Application of Hybrid Silicate as a Film-Forming Agent in High-Temperature Water-Based Drilling Fluids

Ying Li, Maosen Wang, Xianfeng Tan, Yinghui An, Huanan Liu, Ke Gao, and Mingyi Guo*

ABSTRACT: Effective control of shale swelling and lost circulation using drilling fluid is considered the dominant strategy for maintaining borehole stability, especially drilling operations in deep oil and gas wells. In this work, a hybrid silicate that contains lithium silicate and potassium methyl silicate (PMS) was employed as a film-forming additive to reduce shale hydration and filtration loss in the high-temperature drilling fluid. Scanning electron microscopy (SEM) results revealed that a dense quartz crystal film coating on the shale can be formed in a hybrid silicate solution when the temperature exceeds 150 °C. The in situ-formed film on the shale surface with a thickness of 60–130 μm was composed of fibrous crystalline silica. Furthermore, the aqueous hybrid silicate exhibited enhanced hydration inhibition ability by preventing water invasion of the formation. Aqueous hybrid silicate with a concentration of 0.5–3 wt % lithium silicate and 0.1–0.2 mol/L PMS was first chosen to obtain the optimum concentration according to the hydration inhibition ability and film formation characteristics. The hybrid silicate was added into a drilling fluid formulation applicable in high-pressure and high-temperature conditions, and the rheological characteristics and filtration properties were investigated. The results confirmed that drilling fluids with the addition of hybrid silicate can mitigate variation of viscosity and yield point before and after aging at 180 and 220 °C. Besides, the filtration behavior was also improved by adding hybrid silicate into the drilling fluid. A lower filtration loss was observed at the concentration of 1.0 wt % lithium silicate and 0.2 mol/L potassium methyl silicate, which showed 63 and 50% HPHT fluid loss reduction for unweighted and weighted formulations at 205 °C and 3.5 MPa, respectively. In addition, the drilling fluid featured stable rheological and filtration properties and excellent shale hydration inhibition characteristics when exposed to high temperatures, making it a promising candidate for drilling in deep oil and gas wells.

1. INTRODUCTION

Borehole stability is a great scientific and practical challenge in oil and gas exploration and production with increasingly complex geological conditions. As the “blood” of a drilling operation, drilling fluid has long been expected to play a pivotal role in transporting and suspending rock cuttings, cooling and lubricating drilling equipment, controlling subsurface pressure, minimizing fluid loss and lost circulations, and borehole stability.1,2 Although oil-based drilling fluids have many benefits, such as thermal stability and borehole stability in drilling water-sensitive shales, considering the requirements of easy preparation, environmentally friendly nature, and variable rheology, water-based drilling fluids are widely recommended.3,4 However, the critical issue of water-based drilling fluids that needs to be tackled is borehole instability, mainly related to shale hydration and dispersion.5,6 In particular, filtrate from water-based drilling fluid invasion of shale formations and the subsequent shale swelling are the leading causes of wellbore instability.

On the one hand, exploring shale inhibitors based on the aqueous solution, filtration reduction agents, and plugging materials is an effective method to minimize clay swelling. Thus, inorganic salts, such as KCl and CaCl₂, which can weaken the clay hydration via ion exchange,7 and organic compounds, such as oligomeric ether amines and polymeric quaternary amines, have been widely developed.8–11 In the meantime, synthetic and natural polymers,12–14 nanosized particles, are employed as filtration reduction agents by forming a thin layer of solids to prevent water invasion of the formation.15,16 However, in high-temperature drilling conditions, inorganic salts, degradation of the polymeric compounds, and desorption from the clay surface usually lead to a decrease in performance.17–19 In particular, for deep well or geothermal drilling operations, degradation of the
polymer filtration additives occurred at high-temperature downholes, inducing flocculation or dispersion of clay particles, resulting in significantly increased filtration loss. Thus, the additives with great inhibition and plugging property applied in harsh conditions are considered feasible solutions to address the wellbore stability.

On the other hand, forming a protective film on the shale surface is an alternative method. Thus, film-forming drilling fluids that can form a protective layer based on silicate have elicited great concern and been well demonstrated. Ninety years ago, silicates were first employed in water-based drilling fluids to reduce water penetration of fractures or water-out from the fractures into the oil production wells. Gelation and precipitation of soluble silicate come into contact once with multivalent cations \((\text{Ca}^{2+}, \text{Mg}^{2+}, \text{Al}^{3+})\) in formation water or slight acids.

Along with the chemical bonding of silica oligomers, with further gelation and precipitation of silicate colloid onto the surface of drill cuttings and formation, a protective layer can be formed. Localized gelation and precipitation can seal the microfractures, cracks, and rubbles in the formation to prevent the influx of the drilling fluid. The protective silicate drilling fluid has successfully drilled reactive shales despite the difficulties in controlling the rheology and filtration loss. Since the introduction of potassium ions and specific polymers by Wingraves’ group, drilling fluids containing inorganic silicate, with superior performance, optimum inhibition property, and great wellbore integrity, have been widely applied worldwide.

