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EXPERIMENTAL INVESTIGATION OF A HIGH TEMPERATURE RESISTANT AND LOW FRICTION FRACTURING FLUID

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Abstract: The performance of a hydraulic fracturing fluid (HFF) system directly determines the efficiency of stimulation. Since the targeted formations of most oil fields in China are characterized by large depth (~5000 m), high temperature (160 to 180 °C) and tight lithology, newer and suitable HFFs have to be developed. Based on a newly synthetized organo-boron/-zirconium cross-linking agent (Gh-g), a composite temperature stabilizer (WJ-6) and other optimized additives via indoor evaluation, this study introduced a novel HFF, which is thermally stable at high temperature (HT) up to 180 °C and exerted low friction pressures. The performance of HFF was evaluated in the laboratory. The experimental results showed that the HFF system performed well at HTs. It maintained a viscosity of 100 mPa·s or more after 90 min of shearing (170 s^{-1}) at 180 °C. Furthermore, the system exhibited delayed cross-linking. It took 120 s for the cross-linking reaction to complete; therefore, the tube friction was reduced to a large extent. Another characteristic feature of the formulated HFF system was the low friction pressures, where the drag reduction percentage was in the range from 35% to 70%. Moreover, only minor damage was caused by the fluid to the formation core samples. The average core permeability damage was 19.6%. All these qualities ensure that this fluid system is in full compliance with the requirements of the fracturing treatment.

Keywords: *high temperature fracturing fluid, resistance to shearing, hydroxypropyl guar, low friction, delayed crosslinking*

Introduction

A critical factor in the successful stimulation of deep tight oil and gas reservoirs is the performance of HFF. Formulating a HFF system that maintains stable performance under ultra-HT and a prolonged shearing environment remains a challenge for engineers (Li et al., 2003; Zhang et al., 2005; Li et al., 2005; Han et al., 2006).

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Each of the several additives in HFF has its specific function. However, not every component plays a decisive role in the performance of HFF at HT condition (Lagrone et al., 1983; Loveless, 2011). Critical factors affecting the performance of HT resistant HFF include components listed below.

Thickening agent, as a main component of the HFF, is to enhance the viscosity of the aqueous solution. Generally, the greater molecular weight of the thickening agent, the stronger is its thickening ability. Water solubility of viscosifier will be high and the residue after the gel breaks down will be less if the number of hydration groups on the molecular chain of the thickening agent is high (Yang et al., 2004).

Crosslinking agent like organic boron enhances the viscosity of HFF is a widespread practice. However, the organic boron cross-linker is unstable in deep and HT low-permeability reservoirs; cross-linking is gradually ruptured with increase in temperature. Domestic organic boron cross-linkers are not stable at temperatures >140 °C. Reticular gel can be generated with an organozirconium cross-linker; covalent bonds result from the reaction between the transition metal ions and maleinoid form of hydroxyl groups on the galactose branched chain of the polymers. The cross-linking functional group is relatively stable and can endure temperatures up to 260 °C; however, the reforming ability of gel after high-speed shearing is extremely poor. A combination of boron- and zirconium-based cross-linking agents, which compensate for the shortcomings in each other, is a widely used cross-linking agent in HT (>140 °C) HFF formulations (Chen et al., 2007; Wang et al., 2011; Lu et al., 1995).

Temperature stabilizer is a vital component in HT HFF. Modified guar is the preferred thickening agent in HT fracturing liquid. However, the main polysaccharide backbone of the plant guar begins to degrade at temperatures >160 °C and deteriorates rapidly at temperatures >177 °C. A temperature stabilizer is usually added to improve the thermal resistance of the HFF (Zhang et al., 2012; Gupta et al., 2011).

pH adjusting agent is also adopted to regulate the acid-base property of the HFF for a better performance. Hydrolysis of guar gum and its derivatives occurs easily in a low pH environment and, more so, at HT environment. Therefore, the pH value of the HFF should be maintained within a suitable range (Abad et al., 2011; Terracina et al., 1999; Poleski et al., 2013).

Considering the factors in the formation of oil wells in China, a HFF system has been formulated in the laboratory and evaluated on the basis of the above key factors.

