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The Development and Deployment of Degradable Temporary Plugging Material for Ultra-Deepwater Wells

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Abstract: The fractured granite reservoir is well developed in Yongle block, which leads to severe drilling fluid loss-circulation. To solve the technical problem of both plugging and reservoir protection, on the basis of comprehensive literature research and laboratory tests at home and abroad, a polymer with an appropriate molecular weight, an organic crosslinking agent and other auxiliary materials were screened. In addition, a kind of high-temperature resistant loss-circulation plugging gel, which could be formed by timing and self-degradation, was developed. The high-strength gel loss-circulation system can be established by the development of a dynamic covalent borate ester bond crosslinking agent, which can crosslink with polyvinyl alcohol and xanthan gum. This system is of formidable strength and can be used for loss-circulation control in a fractured formation. The dynamic covalent borate ester bond tends to break due to the peroxide glue breaker under low pH levels, which can accelerate the degradation of the plugging gel into small molecules. The degradable temporary plugging material can ensure high-performance sealing and self-degradation capabilities of the fractured granite reservoir. The laboratory results showed that the high-performance degradable gel system was of adjustable gelling time, high gelling strength and high sealing capability. Its pressure-bearing could reach 5.8 MPa under 110 °C with 3.5 mm width of fractured granite core. Before crosslinking, the system also boasted promising thixotropy and rheology. The gel breaking time of the system was short, which could be completely broken with 6.1 h in 6% peroxide solution with pH of 4. The gelation time was related to the type of crosslinking agent, the amount of crosslinking agent and temperature. With the increase of temperature, the gelation time of gel system decreased. With the increase of the amount of the agent, the gelation time of gel system decreased. The gelation time was 105 min when using a 1% dynamic covalent borate ester bond crosslinking agent at 80 °C; the gelation time was 72 min when using a 1% dynamic covalent borate ester bond crosslinking agent at 110 °C; the gelation time was 71 min when using a 2% dynamic covalent borate ester bond crosslinking agent at 80 °C; the gelation time was 65 min when using a 2% dynamic covalent borate ester bond crosslinking agent at 110 °C; the gelation time was 72 min when using a 1% chromium crosslinking agent at 80 °C; the gelation time was 63 min when using a 2% chromium crosslinking agent at 80 °C; and the gel system had good reservoir protection performance. The permeability recovery rate was introduced to evaluate reservoir protection performance. The permeability recovery rate of using the dynamic covalent borate ester bond crosslinking agent was superior to that of using the chromium crosslinking agent. Using the dynamic covalent borate ester bond crosslinking agent, when the fracture width was 1.6 mm, the temperature was 80 °C and the soaking time was 8 h, the permeability recovery rate was 90.32%; when the fracture width was 0.75 mm, the temperature was 80 °C and the soaking time was 8 h, the permeability recovery rate was 84.53%. Using the chromium crosslinking agent, when the fracture width was 1.6 mm, the temperature was 80 °C and the soaking time was 12 h, the permeability recovery rate was 59.58%; when the fracture width was 0.75 mm, the temperature was 80 °C and the soaking time was 12 h, the permeability recovery rate was 45.65%. The viscosity of the residual solution was low and was helpful for reservoir protection during loss-circulation control under the fractured granite reservoir condition. The novel degradable temporary plugging material can solve the loss-circulation problem of the ultra-deepwater fractured granite reservoir. In addition,

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the material can pave the way for the exploration and development of a vast amount of hydrocarbon resources in the South China Sea.

Keywords: deepwater; loss-circulation material; dynamic covalent crosslinking; thixotropy degradation; reservoir protection

1. Introduction

In the South China Sea, there are rich deepwater oil and gas resources, as shown in Figure 1. However, in Yongle deep and ultra-deepwater block, these deepwater resources develop fractured granite formations, the safe density window of drilling fluid is narrow and the loss-circulation problem is prominent and prone to cause drilling fluid to enter the formation through loss-circulation channel. This will not only lead to an extension of the drilling period, an increase in the drilling cost, and an influence on geological logging, reservoir pollution and productivity, but also lead to a series of serious downhole problems such as blowout, stuck pipes, borehole caving and borehole abandonment [1,2]. For fractured loss-circulation, the commonly used plugging method is the adoption of a polymer gel system. Polymer gel plugging technology refers to the use polymer gel to crosslink with each other to form a viscoelastic body, which has strong deformability and can enter the crack and hole space through extrusion deformation without being limited by the loss-circulation channel. In addition, the viscoelastic body can stay at the loss-circulation layer position. The plugging layer is formed by a curing reaction or volume expansion at the loss-circulation zone, which has the advantages of a low density of plugging slurry, adjustable gelling time and strong ability of plugging slurry to control filtration loss [3–8].

Figure 1. Deepwater exploration and development in the South China Sea.

