Study of a Polyamine Inhibitor Used for Shale Water-Based Drilling Fluid

Yuexin Tian, Xiangjun Liu, Pingya Luo, Jinjun Huang, Jian Xiong, Lixi Liang, and Wenfei Li

ABSTRACT: Here, we report a water-soluble shale inhibitor for inhibiting shale hydrate formation. The copolymer denoted as thermogravimetric analysis (TGA) was synthesized via triethanolamine, two maleic anhydrides, and glacial acetic acid. The infrared (IR) and gas chromatography (GC) results indicated that TGA is a low molecular weight polymer inhibitor (IR) and is the most commonly used method to identify compounds and molecular structures qualitatively. It is mainly used to study the molecular structure of organic substances and conduct qualitative and quantitative analyses of organic compounds. The main function of GC is for polymer molecular weight analysis. With the aid of shale rolling recovery experiments, particle size distribution experiments, triaxial stress experiment methods, bentonite slurry rate inhibition experiments, and thermogravimetric experiments to evaluate TGA inhibition characteristics, the inhibition effect of TGA is better than that of the traditional inorganic salt inhibitor KCl, polymer amine inhibitor UHIB, and organic cationic shale inhibitor NW-1. When the mass fraction is 0.2%, the cutting recovery rate increases from 18.3 to 94.1%. The compressive strength of the shale core after adding 1% TGA inhibitor is 177.9 MPa, which is close to the original core compressive strength of 186.5. The wet sodium montmorillonite crystal layer spacing after treatment with 0.5%, 1.5%, and 3% TGA aqueous solution is 1.38, 1.35, and 1.35 nm, respectively, and the sodium montmorillonite crystal layer spacing after diesel treatment is 1.34 nm, indicating that the inhibitory effect of TGA on sodium montmorillonite is equivalent to that of diesel and that TGA can effectively inhibit the hydration and dispersion of sodium montmorillonite. At the same time, the crystal layer spacing and the weight loss rate of sodium montmorillonite modified by TGA inhibitors did not change significantly after adsorption of deionized water, which proved that TGA inhibitors could be adsorbed in the crystal layer space of sodium montmorillonite to inhibit hydration and dispersion of sodium montmorillonite. Field test results show that TGA can significantly improve the inhibition performance of the field drilling fluid, and the effect is better than the strong conventional inhibition water-based drilling fluid system, which solves the problems of wellbore instability and considerable friction in horizontal shale sections and provides a new idea and method for efficient shale gas drilling.

INTRODUCTION

With the increase in world energy demand and the development of drilling technology, the drilling depth is increasing, drilling formations are becoming increasingly complex, and mud shale instability caused by the stability of the well wall is particularly prominent,

which often causes significant difficulties to safe, high-quality, fast, and efficient drilling and puts forward higher requirements for drilling fluid technology. The developed high-performance polyamine water-based drilling fluid system solves the problem of safe drilling in shale formations and successfully replaces expensive and polluting oil-based drilling fluids. The key to developing a high-performance polyamine water-based drilling fluid system is the study of shale hydration inhibitors. It is of great significance for developing high-performance water-based drilling fluids to develop a polyamine inhibitor with excellent inhibition performance and establish a systematic method to analyze the action mechanism of polyamine inhibitors.
At present, the most widely studied chain-like polyamine inhibitors are widely used. They mainly include low molecular weight polyether amines, polyether amine derivatives, or their mixtures. Chain-like polyamine inhibitors are positively charged when exposed to water and adsorb on the negatively charged clay surface by electrostatic and hydrogen bonds. They can exchange hydrated cations between clay minerals and provide multiple amine groups for simultaneous multipoint single-point reactions. The layer adsorbs on the clay surface, effectively inhibiting the adjacent layers of adjacent clay and forming a dense structure.1,13

Hou et al.14 catalyzed polyols and then passed ammonia gas to obtain polymer intermediates containing ether bonds. Under high-temperature conditions, C–C and C–N were used to replace ether oxygen groups to obtain a light brown liquid and named JY-2. Jie et al.15’s performance studies on JY-2 inhibitors show that the introduction of C–C and C–N in the main chain can improve the temperature resistance of the inhibitor. It can maintain good abilities to inhibit hydration and dispersion. Zhang et al.16 catalyzed low molecular weight polymerized alcohol, introduced ammonia gas, and modified it to prepare a light yellow viscous liquid—JAI. The results show that the most apparent characteristic of JAI is that the ether bond can fully enter the interlayer of clay to compress the interlayer spacing. The inhibition of JAI is relatively stable at 93–200 °C in alkaline environments, and it does not need to add other alkaline regulators.

Zhong et al.17 prepared a high-performance polyamine inhibitor by the polymerization reaction of polyether diamine and ethylene oxide and named it SDJA-1. Research on its performance shows that SDJA-1 exhibits strong inhibition in a high-temperature environment of 200 °C. In the shale rolling recovery experiment at 77 °C, the decrease of the third recovery rate is small (54−59.7%), which indicates that the adsorption on the rock surface is very firm, and the action time is long. While ensuring its inhibition, SDJA-1 does not cause performance changes due to incompatibility with anionic treating agents, and it has good compatibility with various types of treating agents.

Wang et al.18 synthesized a new shale inhibitor, LM-1, from small-molecule organic amine (HLA-3), 2-acrylamido-2,2-methylpropanesulfonic acid (AMPS), and dimethyldiallylammonium chloride (DMDAAC). When the mass fraction of LM-1 is 2.0%, the rolling recovery rate of drilling cuttings can reach more than 90%. After adding bentonite to the LM-1 aqueous solution, the dynamic shear force is small, indicating that LM-1 has a good suppression performance; before the temperature reaches 350 °C, LM-1 has no significant thermal degradation and has good thermal stability; LM-1 has good salt resistance and can adapt to drilling operations in high-salt reservoirs.