Materials and methods

Equipment and Materials

Viscosity of HFF systems was investigated by RS6000 rheometer (Germany Haake). Pincee capillary viscometer (HengTong Instrument Co., Ltd., Shanghai, China) was used to measure the viscosity of HFF after breaking. Leak-off coefficient of fluid was tested with HT dynamic fluid loss evaluating device HALS-1 (Huaan scientific equipment corporation, Jiangsu, China). Friction of HFF was evaluated by large-scale friction tester YMC-1 (Huaan scientific equipment corporation, Jiangsu, China).

Samples studied include industrial products (hydroxypropyl guar (BG-1, SG-1, BXT-2), KCl, NaOH, Na_2CO_3, $NaHCO_3$), capsule gel breaking agent (XT-71), emulsion breaker (XH-2), cleanup additive (XT-5), temperature stabilizer (WJ-1, WJ-2, WJ-3) and bactericides (JA-1).

HT cross-linking agent Gh-g was prepared using the following protocol. Pre-determined quantities of borax, sodium gluconate and water were mixed in a three-necked flask. The resulting mixture was agitated and refluxed for 1 h at 80 °C using an oil bath. Subsequently, zirconium oxychloride, lactic acid, triethanolamine, glycerin, citric acid and EDTA were added under an atmosphere of nitrogen. The faint yellow-colored fluid, i.e., the HT cross-linking agent Gh-g, was obtained after agitating and refluxing the mixture at the same temperature (80 °C) for 6 h.

Experimental methods

Formulation of HT resistant HFF

At the beginning, the main additives (thickening agent, cross-linking agent, temperature stabilizer and pH adjusting agent) and other additives were evaluated as the component candidate of HT HFF. Tests were conducted to ensure that the selected additives had no negative effects on the characteristics of the HFF. Subsequently, compatibility evaluation was carried out to see if any flocculates and deposits were observed. The HFFs were formulated with additives that had good compatibility with each other and no negative effects on HFF function. All experiments were implemented in accordance to Standards of Petroleum and Natural Gas Industry of China.

Evaluation of HT resistant HFF

The optimized base fluid was prepared and the components allowed to hydrate for 2 h to ensure complete polymer hydration. To minimize variations in the base fluid, its temperature and pH were measured before use. The viscosity of the base fluid was in the range of 170 s^{-1}. An aliquot of the base fluid was cross-linked. After cross-linking, the fluid was sheared at high speed for an additional minute before being placed in viscometer.

The cross-linked fluid was placed in the RS6000 viscometer and pressure was applied with the nitrogen gas. With a preheated oil bath at the predetermined test temperature, it took ~30 minutes for the sample to reach the designated temperature. The fluid was sheared at 10 s^{-1} to 20 s^{-1} during heating. The shear rate was increased to 170 s^{-1} when the sample attained the test temperature and the shearing was continued for 90 minutes. After recording the initial rheogram, the evaluation was continued until the fluid viscosity dropped below 50 mPa·s.

The friction characteristics of the fluid system were evaluated by large-scale friction tester YMC-1. The inner diameter of coiled flow loop was 1.2 cm. Various additives at the desired concentrations were added to the water and equilibrated for 5 minutes (to disperse, mix and hydrate) before the mixture was released into the flow loop. Pressure drops and flow rates were recorded after every 30 s to 60 s for several minutes while the fluid recirculated through the flow loop. Subsequently, pressure variation in the flow of additive-free water under the same conditions was recorded. The results from the two experiments were compared.

The formation damage potential of the HFF was assessed via regained permeability tests. Tests were performed in accordance to API RP39 recommended practices for measuring the viscous properties of a cross-linked water-based HFF.

Results and discussion

Formulation of HFF system

Thickening agent

Modified plant gum functions as a thickening agent owing to its high viscosity, resistance to HT, leaves less residue and is required in low quantities (GUO et al., 2011). The physical performance of the three widely used gums – imported guar gum BG-1 (1st grade), hydroxypropyl guar gum SG-1 (1st grade) and hydroxypropyl guar gum BXT-2 (1st grade) – under our experimental conditions is shown in Table 1.