Generally, sodium silicate and potassium silicate were used in the silicate drilling fluid. Despite silicate-based drilling fluids having outstanding film-forming and plugging properties, the drilling fluids have drawbacks, such as poor compatibility, uncontrollable viscosity, and increased filtration loss, when they encounter high-temperature conditions, leading to decreased performance. Furthermore, considering the limitations of high viscosity and the lower stability of the SiO_2/M_2O mole ratio of sodium silicate and potassium silicate, a mole ratio lower than 3.3 is generally used to produce gels and precipitate silicas. Thus, there has been a greater emphasis on searching for nonconventional silicate-based drilling fluids.

Lithium silicate was proposed as an alternative solution to enhance the film-forming efficiency and overcome the above disadvantages. Compared to sodium silicate and potassium silicate, lithium silicate can form a stable, low-viscosity solution even at a high SiO_2/Li_2O mole ratio (up to 8.0). Besides, lithium silicate exhibits better film-forming performance at high temperatures and binding ability to various surfaces, which is preferred to sodium and potassium silicates in applications such as concrete surface treatment, specialty coatings, refractory, ceramics, and glazes. In addition, the properties of being waterproof, dry-wet cycle resistance, and self-curing make lithium silicate a promising and preponderant candidate as a film-forming agent.

However, owing to the high content of SiO_2, poor continuity and adhesion of the film formed by lithium silicate were usually reported. To improve the film quality and reduce the potential for efflorescence, a film formation accelerator is necessary. In this research, a water-soluble organic silicate, potassium methyl silicate (PMS), which is usually used as a waterproof reagent to impart water repellency to the building surface, was adopted as an auxiliary additive of drilling fluid for promoting film formation. Moreover, our previous studies showed that PMS exhibited excellent inhibition and film-forming property in water-based drilling fluids.

Also, there are rare reports on the performance of silicate-based drilling fluids at HPHT conditions. In this study, the hybrid silicate could react and form a quartz crystal film to prevent water intrusion into the formation and maintain the borehole stability using the high downhole temperatures. Due to their environment-friendly nature, low cost, excellent temperature resistance, inhibition, and interesting reactions in high-temperature environments, lithium silicate and potassium methyl silicate were demonstrated as film-forming agents in high-temperature drilling fluids. It is a valid approach to reduce water penetration into the formation through the porous structure. Therefore, promotion and use of this drilling fluid have prospects in the process of oil and gas extraction.

## 2. Experimental Section

### 2.1. Materials and Methods

#### 2.1.1. Materials

Sodium bentonite (Na-Bt) was obtained from Rongchang Mining Co., Ltd., P. R. China. Lithium silicate \((\text{SiO}_2/\text{Li}_2\text{O} = 4.8)\) was purchased from Yousuo Technology Co., Ltd., China. Methyl trichlorosilane was obtained from Shanghai Aladdin Bio-chemical Technology Co., Ltd., China. A modified procedure was used to synthesize potassium methyl silicate (PMS). Typically, 600 mL of 18 wt % hydrochloride solution was added into a three-necked bottle, and then 100 mL of methyl trichlorosilane was slowly dropped into the three-necked bottle. The mixture was then stirred for 2 h, and the temperature was kept at 30 °C with an ice bath. The precipitate, methyl silicon alcohol, was filtrated, washed with water three times, and then dried at 100 °C. Then, a 40 wt % potassium hydroxide solution was dropped slowly into the three-necked bottle, which contained dried methyl silicon alcohol. The reaction was kept at 80–90 °C for 2 h, and potassium methyl silicate solution was obtained.

Sulfonated lignite (SPNH), sulfonated asphalt, silicone polymer, sulfonate copolymer 1, and sulfonate copolymer 2 were obtained from Rongsheng Chemical Co., Ltd. (China) and Chevron Phillips Chemical Co., Ltd., and CaCO_3 (1000 mesh) and barite (BaSO_4) were obtained from Jiangxi Kote Fine Powder Co., Ltd., China. Potassium silicate \((\text{K}_2\text{SiO}_3)\), potassium hydroxide \((\text{KOH})\), potassium chloride \((\text{KCl})\), and sodium silicate \((\text{Na}_2\text{SiO}_3)\) were obtained from Sinopharm Chemical Reagent Co., Ltd., China. The mineral compositions of the shale cuttings used in the study are listed in Table 1, and montmorillonite accounts for 15% of the illite/smectite mixed layer.

| Mineral     | Content (%) | Relative content of clay minerals (%) |
|-------------|-------------|-------------------------------------|
| quartz      | 20.4        | illite                              |
| feldspar    | 10.6        | illite/smectite                      |
| dolomite    | 15.6        | chlorite                            |
| calcite     | 9.0         |                                     |
| analcime    | 18.5        |                                     |
| clay minerals | 25.9       |                                     |
| illite      | 51          |                                     |
| illite/smectite | 46       |                                     |
| chlorite    | 3           |                                     |

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2.2. Film Formation on the Shale Surface. Film-forming aqueous solutions were obtained by mixing PMS and lithium silicate (mSiO$_2$/nLi$_2$O = 4.8:1). Lithium silicate and PMS with different proportions were added to 400 mL of deionized water and stirred for 1 h. Then, 20 g of shale cuttings were added into the mixed silicate solutions and then transferred into aging cells, which were kept in a roller oven for 16 h at 150–220 °C. After cooling to room temperature, the shale cuttings were collected and dried in an oven for 5 h at 105 °C. Besides, the parameters concerned with film formation, such as the temperature, pH, run duration, ratio, and concentration of potassium methyl silicate and lithium silicate, were investigated. The optimum film-forming reaction parameters were obtained according to the cuttings’ hot-rolling recovery test.