Wang et al.19 used diethylenetriamine and epichlorohydrin as raw materials to synthesize hydroxylamine shale inhibitors by reacting the hydrolyzed products of epichlorohydrin under acid with diethylenetriamine. When the addition amount of the inhibitor was 1%, the inhibitory effect of this shale inhibitor was similar to that of the foreign inhibitor ULTRAHIB and had a better inhibitory performance. At the same time, the inhibitor had good compatibility with the drilling fluid system and had little effect on the rheological properties of the drilling fluid system, and to a certain extent, it reduced filtration at normal temperature and pressure.

In this paper, a new shale inhibitor, thermogravimetric analysis (TGA), was synthesized with triethanolamine, maleic anhydride, and glacial acetic acid as monomers. Compared with conventional shale inhibitors, TGA can exert a long-term inhibitory effect at low concentrations. Its inhibitory performance was evaluated in the laboratory, its inhibitory mechanism was analyzed, and field tests were conducted. The field test results show that the TGA inhibitor can significantly improve the inhibition performance of field drilling fluid, solve the problems of wellbore instability and large friction in horizontal shale sections, and provide a powerful technical guarantee for safe and efficient drilling of horizontal shale gas wells.

### EXPERIMENTAL SECTION

**Materials.** Triethanolamine (analytical grade), maleic anhydride (analytical grade), and glacial acetic acid (analytical grade) were used.

**Synthesis of Copolymer TGA.** Triethanolamine (78 g) and maleic anhydride (213 g) were added to a four-necked flask with a serpentine condenser, a stirrer, and a thermometer in proportion at room temperature, and the flask was placed in a constant temperature oil bath. The temperature was initially raised to 50–60 °C, which could promote the esterification reaction. After holding for 30 min, the system was heated to 160 °C, and the polymerization of esterification products was started. After the temperature reached the standard, the polymerization reaction started for 5 h. At the same time, because the polymerization of maleic anhydride and triethanolamine was ring-opening polymerization, to avoid water in the system, the water molecules in the system were extracted by vacuum. A vacuum pump was used to keep the pressure in the flask and stirred at 20 mmHg. After polymerization, a certain amount of glacial acetic acid and water was added to the cooling system to approximately 100 °C and stirred for 0.5 h to obtain a certain concentration of the shale inhibitor TGA, with the appearance of a pale yellow viscous liquid. The reaction mechanism was as follows: see Figure 1.

![Figure 1. Reaction mechanism equation.](https://doi.org/10.1021/acsomega.1c01936)

**Characterization of Copolymer TGA.** An appropriate amount of TGA inhibitor product was taken for purification. A certain amount of dilute hydrochloric acid was added into the system, and the incomplete triethanolamine was removed by the reaction of triethanolamine with an inorganic acid. Then, the product was dried in a 105 °C oven to remove HCl and water. After purification, the synthesized TGA inhibitor was analyzed by a WQF-510 FTIR (Beijing Beifen Rayleigh Analytical Instrument Company, resolution 2 cm⁻¹, scanning range 4500–450 cm⁻¹).

**Determination of Molecular Weight.** TGA solution was added to make a 10 mg/mL solution under the condition of a highly pure water mobile phase and a flow rate of 0.8 mL/min. The solution was first ultrasonicated for 30 min at room temperature and then allowed to stand for 3 h to make it fully dispersed. After shaking well, the solution was centrifuged at
5000 r/min for 15 min, and the supernatant was taken to measure its molecular weight by gel chromatography (Alliance e2695, Waters, USA).

**Biological Toxicity Analysis.** TGA inhibitor solution (1.0%) was prepared, and its biotoxicity was determined by a DXY-2 biotoxicity tester (manufactured by the Institute of Soil Science, Chinese Academy of Sciences) according to the standard “GB/T15441-1995 Water Quality Determination of Acute Toxicity of Luminescent Bacteria”.

**Shale Rolling Recovery Experiment.** The shale rolling dispersion experiment was used to evaluate the inhibitor’s hydration and dispersion performance. The cuttings used were taken from the Longmaxi Formation in Weiyuan, Sichuan. Fifty grams of 6–10 mesh dry rock cuttings were added to an aging tank containing 350 mL of 1% inhibitor solution, sealed, and put into a roller furnace for aging (at 77 ± 5 °C for 16 h). After hot rolling, the liquid and rock cuttings were removed and cooled, poured into a 40 mesh standard sieve, wet sieved with tap water for 1 min, dried in a constant temperature drying oven at (105 ± 3) °C for 4 h, removed from the air, and weighed after 24 h. The method was used to determine the mass of the residual rock sample after hot rolling in 350 mL tap water. The rolling recovery rate of cuttings is calculated according to formula 1.

\[ R = \frac{m_2 - m_1}{m_1} \times 100 \]  

where \( R \) is the shale recovery rate, \% \( m_1 \) is the recovered rock sample mass in clean water, \( g \) and \( m_2 \) is the recovered rock sample mass in sample solution, \( g \).

**Particle Size Distribution Experiment.** The particle size distribution is generally used to characterize the inhibitory effect of inhibitors microscopically. A laser particle size analyzer (HODIBA/LA-950A) was used to test the particle size distribution of the prepared bentonite suspension containing a specific concentration of inhibitor. The experiment compared the effect of three inhibitors on the particle size distribution of bentonite at different concentrations. First, the power of the instrument was turned on and warmed for 1 h to ensure that the instrument was stable. At the same time, 100 mL of deionized water was measured, and different mass fractions of inhibitor materials were added (the mass fractions of inhibitors studied in this paper were 1.5% and 3%) and stirred until the materials were fully dispersed. Then, the sample cell was cleaned three times, an empty sample of inserted, the cycle speed to 15 gears was set, and the stirring speed to 15 gears, and clicked to correct. When the red light beam and blue light beam reached 100%, the sample was added until the red light, and blue light reached the measurable range. The click measure after the diameter distribution graph is stable. Before the test, a 4% bentonite-based slurry was prepared, stirred, and prehydrated for 24 h, and then TGA at different doses was added. After full stirring for 24 h, the particle size distribution of the above suspension system was measured by a HODIBA/LA-950A laser particle size analyzer.