Table1 The main properties of different thickening agents

Type	Water-insoluble matter content [%]	Viscosity at 0.6% concentration [mPa·s]	Residue [mg·dm^{-3}]
BG-1	4.39	123	229
SG-1	4.58	108	249
BXT-2	4.25	117	212

Each thickening agent was screened for its water-insoluble content, thickening ability and the quantity of residue remaining. The water-insoluble content and residues of thickening agents BG-1 and BXT-2 was less than that of SG-1 (Table 1), therefore, it is likely that the use of BG-1 and BXT-2 in the HFF will cause less damage to the formation. The relatively high viscosity observed with 0.6% solutions of BG-1 and BXT-2 indicated their strong thickening ability. The lower quantities of thickening agent would be, the stronger thickening ability and the lower damage could cause to the formation because of the lower quantities of residue left behind by the HFF. Although thickening ability of BXT-2 was slightly lower than that of BG-1, the water-insoluble content and the amount of residue was also relatively low. Permeability of block Hui 25 formation is quite low (~0.04×10^{-3} μm^2), therefore, a high residue in the HFF can cause serious damage to the conductivity of proppant and the matrix permeability. Therefore, BXT-2 was selected as the thickening agent in the formulation of HT HFF system.

Cross-linking agent

Reasonable selection of cross-linking agent can greatly enhance the temperature resistance of a HFF. Widely used cross-linking agents for hydroxypropyl guar gum are organoboron compounds. However, these compounds lose the cross-linking ability due to chemical modifications when the temperature exceeds 140 °C. Organotitanium and organozirconium compounds, synthesized from titanium or zirconium ions, respectively, can maintain a relatively strong cross-linking ability at temperatures >140 °C, provided an appropriate pH value is maintained (AINLEY et al., 1993; WANG et al., 2004). Six different cross-linking agents, four of which were organoboron and organozirconium compounds, were evaluated. The remaining two cross-linking agents evaluated were organotitanium compounds.

As a based fluid for conducted experiments was a guar gum fluid containing compounds such as hydroxypropyl guar gum BXT-2 (0.6%), KCl (0.5%), cleanup additive XT-5 (0.5%), demulsifier XH-2 (0.5%), temperature stabilizer (1%), and bactericide JA-1 (0.1%). At room temperature (20 °C), different cross-linking agents (0.30 mL) were added separately to the fluid (100 g) and mixed. The cross-linking time was recorded and the thermal and shear resistance of each of the gel was evaluated. Similar tests were performed with increasing amounts of GH-g (0.40, 0.50, 0.55 and 0.60 mL) for the sake of comparison. The results showed that the cross-linking ability of GH-g was better. The cross-linking time and hang-up characteristics of the gel with various amounts of GH-g are shown in Table 2.

Table2. Characteristics of crosslinking and hang-up ability of HT crosslinker GH-g at different concentration

Formula of basic fluid	Concentration of crosslinker Gh-g[%]	Thickening time[s]	Hang-up time [s]	Gel property
0.6% hydroxypropyl guar BXT-2+0.5%KCl+0.5% cleanup additive+0.5% emulsion breaker +1% temperature stabilizer+0.1%JA-1 bactericide agent	0.3	30	130	easy to hang up
	0.4	26	125	easy to hang up
	0.5	20	126	easy to hang up
	0.6	15	118	can be hung up, slightly friable

Rheological tests at 160 °C and a shear rate of 170 s^{-1} were used for assessing the thermal and shear resistance of the HFFs containing different amounts of GH-g (Figure 1). The bimetallic organo-boron/-zirconium cross-linking agent GH-g showed good performance when used at a concentration of 0.5%–0.6%. The initial viscosity of the fluid rose up to 1000 mPa·s and decreased after 1 h of shearing to 160 mPa·s.