2.3. Hot-Rolling Dispersion. A hot-rolling dispersion test (shale recovery) was used to obtain the optimum film-forming reaction parameters. Typically, 50 g of shale cuttings (size of 1.7–3.35 mm) was added into 350 mL of a hybrid silicate aqueous solution contained in an aging cell made of steel. The aging cell was rolled at 150, 180, and 220 °C for 16 h. Recovered shale cuttings (size larger than 380 μm) were washed with water and dried in a hot air oven for 5 h at a temperature of 105 °C to remove moisture. The shale cutting recovery (R) was calculated using the formula

\[ R = \frac{W}{50} \times 100\% \]  

where W is the weight of the recovered shale cuttings. The percentage of the recovered weight of shale indicates the inhibition ability of the aqueous solution.

2.4. Film-Forming Drilling Fluid Formulation. To apply the film-forming agents in high-temperature drilling fluids and verify their performance, a basic formulation containing sodium bentonite, filtration reducers, and a tackifier agent was introduced based on orthogonal array experiments by following the thermal and rheological stability and minimum filtration loss. Similarly, hybrid silicate-based drilling fluids were prepared with concentrations of 0.2 mol/L PMS and 1.0 wt % lithium silicate, and the compositions of drilling fluids are listed in Table 2.

Drilling fluids were prepared by the following steps:

1. Sodium bentonite was added into distilled water under stirring to form a suspension.
2. Then, the additives shown in Table 2 were added to the above suspension under stirring.

![Flowchart of the study.](https://doi.org/10.1021/acsomega.1c02725)
2.4.1. Rheology Test. Rheological parameters such as apparent viscosity (AV), plastic viscosity (PV), and yield point (YP) were measured according to the American Petroleum Institute (API) recommended practice using a rotational-type rheometer (ZNN-D6B). The drilling fluid was agitated at various shear rates starting from 3 to 600 rpm, and the shear stress was measured at each shear rate. According to the 300 and 600 rpm readings, the rheological parameters were calculated according to the Bingham plastic model by the following equations

\[
AV = \phi 600/2 \text{ (mPa-s)} \tag{3}
\]

\[
PV = \phi 600 - \phi 300 \text{ (mPa-s)} \tag{4}
\]

\[
YP = 0.511 \times (2 \times \phi 300 - \phi 600) \text{ (Pa)} \tag{5}
\]

2.4.2. Filtration Test. The filtration loss behavior was also studied following the API standard at 0.69 MPa and 25 °C using a ZNS 6A filter and at a high temperature and pressure (HTHP, 205 °C, 3.5 MPa) using the OFI testing equipment (OFITE), high-temperature high-pressure (HTHP) filter. In this test, the filtration cell was filled with 350 mL of drilling fluid and loaded in the filtration instrument. The filtrate was collected for 30 min at different time intervals. At the end of 30 min, the pressure was released, and the cake was collected.

In addition, the experimental flowchart of this study is shown in Figure 1.

3. RESULTS AND DISCUSSION

3.1. Characterization of Film Formation on the Rock Surface. 3.1.1. Morphology and Microstructure of the Film. Compared with severe hydration in water, the phenomena of shale swelling and hydration could be greatly suppressed by applying a silicate gelation process, which has been validated in previous research and field applications. But the inhibition characteristics of silicate at high temperatures have rarely been reported.

The optical photos of shale after hot-rolling at 180 °C in different aqueous solutions are shown in Figure 2. The specimens with invisible edges and smooth surfaces indicated that obvious hydration had occurred in water at 180 °C, which is consistent with the low shale recovery (Figure 2b). For the shale after hot-rolling at 180 °C in either lithium silicate or PMS, sharp corners and edges of the shale cutting can be observed, which indicated that the original shale cutting morphology was preserved and hydration of shale cuttings was reduced effectively (Figure 2c,d). Surprisingly, after hot-rolling in the hybrid silicate aqueous solution containing lithium silicate and potassium methyl silicate, a bright glassy film can be seen on the shale cutting surface (Figures 3b,d and 4b). Furthermore, clear edges and complete film coverage can be identified on individual particles. Therefore, it is inferred that as an effective shield, the close coating formed by hybrid silicate on the surface of shale cuttings can prevent water invasion into cuttings and thus reduce shale hydration. Although sodium or potassium silicate polymerization and gelation have been demonstrated within subterranean formations to plug cavities or pores and reduce fluid flow capacity, this is the first time that the shieldlike film was observed in the presence of potassium methyl silicate and lithium silicate.