**Bentonite Flake Test.** A 4% sodium montmorillonite slurry containing 3% TGA inhibitor was prepared and stirred at high speed for 30 min. After standing for 24 h, the suspension was poured onto a 200 mesh sieve, washed with a solvent, and then dried at 105 °C for 4 h to prepare sodium montmorillonite tablets with a thickness of less than 5 mm. After drying, tweezers were used to remove the dried sodium montmorillonite flakes on the screen. A scanning electron microscope was used to photograph the nonscreen contact surface of the sodium montmorillonite flakes to observe the surface morphology of the sodium montmorillonite flakes under different concentrations of inhibitors.

**Inhibition of Bentonite Pulping Experiment.** An aqueous solution of 1% of the three inhibitors TGA, UHIB, and NW-1 was prepared with pure water, and then a certain amount of bentonite was added to the solution, which was stirred at high speed for 60 min to make it a 4% bentonite suspension. The prepared soil slurry was put into an aging kettle and aged in a roller heating furnace at 120 °C for 16 h. After aging, it was cooled to room temperature, and its apparent viscosity was tested with a six-speed rotary viscometer.

\[ \text{Apparent viscosity change rate} = \frac{AV_0 - AV}{AV_0} \times 100\% \]  

where \( AV_0 \) is the apparent viscosity of blank sample, mPa·s; \( AV \) is the apparent viscosity of inhibitor-modified soil, mPa·s; and apparent viscosity change rate is the ratio of the difference between the viscosity of the soil slurry before and after adding the inhibitor to the viscosity of the soil slurry before adding the inhibitor.

**Triaxial Stress Test.** The core at 2380 m of a well in the Longmaxi Formation in the Weiyuan area of Sichuan was made into core columns with a specification of 2.5 cm × 5 cm. The cores were immersed in aqueous solutions with different concentrations of inhibitors for 24 h, and then the core bearing capacity was tested by an RTR-1000 triaxial rock mechanics testing system.

**Zeta Potential Analysis.** Inhibitors with different concentrations were added to the 4% bentonite suspension, stirred for 30 min, closed, and incubated for 24 h. Then, the zeta potential of the bentonite suspension was measured by a ZetaProbe potential-particle size analyzer (produced by American CD Company).

**Thermogravimetric Analysis.** The interlayer water content of montmorillonite is an important indicator of clay hydration. Similarly, in this research, replacing sodium bentonite with shale powder can more intuitively reflect the water-repellent effect of inhibitors.

The suspension containing a specific inhibitor concentration was prepared with 200–300 mesh shale powder, stirred at high speed for 30 min, incubated for 24 h, and centrifuged for separation. The supernatant liquid was poured out, and the lower cuttings were washed with deionized water three times, dried at 105 °C for 16 h, and sieved through 200 mesh to obtain bentonite after TGA treatment. A thermogravimetric analyzer was used for thermal differential analysis (Labsys EVO model of Setaram, France, the atmosphere was nitrogen, and the heating rate was 10 °C/min).

**X-ray Diffraction Analysis.** 4% sodium montmorillonite suspension was prepared; 0.5%, 1.5%, and 3% TSA were added; diesel oil and water were added at the same time for comparison; high speed stirring for 30 min, after standing for 24 h, centrifugation was performed; the supernatant was poured out; the lower layer montmorillonite was directly taken at (23 ± 2) °C for X-ray diffraction (XRD) analysis; and crystal layer spacing (wet state) was measured. After the wet montmorillonite interlayer spacing test, all samples were dried at 80 °C for 16 h and then dried montmorillonite was analyzed by dry XRD at (23 ± 2) °C to determine the interlayer spacing (dry state) of montmorillonite.
Soaking Experiment of Bentonite Mud Cake. A certain amount of sodium bentonite was taken and dried at 105 °C for 4 h. Then, 10 g of sodium bentonite was placed in a steel cylinder of a specific size with filter paper at the bottom. The bentonite was pressed for 5 min with a tablet press under a constant pressure of 10 MPa. After pressing, the bentonite mud cake was removed and placed in the center of a 90 mm Petri dish for use. Two hundred milliliters of an aqueous solution of various inhibitor concentrations were poured into the Petri dish slowly along the edge. After pouring, start timing. After soaking for 2 h and 24 h, images were taken with mobile phones. When taking images, the Petri dish and the square frame should be cut inside as far as possible to ensure the same size standard as far as possible.

RESULTS AND DISCUSSION

Characterization of Copolymer TGA. Figure 2 shows the infrared (IR) spectrum of the TGA inhibitor and the strong and broad absorption peak produced by −OH stretching vibration at 3420 cm\(^{-1}\). The absorption peaks at 2955 and 2856 cm\(^{-1}\) are derived from the antisymmetric stretching vibration and symmetric stretching vibration of C−H bond in −CH\(_2\), and 1690 cm\(^{-1}\) is the absorption peak produced by the stretching vibration of C=O and C=C. The peak at 1550 cm\(^{-1}\) is the absorption peak of the in-plane bending vibration of amine N−R, and 1300−1400 cm\(^{-1}\) is the in-plane bending vibration of CH on organic acid.

Molecular Weight of TGA. The results are shown in Figure 3 and Table 1.

As shown in Figure 3 and Table 1, the highest peak molecular weight of TGA was 1370, the number-average molecular weight was 1175, and the weight-average molecular weight was 1400. It can be judged that the molecular weight of the synthesized product is basically in line with the design principle of the inhibitor molecular structure.\(^{20}\)

| Mn  | M\(_{\text{w}}\) | M\(_{\text{p}}\) | M\(_{\text{z}}\) | M\(_{\text{z}} + 1\) |
|-----|--------------|--------------|--------------|-----------------|
| 1175| 1400         | 1370         | 1642         | 1914            |

Figure 2. TGA inhibitor IR spectra.

Figure 3. TGA autoscale chromatogram.
**Biological Toxicity of TGA.** The test results are shown in Table 2.