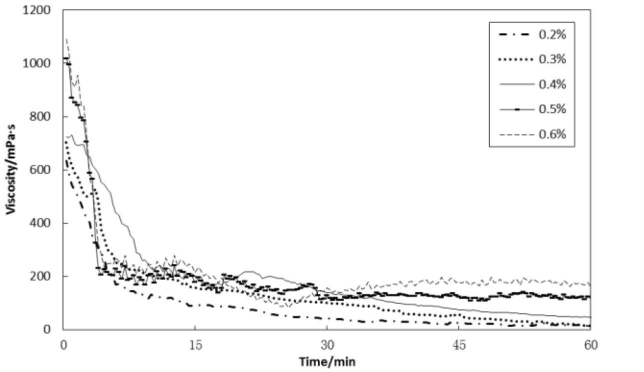

Fig.1. Rheological curve of HFF with different amount of GH-g at 160˚C

Temperature stabilizer

Temperature resistance of cross-linked guar-based fluid degrades greatly when the temperature exceeds 120 °C. Therefore, a temperature stabilizer is typically added to enhance the temperature resistance and reduce the degradation rate of the cross-linked guar-based fluid at HT condition. Three temperature stabilizers, WJ-1, WJ-2 and WJ-3, were tested to identify which of them causes the greatest enhancement in temperature tolerance of cross-linked guar gum-based fluid. WJ-1 was a thiosulfate, WJ-2 was a ketoxime and WJ-3 was a hydrazine. The results showed that none of these temperature stabilizers can improve the thermal stability individually.

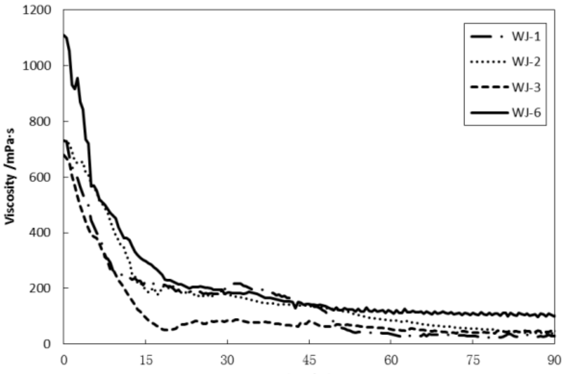

Fig. 2. Effect of different temperature stabilizer on the HT resistance at the concentration of 1%

Rheological curves of the three temperature stabilizers are shown in Figure 2. Thiosulfate had a good assistant effect in temperature tolerance at low temperature conditions and the ketoxime, WJ-2, was relatively stable. Although hydrazine was expensive, its strong reducibility could improve the thermal stability of the HFF effectively. Therefore, various combinations of WJ-1, WJ-2 and WJ-3 were tested for their ability to enhance the temperature resistance of the fluid system. According to results from the rheological tests, the optimal enhancement in thermal stability was observed when the ratio of the three temperature stabilizers WJ-1:WJ-2:WJ-3 was 5:3:2. This combination of WJ-1, WJ-2 and WJ-3 was designated as WJ-6. On evaluation of its prolonged stability, no change in color or the emergence of flocculates and deposits were observed. As evident from Figure 2, when temperature and shearing rate were 160 °C and 170 s^{-1}, respectively, WJ-6 enhanced the temperature tolerance and shearing resistance significantly. Thus, WJ-6 was selected as the temperature stabilizer in the HT HFF system. WJ-6 provided thermal stability by two mechanisms. To begin with, the temperature stabilizer could take off the free oxygen in the fluid, thereby weakening the accelerating of thermal degradation and, consequently, enhancing the thermal stability of thickening agent. Additionally, the temperature stabilizer was able to react with the free radical of the polymer to improve the substantivity between cross-linker and polymer hydroxyl group, thus allowing the HFF to be stable at HT. These two mechanisms provide the thermal stability to the gel HFF system.

pH adjusting agent

The pH has a great effect on the characteristics of HT HFFs. Hydroxypropyl guar is hydrolyzed in solutions with low pH value and, more heavily, at HTs. Generally, polymers such as guar form cross-links only in an alkali environment. Rheology tests were performed on HFFs containing various amount of Na_2CO_3, $NaHCO_3$ and NaOH to analyze the temperature tolerance and shear resistance. Analysis of the rheological curve suggested that GH-g had the optimal cross-linking effectiveness with 0.15% NaOH.