Figure 3 shows the photos of shale cuttings after hot-rolling in a hybrid silicate solution of different concentrations at 180 °C. A white powder fell off the surface of the cuttings in the hybrid silicate solution with 0.2 mol/L PMS as the concentration of lithium silicate was increased from 0.5 to 3.0 wt %, as shown in Figure 3c,d, indicating poor compactness and weak film coating continuity. Besides, in the hybrid silicate solution with 0.5–1.0 wt % lithium silicate, dense and smooth thin coatings on the cuttings can be observed at the concentration of 0.2 mol/L PMS.

To further inspect the effect of temperature on film formation of hybrid silicate, hot-rolling at different temperatures was conducted. When the temperature is lower than 150 °C, there is no obvious film on the surface of cuttings, and even original edges and corners can be preserved. As shown in Figure 4, a film coating on the shale cuttings can be observed at a temperature higher than 150 °C; furthermore, the film thickness increased with the increase of temperature. A visible powder covering the cuttings can be seen after hot-rolling at 220 °C, and only a bright glassy film can be seen after hot-rolling at 180 °C.

Optical microscopy is used to observe the detailed information of the film on the shale cutting. In contrast to the rough surface of the original cuttings, a smooth and compact surface of the cuttings can be seen after hot-rolling in the hybrid silicate solution, and the clear boundary between the film and shale can be seen from the cross section (see Figure 5f), with the thickness of about 100 μm. Also, there are no cracks on the film, indicating that the film could be completely covered on the cuttings, which can greatly enhance the ability to prevent water invasion into the shale.

The features of the film including thickness and detailed microstructure were assessed using SEM that revealed interesting results (see Figure 6). The film formed on the surface of cuttings and glass microscope slides was examined. Clay minerals with a lamellar structure can be seen on the rough surface of the original cuttings, as well as pores formed by lamellar plate alternating stacking. After hot-rolling at 180 °C, the edges and corners of the sample can be clearly distinguished. The height of individual cuttings is reduced, which indicates that the cutting surface was deformed by the applied pressure. The cutting surface is smooth and uniform, and no cracks or pores can be observed. The lamellar plate of clay minerals is stacked vertical to the surface, and the thickness is about 100 μm, indicating that the film formed by hot-rolling at 180 °C could provide a barrier to prevent water invasion into the shale.
it can be seen that instead of lamellar clay minerals, the smooth film with lower porosity on the shale surface is composed of fibrous wires and a small number of spherical particles. As can be seen from Figure 6, fibers with a diameter of around 20 nm and a length of several micrometers were obtained. To eliminate the interference of minerals in cuttings with formation of the film, the surface of the glass slide after hot-rolling in the hybrid silicate was examined, which showed that the top-layer film was made up of cross-linked fibers and some even embedded in the rock pore.

In addition to the results discussed above, the characteristics of the film formed on the cuttings were affected by the aging temperature. It can be seen in SEM images, as given in Figure S1, that as the aging temperature increases, the diameter of the crystalline quartz fiber increases, which is consistent with the principle of temperature affecting the growth rate of crystals. The thickness of the film on the shale cuttings was 60–130 μm, which was confirmed by the cross-sectional view of SEM images (see Figure 7). It can be seen from the rock–film interface that the film was closely integrated with the shale.

Figure 3. Surface state of shale in hybrid silicate solution with different concentrations at 180 °C (a, 0.1 mol/L PMS + 0.5 wt % lithium silicate; b, 0.2 mol/L PMS + 0.5 wt % lithium silicate; c, 0.3 mol/L PMS + 0.5 wt % lithium silicate; d, 0.2 mol/L PMS + 1.0 wt % lithium silicate; e, 0.2 mol/L PMS + 2.0 wt % lithium silicate; and f, 0.2 mol/L PMS + 3.0 wt % lithium silicate).

Figure 4. Images of shale after hot-rolling in hybrid silicate solutions at different temperatures (1.0 wt % lithium silicate and 0.2 mol/L PMS; a, 150 °C; b, 180 °C; and c, 220 °C).

Figure 5. Optical microscopy images of the shale cutting surface at different magnifications (a, d, original shale; b, c, e, the film on the shale surface; and f, the shale cross section).
cutting surface, indicating that the cross-linked network could be embedded in the pore of the shale cutting and the film might be grown on the shale surface, and thus the obtained silica coating was wash-resistant and able to act as a protective shield.

3.1.2. Identification of the Film. To identify the film’s chemical composition formed in the hybrid silicate solution, XRD and FT-IR spectroscopy were used to analyze the original shale cuttings and the film formed on the cuttings at 180 and 220 °C. Although severe hydration of the cuttings can be observed after hot-rolling in water, the chemical composition and crystal structure of minerals are still maintained. As illustrated in X-ray diffraction patterns (see Figure 8a), it can be seen that peaks of the original shale cuttings and the cuttings after hot-rolling in water correspond to illite, calcite, analcime, quartz, dolomite, and feldspar. The XRD spectra of the shale after hot-rolling in the hybrid silicate solution with a concentration of 0.2 mol/L PMS and 0.5 wt % lithium silicate revealed enhanced sharp peaks corresponding to quartz.