According to the average value of the relative luminous intensity corresponding to each concentration of the measured result, the unitary linear regression equation fitting the average relative luminous intensity and concentration is \( T = 106.41277 - 0.00122C \).

Substituting \( T = 50 \) into the equation, the calculated EC50 \( \approx 50,041 \text{ mg/L} \), that is, the EC50 of 1.0% TGA solution = 50,041 mg/L. According to the biological toxicity classification standards of oilfield chemicals and drilling fluids in Table 3, 1.0% TGA solution is nontoxic (see Table 4).

**Shale Rolling Recovery Experiment.** Shale rolling dispersion results are shown in Figure 4. Figure 4a shows that the inhibitor TGA shows excellent inhibition performance. When the mass fraction was 0.2%, the cutting recovery rate increased from 18.3 to 94.1%, and the recovery rate did not change much with increasing inhibitor mass fraction. The recoveries when the dose was 1.5 and 3% (mass percentage concentration) were 95.12 and 96.04%, respectively. Under the effect of the same organic amine inhibitor concentration, the first-time recovery rate of TGA was the highest. At the same time, under the same experimental conditions, the one-time recovery rate after mixing with 7% KCl and 3% UHIB was 83.6%. The results show that the TGA inhibitor has a good effect in inhibiting shale hydration and dispersion at low mass fractions, and its inhibition is better than that of the traditional inorganic salt inhibitor KCl and polyamine inhibitor.

Comparing Figure 4a,b, it can be found that with the increase of test times, the recovery rate of cuttings treated by NW-1 and UHIB gradually decreases. In contrast, the secondary recovery rate of cuttings treated by TGA is more than 99% compared with the first-time recovery rate of the same concentration, indicating that the inhibitor has stable and firm adsorption on the surface of cuttings, is not easy to desorb, and has longer effective action time. NW-1 is the common name of glycidyl trimethyl ammonium chloride as a cationic shale inhibitor; UHIB is a kind of organic cationic amide polymer complex that is copolymerized by the cationic monomer dimethylallylammonium chloride and acrylamide monomer. It has an affinity and can adsorb with many substances (can play the role of "charge neutralization" and "adsorption bridge" for negatively charged particles in water).

**Particle Size Distribution Experiments.** The experimental results of the particle size are shown in Figure 5.
Figure 5 shows the particle size distribution of the 4% bentonite-based slurry after adding different amounts of TGA. The results show that the 4% bentonite-based slurry has a multipeak distribution in the range of 0.1−100 μm, a narrow and sharp single peak distribution in the range of 0.1−1 μm, and the remaining two broad peaks in the range of 1−100 μm. The median particle size and average particle size of the 4% blank base slurry are 1.84671 and 5.64710 μm, respectively. When the TGA concentration was increased to 0.5%, the peak height in the range of 0.1−1 μm decreased gradually, the two peaks in the range of 1−100 μm merged into one peak, and a slightly prominent peak appeared at approximately 100 μm. At this time, the median particle size D50 and average particle size were 5.71874 and 8.97673 μm, respectively. Compared with the base slurry, the effect of inhibiting the hydration and dispersion of bentonite particles is not apparent. With increasing TGA concentration, the particle size distribution of bentonite began to change significantly. The height of a single peak in the range of 0.1−1 μm began to decrease significantly, and a relatively high peak and a relatively low peak appeared in the ranges of 10−100 and 100−3000 μm, respectively. As the TGA concentration increases from 1.0 to 3.0%, the peak height within 0.1−1 μm decreases, and the relatively low peak height within 100−3000 μm increases. The above phenomenon shows that the addition of TGA reduces the number of small bentonite particles and increases the number of large bentonite particles. The essence is that TGA effectively uniformly adsorbs on the surface of the bentonite particles at multiple points to inhibit their dispersion.

**Bentonite Flake.** From Figure 6, we can see that the particle morphology of sodium montmorillonite has changed greatly. From the scanning electron microscopy (SEM) images of sodium montmorillonite-based slurry, it can be seen that the
hydration degree of sodium montmorillonite is severe. There is a bright hydration shell on the surface, and no apparent particles can be observed under the low-power microscope. However, only a small amount of hydration shell on the surface of sodium montmorillonite particles was modified by a 3% TGA inhibitor.

At low magnification, uniform and regular particles can be seen. On the other hand, comparing the electron micrographs of the clay sheet treated with the TGA inhibitor with those of the untreated clay sheet, it is found that when the electron micrograph light irradiates the surface of the clay sheet due to the severe hydration of the untreated clay, the surface of the clay sheet is relatively smooth, with low convexity and concavity, weak stereoscopic sense, and poor imaging.

Comparing the surface morphology of the inhibitor clay sheet observed by SEM with the strength test results of shale core, it is found that the severe hydration of clay, affected by the expansion stress, reduces the cementation degree of shale, resulting in the change of rock mechanical properties and the decrease of compressive strength. In contrast, if clay hydration can be well restrained, the reduction in shale compressive strength can be controlled, and the wellbore can be stabilized during drilling. The above results show that the clay slice microscanning method is an effective and feasible method to evaluate the effect of inhibitors.

Inhibition of Bentonite Pulping Experiment. The experimental results show that the three inhibitors have a certain improvement effect on the rheology of the base slurry, and the changes are significant. Compared with inhibitors UHIB and NW-1, TGA inhibitors have the best effect on the rheology control of bentonite, and the apparent viscosity change rate reaches 90%. This shows that TGA can better inhibit the bentonite slurry rate and make the drilling fluid system easier to maintain.

Triaxial Stress Test. The results are shown in Table 5.

