of nano based drilling fluid for shale swelling inhibition, Petrol. Sci. Technol. 40 (2022) 2710–2736, https://doi.org/10.1080/10916466.2022.2048014.