Additionally, the diffraction peaks of the samples stripped from the surface of the cuttings and the slide can be assigned to quartz and are consistent with the JCPDS standard patterns of...
quartz and moganite (PDF Nos. 46-1045 and 52-1425). Diffraction peaks of 2θ at 26.64, 35.86, 45.25, 51.28, and 55.05 were assigned to quartz (see Figure 8b). We are convinced that the film formed on both the shale cuttings and the glass slides is crystalline silica polymorphs. The inhibition of silicate-based drilling fluid was usually attained at room temperature through the chemical bonding of silica oligomers with drilling cuttings or fracture surfaces, resulting in an amorphous silica layer or precipitation to reduce invasion of water into the formation. Although the hydrothermal preparation of crystalline silica from amorphous silica has been intensively studied, the preparation of crystalline silica films from hybrid silicates has been rarely reported. The crystalline silica film formed on the cutting surface in hybrid silicate at high temperatures shows superior hydration inhibition characteristics.

As organic species can be used to alter the dielectric constant of the solvent and accelerate silicate gelation, in this study, PMS was applied to form the crystalline silica film. To further analyze the composition of the film, FT-IR absorption spectra over the range of 4000–400 cm\(^{-1}\) of the original shale cutting, the film formed on the cutting, and the film formed on the glass slide are illustrated in Figure 9.

The broad bonds at 3430 cm\(^{-1}\) and the peak at 3623 cm\(^{-1}\) correspond to the stretching vibration of Si–OH and Si–O of the shale cutting and the film formed with hybrid silicate. The predominant absorbance peak at 1032 cm\(^{-1}\) is caused by Si–O–Si in shale cutting. The band at 916 cm\(^{-1}\) is due to the bending vibration of –OH in Al–Al–OH, and the absorption band of CO\(_3^{−2}\) is shown at 1453 cm\(^{-1}\), corresponding to dolomite in the shale. Additionally, other peaks such as those at 465, 520, and 792 cm\(^{-1}\) are due to the absorption bands of quartz. The dominant band at 1082 cm\(^{-1}\), shown in Figure 9b,c, is related to the stretching vibration of Si–O–Si of the crystalline silica, which confirmed the formation of crystalline silica. The peaks located at 2852 and 2923 cm\(^{-1}\) can be assigned to the symmetric and antisymmetric stretching vibration of C–H from the methyl of PMS, respectively. The peaks at 1384 and 1465 cm\(^{-1}\) can be attributed to the bending vibration of –CH\(_3\) of PMS, indicating that PMS has participated in the formation of the film layer and that the methyl groups of PMS exist on the surface of crystalline silica.

3.1.3. Film-Forming Mechanism. Crystallization from alkaline silica to quartz under hydrothermal conditions has been investigated for years. Generally, gelation from SiO\(_4\) monomer to chains, three-dimensional oligomers, and eventually polymers occurs by changing the pH or adding metal salts. As the solution SiO\(_2\)/Li\(_2\)O mole ratio is 4.8, three-dimensional oligomeric species could be the dominant component, which was used for the production of gels and precipitated silica colloids. Based on the previous study on the hydrothermal synthesis of quartz from amorphous silica, the possible reaction path is listed below as far as they occurred under hydrothermal conditions

\[
\text{Li}_2\text{O} \cdot n\text{SiO}_2 + (2\pi + 1)\text{H}_2\text{O} \rightarrow 2\text{LiOH} + n\text{Si(OH)}_4
\]  

(6)

\[
\text{Si(OH)}_4 \rightarrow \text{SiO}_2 \text{(colloidal silica)} + 2\text{H}_2\text{O}
\]  

(7)

\[
\text{SiO}_2 \text{(amorphous silica)} \rightarrow \text{quartz}
\]  

(8)

As shown in Figure 10, the possible mechanism of film formation with hybrid silicate on the shale surface is presented. First, lithium silicate was hydrolyzed in an aqueous solution, condensation of the SiO\(_4\) monomer species formed three-dimensional oligomers, and then thermal dihydroxylation of colloidal silica was carried out to form crystalline quartz. In the meantime, CH\(_4\)Si(OH)\(_2\)O participated in the formation of intermolecular reaction polymer chains and resulted in the formation of fibrous quartz due to the surface confinement effect of the –CH\(_3\) hydrophobic group.

SEM images of shale cuttings aged at 180 °C with different time intervals are presented in Figure 11 to provide insight into the crystallization process of aqueous hybrid silicate to quartz. The precipitated silica colloids can be observed on the cutting surface after aging for 6 h. Moreover, the crystalline fibrous
quartz can be seen after aging for 8 h. Furthermore, the compacted nanofibrous crystallized quartz was formed after aging for 10 h. Besides, XRD patterns confirmed that the crystallinity increased along with the aging time. As shown in Figure 12, no apparent enhancement of the peak of quartz can be observed for the sample collected from the shale cuttings, which was aged in the solution of 0.2 mol/L PMS and 0.5 wt % lithium silicate for 2 h. The strong diffraction peaks corresponding to crystallized quartz confirmed that the reaction required at least 6 h at 180 °C.