Table 5 shows that the core shows good compressive strength before soaking, and the compressive strength reaches 186.5. After soaking with clean water, the compressive strength of the core decreases significantly to only 114.7 MPa, indicating that serious hydration occurs inside the core, and the compressive strength decreases by 38.5% due to hydration expansion inside the core (Figure 7). After adding 1% inhibitor TGA, the compressive strength of shale core is 177.9 MPa, which is higher than that after soaking in clean water and other three kinds of treatment agents (the concentration gradient of KCl shows that the compressive strength of shale core is positively correlated with KCl concentration), which is close to the compressive strength of the original core, indicating that TGA has not only excellent inhibitory effect on the hydration of clay but also has an outstanding effect on the improvement of the strength of shale rock. The effect is better than the amine inhibitors UHIB, NW-1, and KCl.

Zeta Potential Analysis. DLVO theory can be used to judge the stability of this complex colloid. The stability of the colloidal system is determined by the attraction and repulsion between the colloidal particles, while the repulsion of the colloid is controlled by the zeta potential. The greater the absolute value of the zeta potential of the clay particles, the higher the dispersion of the colloidal system and the more stable the system. In addition, the study by Lin et al.21 showed that reducing the charge contained in the clay layer by 20% can make clay minerals insensitive. The organic amine inhibitors are partially dissociated into −NRiesz groups and OH− groups in water so that the solution is weakly alkaline. Generally, the isoelectric point is −15454

![](https://doi.org/10.1021/acsomega.1c01936). Copyright 2020.

**Table 5. Triaxial Experimental Results after Soaking in Different Inhibitor Solutions**

| core status              | confining pressure/MPa | temperature/°C | Poisson’s ratio | elastic modulus/MPa | stress value/MPa |
|-------------------------|------------------------|----------------|-----------------|---------------------|-----------------|
| the original water      | 25                     | 80             | 0.273           | 17,469.2            | 186.5           |
| 0.5% TGA solution       | 25                     | 80             | 0.364           | 13,471.3            | 114.7           |
| 1% TGA solution         | 25                     | 80             | 0.392           | 17,143.4            | 169.8           |
| 3% TGA solution         | 25                     | 80             | 0.257           | 17,250.0            | 179.1           |
| 0.5% NW-1 solution      | 25                     | 80             | 0.376           | 16,849.1            | 152.1           |
| 1% NW-1 solution        | 25                     | 80             | 0.443           | 17,158.4            | 158.9           |
| 3% NW-1 solution        | 25                     | 80             | 0.317           | 14,350.4            | 162.7           |
| 0.5% UHIB solution      | 25                     | 80             | 0.351           | 15,741.7            | 130.7           |
| 1% UHIB solution        | 25                     | 80             | 0.289           | 16,846.3            | 153.3           |
| 3% UHIB solution        | 25                     | 80             | 0.371           | 13,214.0            | 149.6           |
| 1% KCl solution         | 25                     | 80             | 0.402           | 14,792.5            | 143.4           |
| 3% KCl solution         | 25                     | 80             | 0.343           | 15,319.8            | 155.9           |
| 5% KCl solution         | 25                     | 80             | 0.389           | 16,719.4            | 165.8           |
| 7% KCl solution         | 25                     | 80             | 0.421           | 15,971.2            | 170.7           |

**Figure 7.** Core state before and after the test "Photograph courtesy of Yuepeng WANG. Copyright 2020."
point of clay particles is 6–8. When the pH of the drilling fluid system is greater than 6–8, the clay surface is negatively charged. The \(-\text{NR}^+\) dissociated from polyamine in water forms a chemical potential difference with the cations between clay layers. Driven by this potential difference, organic amine molecules enter the interlayer and displace inorganic hydrated cations through ion exchange, thus reducing the zeta potential of clay.

From the curve distribution in Figure 8, it can be seen that with the increase of the concentration of NW-1, the absolute value of the zeta potential of clay particles decreased rapidly, and the electrical properties reversed. Several other inhibitors cannot make the clay particles have an electrical reversal, and the clay particles’ zeta potential is still negative. For TGA, the absolute value of the zeta potential of clay particles can be reduced at low concentrations, and the potential change of clay particles can reach approximately 50 at 0.5% concentration. When the concentration reaches 1%, the zeta potential tends to be stable, and the potential at this time is the saturation potential of clay. This is due to the neutralization between the positive charge of TGA and the negative charge of the clay surface (inside and outside), which reduces the repulsive force of the first hydration film on the clay surface to control the lattice expansion. The hydrolysis process of TGA in an aqueous solution is as follows

\[
\text{RN(CH}_2\text{OH)}_2 + \text{H}_3\text{O}^+ \rightleftharpoons \text{RN(CH}_2\text{OH)}_2\text{H}^+ + \text{H}_2\text{O}
\]

Therefore, TGA can reduce the negative charge of clay particles, reduce the electrostatic repulsion of the clay surface, and inhibit the hydration expansion of clay. At the same time, TGA has a relatively mild effect on the electrical properties of clay particles and increases the compatibility with other treatment agents.

**Thermogravimetric Analysis.** The test results are shown in Figure 9.

From the thermogravimetric curve in Figure 9, it can be seen that the thermogravimetric curve of cuttings can be divided into four typical weightless stages: the first stage is the weight loss of adsorbed water; the second stage is the desorption of water molecules between cuttings and the surface of hydrated ions of clay minerals, in which the weightlessness in the first and second stages is generally in the range of room temperature to 200 °C; the third stage is the thermal decomposition of organic matters adsorbed between cuttings; and the fourth stage is the dehydroxylation of clay minerals and the decomposition of organic matter. Because the swelling and hydration of clay minerals in cuttings have an important influence on the dispersion of shale, the weight loss in the first and second stages is mainly discussed here. Comparing Figure 9a, b, it is found that from room temperature to 200 °C, the weight loss is mainly in the first and second stages. After 3% TGA treatment, a very small amount of adsorbed water is removed from the cuttings, and the weight loss rate is 0.6%, while the weight loss of the cuttings without the inhibitor is 2.41% from room temperature to 200 °C, and there is a slight weight loss process between 200 and 300 °C. It is considered that the weight loss is due to the desorption of the hydrated crust of clay minerals. It is found that TGA can change the weight loss process of cuttings in the first and second stages.