Formulation of HT HFF system

After the identification and concentration optimization of thickening agent, cross-linker, temperature stabilizer and pH adjusting agent, the type and concentration of other additives were also determined. Compatibility tests showed that all the above listed additives have good compatibility with each other and present no flocculates or deposits. In addition, the other additives selected, i.e., cleanup additive, clay inhibitor, emulsion breaker and bactericide agent, had no negative effects on the properties of the HFF. As a result, the HT HFF system was a water-based fluid containing hydroxypropyl guar BXT-2 (0.6–0.65%), emulsion breaker XH-2 (0.5%), cleanup additive XT-5 (0.5%), clay inhibitor KCl (1%), bactericide agent JA-1 (0.1%), temperature stabilizer agent WJ-6 (1%), pH adjusting agent NaOH (0.10–0.15%), capsule gel breaker XT-71 (with “wedge” additional breaker technology, 0.0002%–0.2%) and cross-linker GH-g (0.5–0.6%).

Evaluation of HT HFF

The evaluation of the characteristics of the HT HFF was performed according to the requirements of Standards of Petroleum and Natural Gas Industry of China. The HFF was the water-based fluid containing hydroxypropyl guar BXT-2 (0.6%), bactericide agent JA-1 (0.1%), cleanup additive XT-5 (0.5%), pH adjusting agent NaOH (0.12%), clay inhibitor KCl (1%), emulsion breaker XH-2 (0.5%), temperature stabilizer agent WJ-6 (1%), cross-linker GH-g (0.5%) and capsule gel breaker XT-71 (0.1%).

Characteristics of base fluid and cross-linking fluid

Apparent viscosity and pH value are two important evaluation index for the base fluid of HFF. When the pH value was 12–13, at a temperature of 25 °C and a shearing rate of 170 s^{-1}, the apparent viscosity of HFF was 105 mPa·s to 115 mPa·s. Since there was no alkali-sensitivity in Hui 25 block, this fluid system will be suitable for stimulation.

Vortex sealing method, which mainly measures the cross-linking time and the state after gel formation, was used to investigate the characteristics of cross-linking fluid. The HT HFF system started to form the gel after 20 s. At 120 s, the cross-linking was complete. All of this displayed a good delayed cross-linking characteristic. Furthermore, the surface of gel was smooth and showed no wall-hanging feature.

Resistance to temperature and shearing

Thermal and shear resistance of the fluid system was evaluated by simulating the treatment conditions (XIONG et al., 1996). Changes in apparent viscosity of HFF determines whether the rheological properties of HFF can meet the requirement of process design. Temperature and shearing resistance of the HFF system was measured at 180 °C and 170 s^{-1}, respectively, using a HAAKE RS6000 rheometer. As shown in Figure 3, after 90 min of shearing at the corresponding temperature, the results indicated that the viscosity of HT HFF remained at or above 100 mPa·s, which was in full compliance with the requirements of the fracturing treatment.

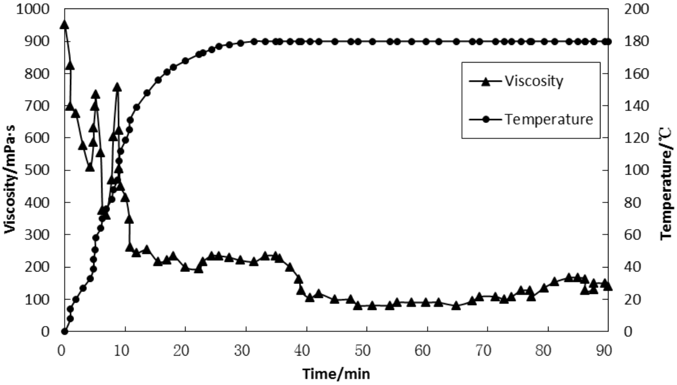

Fig. 3. Rheological curve of HT HFF at 180˚C and 170s^{-1}

Evaluation of friction characteristics

Both the choice of pumping equipment and the effectiveness of hydraulic power transmission are markedly affected by the friction produced as fluids flow through the pipes. More problems emerge in treatment when a HFF generates high friction. The targeted formation in well Hui 25 area lies ~5,000 m underground. The delayed cross-linking fluid will greatly reduce the friction by slowing down the process of cross-linking. Here, the friction resistance of HFF is marked by Drag Reduction Ratio – ratio of friction value difference between HFF friction and water to water friction. Results from the YMC-1 large-scale friction tester indicated that the developed HFF system can effectively reduce friction.