Figure S2 shows the status of different shale cuttings immersed in water for a month, and the results indicated that the shale cuttings without the film coating were completely hydrated, while the film-coated cuttings maintained the original morphology without hydration and dispersion. The film showed great water resistance, and the decrease of porosity of rock due to further matrix densification by condensation of a highly cross-linking network was also confirmed.

3.2. Shale Hydration Inhibitive Property of Hybrid Silicate. 3.2.1. Shale Dispersion Test. Inhibition of silicate-

Figure 10. Schematic mechanism to illustrate film formation through the hybrid solution on shale surface.

Figure 11. SEM images of the surface crystallization degree on the shale after reacting in the hybrid silicate solution at 180 °C at different time intervals (a, 0 h; b, 2 h; c, 4 h; d, 6 h; e, 8 h; f, 10 h; g, 14 h; and h, 16 h).

Figure 12. XRD spectra of the original shale cuttings and the film crystallized on the shale in hybrid silicate solution (a, 2 h; b, 6 h; c, 10 h; and d, 14 h).
based fluid is usually due to silicate gelation that results in inorganic silica polymer structures, forming a protective layer on the cutting and the well surface.

The shale cutting recovery test of shale was applied to evaluate the hydration inhibition ability of the hybrid silicate. As illustrated in Figures 13 and 14, the recovery rate of shale cutting in water after hot-rolling was observed in the hybrid silicate solution with the concentration of 0.2 mol/L PMS and 0.5−1.0 wt % lithium silicate, indicating better film formation instead of clay hydration. The above results depicted that the synergism of inorganic and organic silicate enhanced the film-forming reaction.

Moreover, the effect of the hot-rolling temperature on the recovery rate was also investigated. As shown in Figure 14, the recovery rate of shale cutting in water was about 20% (18.8−22.7% as the temperature rose from 150 to 220 °C). The recovery rate increased from 99.1 to 113.2% in the hybrid silicate solution with 0.2 mol/L PMS and 1.0 wt % lithium silicate as the hot-rolling temperature was increased from 150 to 220 °C, and a compact film covering on the cuttings can be observed as shown in Figure 4. This film coating formed in the hybrid silicate solution at a high temperature prevents hydration swelling and dispersion of shale cutting and causes the recovery rate to be higher than 100%. It is expected that the crystalline silica formed on the cutting surface can plug the pores in the formation and improve the integrity of the cutting.

Furthermore, both the original shale and the cuttings after aging in hybrid silicate were soaked in water, as shown in Figure S2. After only 30 min, the original cuttings hydrated severely and dispersed in water, while the film-coated cuttings, even after a month, were integrated and no hydration could be observed, which further showed that the surface film effectively prevented hydration and water invasion into the shale, and thus dramatically improved the inhibition property.

3.2.2. Clay Pellet Disintegration Test. To further investigate the inhibition property of the hybrid silicate solution, potassium chloride and other silicates, for instance, sodium silicate and potassium silicate, were used for comparison. As shown in Figure S3, the mud pellet, made of Na-bentonite, was immersed in different solutions at the concentration of 0.2 mol/L. The mud pellet swelled, and the clay particles dispersed in the water, but the mud pellets completely collapsed in KCl and potassium silicate solution within 2 h.

Although no significant hydration swelling of clay particles was observed, which can be attributed to the ion exchange between clay and potassium ions, water permeated into the mud pellet due to electrolyte concentration, resulting in the collapse of the mud pellet. The mud pellet in sodium methyl silicate also disintegrated, while the pellet in PMS solution showed low hydration swelling, and the original shape was maintained for 2 h. The results revealed that PMS could mitigate clay hydration swelling and effectively prevent water invasion into the interior of the mud pellet. To further evaluate the inhibition ability of the hybrid silicate aqueous solution, the mud pellet was immersed in a hybrid silicate solution with different concentrations. As exhibited in Figure 15, the mud pellet in water completely swelled due to intense hydration after 48 h. PMS showed a higher inhibition ability compared with lithium silicate at the same concentration, while when lithium silicate was added into PMS, the hydration swelling of the clay pellet was significantly reduced in hybrid silica
solution. There is no obvious hydration and collapse that can be observed in a mixture of 0.2 mol/L PMS and 0.5—1.0 wt % lithium silicate for 48 h.

As shown in Figure 16, the status of mud pellets removed from the solutions and dried at room temperature for 24 h can be observed. Slight spalling can be observed on the surface of the clay pellet that was soaked only in PMS solution while in 0.2 mol/L PMS with 0.5 wt % lithium silicate, there is no crack on the surface of the clay ball. On increasing the concentration of lithium silicate to 1.0 or 2.0 wt %, some cracks can be seen, and the clay ball’s shell was spalled. The K+ ions from PMS can be trapped in coordination cages composed of surface hexagons and water molecules in a smectite interlayer, which leads to the clay-swelling inhibition property. Furthermore, the methyl group of PMS can change the hydrophilic silicate layers into hydrophobic ones. The synergistic effect of PMS with lithium silicate led to a compact film on the surface, resulting in the original morphology being retained.