**Figure 8.** Effect of different inhibitors on the zeta potential of bentonite slurry (pH = 9).

**Figure 9.** TG-DTG curve of cuttings before and after 3% TGA treatment: (a) after treatment with TGA inhibitor and (b) cuttings powder.
stages, which proves that TGA can effectively prevent water from entering into the clay crystal layer space by preventing cation exchange. At the same time, it can replace most of the interlayer water, reducing the interlayer water content, to achieve the effect of efficient inhibition.

**XRD Analysis of TGA.** Comparison of the Inhibitory Effects of TGA and Diesel on Sodium Montmorillonite. Figure 10 shows that after full hydration of sodium montmorillonite, the crystal layer spacing of montmorillonite increases from 1.19 to 2.04 nm due to sodium ions in the crystal layer space in the form of larger hydrated ions. The inorganic salt ions and small molecular cations (protonated amino) adsorbed on the surface of clay particles can exchange the hydrated cations in the crystal layer of clay and the adsorbed hydrated shell, which reduces the interlayer spacing of clay and leads to a decrease in the interlayer spacing. The wet sodium montmorillonite crystal layer spacing after treatment with 0.5, 1.5, and 3% TGA aqueous solution is 1.38, 1.35, and 1.35 nm, and the sodium montmorillonite crystal layer spacing after diesel treatment is 1.34 nm, indicating that the inhibitory effect of TGA on sodium montmorillonite is equivalent to that of diesel. In addition, the crystal layer spacing of wet sodium montmorillonite is 2.04, and the crystal layer of sodium montmorillonite treated with different concentrations of TGA decreases in the range of 0.66–0.70 nm, indicating that TGA can penetrate the interior of sodium montmorillonite and enter into the crystal layer of sodium montmorillonite through intercalation to inhibit surface hydration.

**Comparison of the Inhibitory Effects of Different Types and Amounts of Inhibitors on Sodium Montmorillonite.** Different kinds and concentrations of inhibitors were added to investigate the inhibitory effect of sodium montmorillonite by comparison with TGA. The experimental results are shown in Figure 11.

It can be seen from Figure 11 that with the increase of TGA concentration, the crystal layer spacing of wet sodium montmorillonite gradually decreases. The crystal layer spacing of sodium montmorillonite modified by 3% TGA is 1.35 nm, which proves that the inhibitor molecules can enter the crystal layer space and expel the adsorbed water in the crystal layer space by ion replacement, but the change of interlayer spacing tends to be gentle with the increase of concentration. In the dry state, with the increase of inhibitor concentration, the interlayer spacing of sodium montmorillonite gradually increases. When the TGA concentration is 1.5%, the interlayer spacing of sodium montmorillonite increases from 1.19 to 1.36 nm, and then the change is not evident with increasing concentration, indicating that TGA reaches adsorption equilibrium among montmorillonite layers. Comparing the crystal layer spacing changes of sodium montmorillonite treated with three inhibitors before and after drying, it can be seen that the change value of crystal layer spacing of sodium montmorillonite before and after drying is very small. This indicates that the crystal layer space of sodium montmorillonite modified by inhibitors only contains a small amount of adsorbed water, which further proves that amine inhibitors have a strong ability to inhibit hydration in the crystal layer space of sodium montmorillonite.

**Soaking Experiment of Bentonite Mud Cake.** Figure 12 shows the appearance and morphology of bentonite mud cake soaked in clean water for 2 and 24 h. Obviously, after 2 h of full soaking, the upper surface of the bentonite mud cake has small holes and lines caused by the infiltration of water. At the same time, the edge of the bentonite mud cake has evident layered expansion. The closer to the edge, the more serious the

![Figure 10. XRD analyses of the reaction montmorillonite layer spacing diagram: (a) wet montmorillonite and (b) dry montmorillonite.](https://doi.org/10.1021/acsomega.1c01936)

![Figure 11. Different inhibitors of the sodium montmorillonite layer spacing effect.](https://doi.org/10.1021/acsomega.1c01936)
Soaking experiment of bentonite cake in the clear water group (Figure 12). As the amount of TGA increased, the hydration degree of the bentonite cake in the corresponding solution was gradually suppressed. When the added amount of TGA is 2.5%, the edges of the bentonite cake soaked for 24 h have seldom scattered lumps, and the whole is several larger bentonite blocks, which are close to each other. In general, the bentonite cake soaking experiment intuitively reflects that a certain TGA concentration can effectively inhibit the hydration expansion of bentonite and limit its dispersion.

**Mechanism Analysis.** The shale inhibitor TGA mechanism is mainly to inhibit the hydration expansion of sodium montmorillonite by inhibiting interlayer hydration. The amine group of the inhibitor molecule is dissociated into ammonium cations after hydration and then forms a chemical potential difference with the inorganic cations in the clay crystal layer. Under this chemical potential difference, the ammonium cations replace the inorganic cations in the clay layer and reduce the negative charge of the clay surface. At the same time, the ammonium cation easily forms a hydrogen bond with the siloxane on the clay surface, which makes its adsorption on the clay surface play an important role. Therefore, the adsorption is irreversible and is not exchanged by other ions. The hydration repulsion between clay layers decreases under the double action of electrostatic forces and hydrogen bonds. At this time, the interlayer spacing of clay is compressed and squeezed out of the interlayer part of adsorbed water, and the hydration of clay is weakened. At the same time, the protonated amino group in the inhibitor molecule can compete with the water molecule and bond to the surface of clay crystals to destroy the structure of water. In addition, the hydrophobic groups in TGA molecules cover the surface of the clay crystal layer tightly, forming a hydrophobic barrier to prevent the entry and adsorption of water molecules, thus further inhibiting the hydration of clay.22,23