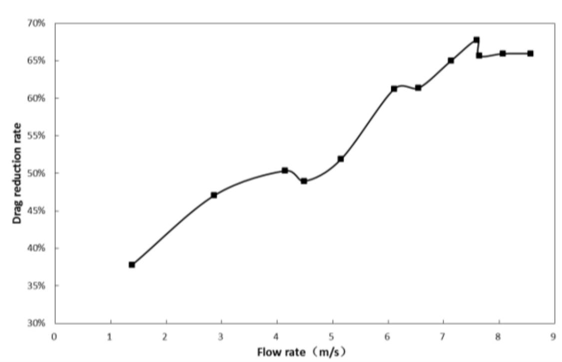

Fig. 4. Drag reduction of the HFF system at various flow rate

As evident from Figure 4, drag reduction ratio of the fluid varied between 35% and 70%, resulting from the different flow rates. Higher values of the ratio were observed for higher flow rates. However, when the average flow rate was >8 m s^{-1}, the drag reduction ratio remained constant. Formation of whirlpools or transitions from a large whirlpool to a small one were hindered in pipe flow because of the swelling of HPG molecule in water, therefore, friction was reduced as a result of low energy loss. The reduction of friction was limited at higher flow rates, as the structural stability of HPG molecule was weakened by the increased shear force exerted on the fluid by walls of the tube.

Evaluation of gel breaking

The performance of flowback and the ultimate stimulation effect are largely influenced by the ability to break the gelled HFF. The compatibility of this HFF system with formation water was confirmed by experimentation, wherein the final solution was clear and contained no emulsion or sediments. The viscosity of fluid after breaking was only 4 mPa·s, which was in full compliance with industrial standard.

Evaluation of formation damage

Cores from the well at Hui 25 area in China were used as samples to evaluate the performance of HFF. The damage caused by the HFF to the formation should be limited, since the lithology in this area was so tight that the average determined core permeability was 0.04×10^{-3} μm^2. Six cores from the intended zone were evaluated for the damage to core permeability brought about by the filtrate of this fracture fluid. The extent of damage to the core permeability varied between 10.0% and 33.8%, while the mean damage percentage was only 19.6% (Table 3), which meets the requirements of industrial standards.

Table 3. Results of experiments for evaluating damage on cores of HT-tolerant HFF

Core label	Original permeability [10^{-3} μm^2]	Permeability after experiment [10^{-3} μm^2]	Damage percentage [%]	Average damage percentage [%]
1#	0.043	0.037	14.5	19.6
2#	0.045	0.039	12.7	
3#	0.035	0.025	29.4	
4#	0.056	0.050	10.0	
5#	0.025	0.017	33.8	
6#	0.041	0.034	17.2	

Conclusions

The variety and dosage of additives in HFF that can influence its properties were selected and optimized through in-lab experiments. The optimized formulation of a HT resistant HFF system was a water-based fluid containing hydroxypropyl guar gum BXT-2 (0.6%), emulsion breaker XH-2 (0.5%), clean up additive XT-5 (0.5%), clay inhibitor KCl (1%), bactericide JA-1 (0.1%), temperature stabilizer WJ-6 (1%), pH adjusting agent NaOH (0.10–0.15%), encapsulated gel breaker XT-71 (wedge-like adding advised, 0.0002–0.2%) and cross-linking agent GH-g (0.5–0.6%). The in-lab performance evaluation of the formulated HT resistant HFF indicated that this fluid system can meet the demands of stimulation. Evidence for the same is follows. The observed delayed cross-linking attribute was favorable to reduce friction and cross-linking of the molecular chains in guar gum started after 120 s. In addition, the HFF exhibited excellent temperature and shearing resistance and its viscosity was 100 mPa·s even after 90 min at a temperature of 180 °C and shearing rate of 170 s^{-1}. Moreover, the gel broke down completely and the viscosity of the solution after gel breaking was only 4 mPa·s. Furthermore, the formulated HFF exhibited low friction quality while tube friction just took up 35–70% of water friction. At last, the formulated HFF caused little damage to the formation of well of Hui 25 area and average damage percentage of core permeability was only 19.6%.

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