3.2.3. XRD Analysis on the d-Spacing of Clay Mineral. XRD patterns presented in Figure 17 display the d-spacing of the original clay minerals and hydrated clay in water and hybrid silicate with 0.2 mol/L PMS and 0.5 wt % lithium silicate for 24 h. As shown in Table 3, montmorillonite (Mnt) is the primary component of the clay minerals used for inhibition ability evaluation. The d_{(001)} spacing of Mnt increased from 1.52 to 2.19 nm after swelling in water and decreased from 1.52 to 1.42 nm in aqueous hybrid silicate. The results further confirmed the synergistic hydration inhibition ability of hybrid silicate.

3.3. Water-Based Film-Forming Drilling Fluid Formulation. To evaluate the performance of the hybrid silicate applied in a basic formula of high-temperature drilling fluid,
the variation of performance before and after hot-rolling was studied.

Considering the rheological and filtration properties of drilling fluids, it is vital to evaluate the variation in performance on adding hybrid silicate in the drilling fluid; thus, the rheology parameters, LPLT, and HPHT filtration loss before and after hot-rolling at high temperature (150, 180, and 220 °C) were demonstrated. Table 4 presents the measured rheological properties, AV, PV, YP, and filtration loss of the formulations with and without hybrid silicate before and after aging. As can be seen, the stable viscosities of the hybrid silicate-based drilling fluid formulations were retained after hot-rolling at high temperatures. Compared with the base drilling fluid formulation, the drilling fluid with the addition of hybrid silicate exhibited an obvious influence on the viscosity: the apparent viscosities of unweighted and weighted formulation (\(\rho = 1.66\) g/cm\(^3\)) were decreased by 40 and 38% before aging. The plastic viscosity and yield point were also decreased due to hybrid silicate in the formulations, though desirable rheological properties were retained. As the aging temperature increased, the API LPLT filtration loss of formulation without hybrid silicate decreased by 11 and 17.8% after aging at 150 and 180 °C, respectively. However, the viscosity drastically increased and led to high flow resistance. Furthermore, the API LPLT filtration loss increased by 51.8% after aging at 220 °C, while the viscosity decreased after aging at 220 °C, which could be attributed to polymer chain desorption from the clay particles or polymer degradation; then, flocculation of bentonite platelets occurred, which has been justified before. After adding hybrid silicate in formulation 1, the LPLT filtration volume slightly increased, which might be due to the presence of the electrolyte (K\(^+\) ions), and decreased by 36.5% compared to the control formulation after aging at 220 °C. The filtration volume was less than 5 mL after aging at 180 °C. At the same time, rheological properties were well maintained.

To understand the filtration characteristic at high temperature and pressure, the HPHT filtration test was performed at 3.5 MPa and 205 °C. The HPHT filtration volume of the base drilling fluid reached 38 mL/30 min, while after adding hybrid silicate (0.2 mol/L PMS and 1.0 wt % lithium silicate) into the fluid, the filtration loss decreased by 63% (14 mL/30 min).

Moreover, for the weighted formulation without hybrid silicate, the HPHT filtration volume was 24 mL, while it decreased by 50% to 12 mL with the addition of the hybrid silicate. Several factors, such as the thermal stability of additives and cake compressibility, affect the HPHT filtration performance. Generally, flocculation of bentonite platelets at higher temperatures is regarded as the main factor for the increase in the HPHT filtrate loss, which can also be confirmed by the loose filter cake presented in the following section. The HPHT test at 220 °C was not performed due to the limitations of the instrument’s capability; however, the data after aging implied that hybrid silicate has great potential to reduce the water influx into high-permeability formations.

Filter cake plays an essential role in stabilizing porous permeable formations, and it provides information on the performance of the drilling fluid. The prominent features of filter cakes, including thickness, compactness, and surface texture, affect the volume of filtrate. As shown in Figure 18, after aging at 220 °C, a loose and thick (about 8 mm) filter cake was obtained from the base formulation, while a dense and smooth filter cake less than 1 mm was observed once hybrid silicates were employed in the drilling fluid. Furthermore, after being dried in air for 72 h, the filter cake of the base formulation was wrinkled and fractured, and a smooth and compact morphology was maintained after adding hybrid silicate. The microstructure of the dried filter cakes was demonstrated by SEM, as shown in Figure 19. There are many micrometer-sized pores in the filter cake of the drilling fluid without hybrid silicate, and lamellae and stacks of bentonite can be seen on the surface. Once hybrid silicate was added, a smooth and compact surface indicated that the pores were plugged with nanosized particles formed by hybrid silicate during the hot-rolling process. Moreover, it suggests that the improved quality filter cake was attributed to the reduction of HPHT filtrate loss.

| mineral | content (%) | the relative content of clay minerals (%) |
|---------|-------------|-----------------------------------------|
| quartz  | 12.1        |                                         |
| feldspar| 4.9         |                                         |
| calcite | 5.2         |                                         |
| clay minerals | 76.5 | montmorillonite 97 |
|          |             | chlorite 3                               |