**Field Application.** The lithology of the Weiyuan area is mainly shale, in which the shale mainly consists of black silty shale, carbonaceous shale, and siliceous shale. At the same time, microfractures are relatively developed in this area, which is prone to hydration and dispersion, leading to collapse. The leakage phenomenon is serious in horizontal well drilling, and ball up and sticking accidents bring great inconvenience to drilling construction and drilling cycles, resulting in huge economic losses. The formula of the polyamine water-based drilling fluid system is 3−5% bentonite + 0.2% KOH + 7% KCl + 3% SMP-II + 4% sulfonated asphalt + 1% TGA + 0.5% KPAM + 5% CaCO3 + 0.5% CMC + 1.5% PAC-LV + weighting agent (according to density requirements), field test in Weiyuan 202H10-7 well. Well 202H10-7 has a depth of 5369 m, in which the horizontal section is 1700 m. After applying the system, it was compared with the same type of wells in the block (the drilling fluid system of the three-well section in the same stratum is potassium polysulfonate drilling fluid), and its formula is well slurry + 0.1−0.3% NaOH + 0.05−0.1 KPAM + 0.5−0.8% PAC-LV + 3−5% RSTF + 3−5% SMP-1 + 3−5% FRH + 2−4% FK-10 + 0.2−0.3% SP-80 + 0.3−0.5% CaO + 5−7% KCl + weighting agent (according to density requirement). During drilling, there was no wall falling phenomenon. Compared with the potassium polysulfonate drilling fluid system in the same
Table 6. Drilling Fluid System Performancea

| performance index                      | \( \rho \) (g/cm³) | PH  | FV (s) | PV (mPa·s) | YP (Pa) | gel (Pa·s/Pa) | FLAPI | FL_{\text{API}} (ml) | lubrication coefficient |
|----------------------------------------|---------------------|-----|--------|------------|---------|---------------|-------|----------------------|------------------------|
| polyamine water-based drilling fluid   | 1.27                | 9.0 | 59     | 19         | 11      | 3.0/15.0      | 4.3   | 16.7                 | 0.072                  |
| strongly inhibited water-based drilling fluid on site | 1.30                | 9.0 | 62     | 23         | 16      | 4.5/20.0      | 6.4   | 23.1                 | 0.096                  |

The well slurry comes from the third opening section of well 202H10-7.

CONCLUSIONS

1. The results of the rolling recovery test, triaxial stress test, bentonite inhibition pulping test, and XRD diffraction test show that the inhibitory performance of TGA is better than that of the traditional inorganic salt inhibitor KCl, amine inhibitor UHIB, and organic cationic shale inhibitor NW-1.

2. With experimental methods such as X-ray diffraction analysis, zeta potential tests, and thermogravimetric analysis, the microscopic mechanism of TGA inhibitors is studied: TGA inhibitors undergo protonation after contact with water, and they are positively charged and enter the clay by intercalation. The crystal layer space is adsorbed on the clay surface through electrostatic interactions and hydrogen bonding. The protonated amine groups and the cations between the clay layers perform ion exchange, exchange hydrated ions between the clay layers, and reduce the electrostatic repulsion on the clay surface and between the clay layers. The repulsion force compresses the diffusion double layer of clay and the space of the clay crystal layer to the maximum extent.

3. Field tests show that the system can solve the problems of wall instability and large sticking friction during horizontal well drilling in the Weiyuan area and meet the technical requirements for field implementation of water-based drilling fluid for shale gas horizontal wells.

AUTHOR INFORMATION

Corresponding Author

Xiangjun Liu — State Key Laboratory of Oil and Gas Reservoir Geology and Exploitation, Southwest Petroleum University, Chengdu, Sichuan 610500, China; orcid.org/0000-0002-0633-0989; Email: 13880093092@163.com

Authors

Yuexin Tian — State Key Laboratory of Oil and Gas Reservoir Geology and Exploitation, Southwest Petroleum University, Chengdu, Sichuan 610500, China; orcid.org/0000-0002-1139-7774

Pingya Luo — State Key Laboratory of Oil and Gas Reservoir Geology and Exploitation, Southwest Petroleum University, Chengdu, Sichuan 610500, China

Jinjun Huang — State Key Laboratory of Oil and Gas Reservoir Geology and Exploitation, Southwest Petroleum University, Chengdu, Sichuan 610500, China

Jian Xiong — State Key Laboratory of Oil and Gas Reservoir Geology and Exploitation, Southwest Petroleum University, Chengdu, Sichuan 610500, China

Lixi Liang — State Key Laboratory of Oil and Gas Reservoir Geology and Exploitation, Southwest Petroleum University, Chengdu, Sichuan 610500, China

Wenfei Li — State Key Laboratory of Oil and Gas Reservoir Geology and Exploitation, Southwest Petroleum University, Chengdu, Sichuan 610500, China

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.1c01936

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors thank the National 13th Five-Year Major Science and Technology Project of China “Research and Test of Water-based Drilling Fluid for Horizontal Shale Gas Wells” (no. 2016ZX05022001-002) and for the financial support.

GLOSSARY

bentonite: it has multipurpose additives to control filtration, suspend barite, and provide enough viscosity to ensure well cleaning ability

KOH: adjust the pH value of the drilling fluid and provide K⁺

KCl: it has a strong ability to inhibit shale permeation and hydration and reduce the fluid loss of drilling fluid. It mainly provides K⁺, which can significantly reduce the particle size of the solid phase, help to enter the formation voids and fractures, and improve the plugging efficiency and strength. It has strong salt and calcium resistance. It is a new type of high-temperature and salt resistance fluid loss agent for drilling fluid at high temperature and high pressure

SMP-II: it can effectively seal microfractures in the formation, prevent exfoliative shale from collapsing, and inhibit shale hydration. At the same time, it also has good lubrication, emulsification, reduction of fluid loss, and high-temperature stability. It can also be used as a lubricant with low lubrication coefficient, especially to reduce the effect of mud cake adhesion. Prevent the pressure difference from sticking
it is a weighting agent mainly barite, which is a weighting agent for PAC-LV, it has strong water solubility, excellent salt CaCO3, it can improve fluid density of the drilling fluid. CMC, it can reduce fluid loss and increase viscosity. When the drilling fluid has a high viscosity, it also has a certain ability to inhibit shale hydration and expansion PAC-LV, it has strong water solubility, excellent salt resistance, and fluid loss reduction ability, especially in the saturated brine drilling fluid; it has a very good fluid loss reduction effect overcoming the disadvantages of PAC-LV, improving cementation, increasing lubrication, and having a high pressure tolerance. 