Table 3. Compositions of Clay Minerals Used for Inhibition Ability Evaluation

Table 4. Properties of Drilling Fluid with and without Hybrid Silicate before and after Aging at Different Temperatures**

| formula | \(\rho\) (g/cm\(^3\)) | aging temperature (°C) | AV (mPa·s) | PV (mPa·s) | YP (Pa) | FL\(_{API}\) (mL) | shale recovery (%) | FL\(_{HPHT}\) (mL) |
|---------|------------------------|------------------------|-------------|-------------|--------|----------------|-------------------|--------------------|
| 1       | 1.03                   | 25                     | 75.0        | 60.0        | 125.0  | 4.5            | 18                | 38                 |
| 1       | 1.03                   | 150                    | 145.0       | 120.0       | 205.0  | 5.0            | 18                | 38                 |
| 1       | 1.03                   | 180                    | 180.0       | 150.0       | 180.0  | 5.0            | 18                | 38                 |
| 1       | 1.03                   | 220                    | 78.5        | 60.0        | 125.0  | 95             | 18                | 38                 |
| 1-H     | 1.03                   | 25                     | 45.0        | 30.0        | 75.0   | 4.5            | 18                | 38                 |
| 1-H     | 1.03                   | 150                    | 145.0       | 120.0       | 205.0  | 5.0            | 18                | 38                 |
| 1-H     | 1.03                   | 180                    | 180.0       | 150.0       | 180.0  | 5.0            | 18                | 38                 |
| 1-H     | 1.03                   | 220                    | 78.5        | 60.0        | 125.0  | 95             | 18                | 38                 |
| 2       | 1.66                   | 25                     | 97.0        | 72.0        | 125.0  | 4.5            | 18                | 38                 |
| 2       | 1.66                   | 150                    | 145.0       | 120.0       | 205.0  | 5.0            | 18                | 38                 |
| 2-H     | 1.66                   | 180                    | 180.0       | 150.0       | 180.0  | 5.0            | 18                | 38                 |
| 2-H     | 1.66                   | 220                    | 78.5        | 60.0        | 125.0  | 95             | 18                | 38                 |

**Note: \(\rho\), AV, PV, and YP refer to the density, apparent viscosity, plastic viscosity, and yield point, respectively. FL\(_{API}\) refers to the filtration of the drilling fluid at 0.69 MPa and 25 °C, and FL\(_{HPHT}\) refers to the filtration of the drilling fluid at 205 °C and 3.5 MPa.
4. CONCLUSIONS

In this study, a hybrid silicate containing inorganic and organic silicate was introduced as a film-forming agent that can be applied in water-based high-temperature drilling fluids for improving well stability. Hybrid silicate containing high-molar-ratio lithium silicate (SiO$_2$/Li$_2$O = 4.8:1) and water-soluble potassium methyl silicate was employed for the first time as a drilling fluid inhibitor by forming a film on shale.

The following conclusions can be drawn.

(1) The fibrous crystalline quartz film, with a thickness of 60–130 μm, can be formed on the shale surface in the presence of hybrid silicate at a temperature higher than 150 °C. The film features and shale recovery rate were greatly influenced by the concentration and proportion of lithium silicate and potassium methyl silicate and the aging temperature.

(2) Higher than 100% shale recovery was achieved due to the film formed by hybrid silicate at high temperatures, and the clay pellet disintegration test verified synergistic inhibition effects of the inorganic and organic silicate.

(3) The addition of hybrid silicate into a base HTHP drilling fluid can mitigate variation of viscosity and the yield point before and after aging at 180 and 220 °C. A lower filtration loss can also be observed by adding 1.0 wt % lithium silicate and 0.2 mol/L potassium methyl silicate into the base HTHP drilling fluid, and 63 and 50% HPHT fluid loss reduction for unweighted and weighted formulations (205 °C, 3.5 MPa) can be obtained, respectively.

(4) It can be speculated that hybrid silicate would be a promising candidate for developing high-performance drilling fluids that can be applied at high-temperature, high-permeability formations.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c02725.

SEM images of the film formed on the shale surface at various temperatures; status of dried shale cuttings immersed in water for 1 month; and status of clay pellets immersed in different inhibitor solutions after 2 h (PDF)

AUTHOR INFORMATION

Corresponding Author
Mingyi Guo – College of Construction Engineering, Jilin University, Changchun 130021, China; orcid.org/0000-0002-3465-4585; Email: guomingyi@jlu.edu.cn

Authors
Ying Li – College of Construction Engineering, Jilin University, Changchun 130021, China
Maosen Wang – College of Construction Engineering, Jilin University, Changchun 130021, China
Xianfeng Tan – Faculty of Engineering, China University of Geosciences, Wuhan 430074, China; Lunan Geo-Engineering Exploration Institute, Shandong Province, Jining 253015, China
Yinghui An – College of Construction Engineering, Jilin University, Changchun 130021, China
Huanan Liu – School of Prospecting and Surveying, Changchun Institute of Technology, Changchun 130012, China
Ke Gao – College of Construction Engineering, Jilin University, Changchun 130021, China

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.1c02725

Notes
The authors declare no competing financial interest.

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