**REFERENCES**

(1) Kok, M. V.; Uyar, T. T. A Geomechanical Wellbore Stability Assessment for Different Formations in Petroleum Fields. *Pet. Sci.* 2014, 32, 2355.

(2) Matsuura, Y. Case studies of borehole stability problems-Drilling through shale and volcanic formation. *J. Jpn. Assoc. Pet. Technol.* 2002, 67, 475.

(3) Zhao, F.; Tang, H.; Meng, Y.; Li, G.; Xu, H. Study on the influence of micro geological features on the stability of hard and brittle mud shale well walls and countermeasures. *Drill. Prod. Technol.* 2007, 16–18.

(4) Wan, W.; Ge, L. Research and application of high-performance water-based drilling fluid in Changning shale gas block. *Drill. Prod. Technol.* 2019, 42, 83–86.

(5) Xianbin, H.; Haokun, S.; Jinsheng, S.; Kahe, L.; Jingping, L.; Xiaodong, D.; Shaojie, L. Nano laponite as a potential shale inhibitor in water based drilling fluid for stabilizing wellbore stability and mechanism study. *ACS Appl. Mater. Interfaces* 2018, 10 (39), 33252–33259, DOI: 10.1021/acsami.8b11419.

(6) Zhong, H.; Huang, W.; Lin, Y.; Qiu, Z.; Liu, G.; Zhang, G. Performance evaluation of new polyamine shale inhibitor. *Pet. Drill. Technol.* 2011, 06, 48–52.

(7) Wang, Z.; Wang, Z. Some knowledge about polyamine and “polyamine” drilling fluid. *China Foreign Energy* 2012, 17, 36–42.

(8) Qiu, Z.; Zhang, D.; Fu, J.; Tong, S.; Zhong, H.; Xing, Y. Research and Application of Polyamine Drilling Fluid in Long Open Hole Section of Tahe Oilfield. *J. Liaoning Univ. Pet. Chem. Technol.* 2016, 6, 33–38.

(9) Zhang, G.; Xu, J.; Zhan, M.; Liu, G.; Zhong, H.; Ma, P. Research and application of new polyamine water-based drilling fluids. *Drill. Fluid Completion Fluid* 2013, 30, 23–26.

(10) Li, Y.; Yang, G.; Fan, Z.; Wang, Q.; Wang, F.; Wang, X.; Chen, G. Research on polyamine inhibiting anti-collapse drilling fluid and its application in western Sichuan. *J. Oil Gas Technol.* 2014, 36, 137–142.

(11) Tian, L.; Li, S.; Wang, B.; Xue, Y.; Li, T. Application of Polyamine Drilling Fluid System in Dingbei Block. *Drill. Prod. Technol.* 2014, 37, 97–99.

(12) Rana, A.; Afaj, M. K.; Saleh, T. A. Advanced developments in shale inhibitors for oil production with low environmental footprints - A review. *Fuel* 2019, 247, 237–249.

(13) Du, W.; Sun, J.; Pu, X.; Zhang, J.; Chen, G. Research status and development trends of clay hydration inhibitor athome and abroad. *Chem. Ind. Eng. Prog.* 2018, 37, 4013–4021.

(14) Hou, J.; Liu, Y.; Song, G.; Song, T.; Yan, J.; Zhao, X. Synthesis and application of a new high temperature high performance salt resistant shale inhibitor. *Drill. Fluid Completion Fluid* 2016, 33, 22–27.

(15) Zhang, H.; Zuo, F.; Tian, Y.; Jia, D.; Liu, Y.; Wen, J.; Zhang, L.; Song, L. Investigation and application of new amine salt inhibitor. *Oilfield Chem.* 2012, 4, 390–393.

(16) Zhong, H.; Qiu, Z.; Huang, W.; Lin, Y.; Li, H.; Zhang, G. The Development and application of a novel polyamine water-based drilling fluid. *J. Xi’an Shiyou Univ., Nat. Sci. Ed.* 2013, 28, 72–77.

(17) Wang, Z.; Zhang, X.; Zhang, P.; Wang, X.; Ma, C. Synthesis and application of zwitterionic shale inhibitor LM-1. *Sci. Technol. Eng.* 2020, 2, 563–568.

(18) Wang, W.; Yu, H.; Li, D.; Wang, Y. Synthesis and performance of hydroxylamine shale inhibitor. *Adv. Fine Petrochem.* 2019, 20, 4–7.

(19) Li, X.; Li, B.; Fan, J.; Li, J. Study on new methods of biological toxicity detection and toxicity classification standards for oilfield chemicals and drilling fluids. *Drill. Fluid Completion Fluid* 2004, 06, 46–48.

(20) Qu, Y. Research on New Amine-based Inhibitors (1)—Molecular Structure Design and Synthesis. *Drill. Fluid Completion Fluid* 2010, 01, 1–3.

(21) Lin, B.; Gao, M. Study on clay stability of MD film flooding agent I. Static test. *Acta Pet. Sin., Pet. Process. Sect.* 2006, 03, 79–84.

(22) Zhong, H.; Qiu, Z.; Huang, W.; Lin, Y.; Li, H.; Zhang, G. Development and application of a new type of polyamine shale hydration inhibitor. *J. Xi’an Shiyou Univ., Nat. Sci. Ed.* 2013, 28, 72–77.

(23) Xie, G.; Xiao, Y.; Deng, M.; Luo, Y.; Luo, P. Low Molecular Weight Branched Polyamine as a Clay Swelling Inhibitor and Its Inhibition Mechanism: Experiment and Density Functional Theory Simulation. *Energy Fuels* 2020, 34, 2169.