The commonly used polymer gel plugging system usually has strong viscoelasticity and deformability [9], and it has been successfully applied in some areas, such as the fractured vicious loss ground layer in northeast Sichuan and other places. In 2018, Bai Yang et al. [10] put forward gel lost circulation slurry and lost circulation slurry for drilling. This slurry has the characteristics of a short static waiting time and quick effect. In addition, the slurry can quickly form a structure at the fracture of the loss-circulation formation. In 2020, Zhang Hongxu et al. [11] proposed a semi-interpenetrating network gel plugging material for oil and gas fields. This material has high gel-forming strength, high shear strength, high pressure bearing capacity and an excellent plugging effect at high temperatures. However, the degradation performance of these different types of gel systems has not been tested. For example, the degradation performance does not meet the requirements, the degradation efficiency in the reservoir is low and the degradation time is long, which is prone to cause serious damage to the oil and gas reservoir. In 2011, Zheng Yan et al. [12] proposed a kind of gel plugging material which is temperature-resistant, crosslinked and degradable. This solvent can form a structural gel with good shear dilution after dissolving, which is a liquid that can be pumped and flow without crosslinking, thus realizing fluid plugging and convenient construction. In 2017, Guo Yongjun et al. [13] proposed a non-crosslinked gel plugging system in which the non-crosslinked polymer forms gel through physical crosslinking, which has viscoelasticity. However, these non-crosslinked gel plugging systems have low strength and relatively weak pressure-bearing capacity. Polymer gel plugging technology has a wide range of applications at home, such as rapid gel formation for shallow wells [14], high-temperature gel for deep wells [15–18], gel formation for high-salt strata [19], timing gel formation [20], etc. Abroad, Sweatman et al. [21] developed a polymer gel loss-circulation plugging system (CP), which is formed by crosslinking two polymers. Lecolier et al. [22,23] developed a crosslinked polymer type bridge plugging material (CACP), which is mainly made of polymer gel and is filled with inert fibers, particles and other materials for bridging. When using the above CACP plugging material [24,25], mud cake in the loss-circulation channel should be removed. This will enable CACPs to play a better role in plugging leaks. In recent years, gel plugging technology has achieved a good application effect in some lost well sections in some areas, but many gel plugging agents still have some shortcomings, such as poor pumpability, easy dilution by the formation water, short gel formation time, poor temperature and salt resistance. Therefore, it is of great significance to develop a kind of gel plugging agent with high temperature resistance, salt resistance, high pressure capacity, good pumpability and controllable forming time for plugging the bottom hole loss-circulation.

Many gel systems in the past have been mainly based on ionic crosslinking and covalent crosslinking [26–28], where the polymer crosslinking structure is stable, difficult to degrade and causes great pollution and damage to oil and gas reservoirs. Therefore, the polymer crosslinking structure is not suitable for plugging operations in reservoirs but is mainly used for plugging in fractured drilling in non-reservoirs [29]. Therefore, aiming at the plugging problem of fractured granite formations in Yongle deepwater block, a gel material with high degradation efficiency was developed. The material has a controllable gel forming time and high gel forming strength and can achieve the goals of pressure-bearing plugging for fractured reservoirs and preventing loss-circulation. In addition, when the pH value of the external environment changes, the bond of this material is prone to break under the action of peroxide gel breaker. Moreover, the bond quickly degrades into small molecular substances so that it can be reverse displaced, thus realizing the plugging removal of reservoir fractures, reducing the damage to fractured oil and gas reservoirs and finally achieving the goal of both loss-circulation prevention and plugging and reservoir protection in drilling process of fractured oil and gas reservoirs. The gel plugging and rubber-breaking technology can seal the loss-circulation channel, has a strong bearing capacity, shorten the drilling cycle, save the cost of plugging and protect the oil and gas layer. In addition, other aspects have achieved the expected effect to achieve the desired purpose. The main objective of the research is to develop a dynamic covalent borate ester bond crosslinking agent which can be physically and chemically crosslinked with polyvinyl alcohol and xanthan gum in a controllable time by means of dynamic covalent bond crosslinking, resulting in a high-efficiency degradable gel with certain strength which can be used for plugging fractured formations of Yongle blocks.

2. Experiment

2.1. Experiment Materials

Polyvinyl alcohol (number-average molecular weight: 120,000), xanthan gum and a dynamic covalent borate ester bond crosslinking agent (organic chromium, sodium bisulfite, sepiolite fiber (fiber length: 2–4 mm), potassium persulfate, NaOH and HCl) were used as materials in the experiment. Among them, the dynamic covalent borate ester bond crosslinking agent was self-made in the laboratory. The preparation method was as follows: weigh monomer 1 dissolved in hot water at 70 °C; while stirring, sodium hydroxide was gradually added to make the mass ratio of monomer 1, sodium hydroxide and water 1 equal to 1:3.5. When the water was heated to 90 °C and stirred for 150 min, a light-colored transparent solution was obtained. When the temperature of the reaction solution was naturally cooled to 40 °C, a certain amount of monomer 2 was gradually added at a stirring speed of 300 rpm, and the mass ratio of component 1 to component 2 was kept at 1:1.5. The temperature of the reaction solution was heated to 95–98 °C, the stirring rate was slowly reduced to 100 rpm and the solvent was left to react for 180 min. At this time, the dynamic covalent borate ester bond crosslinking agent was prepared.

2.2. Experiment Apparatus

An electric mixer MYP19150, thermostat water bath HHWO-50L, HAAKE rheometer, and high-temperature and high-pressure pressure plugging apparatus were included in the experiment.

2.3. Preparation Method of Efficient Degradation Gel Plugging System

Principal. Under 90 °C temperature conditions, water-soluble polymer molecules and a crosslinking agent with a special structure can crosslink physically and chemically in 2 h through dynamic covalent bonding, forming a gel with high strength. The dynamic covalent borate ester bond crosslinking agent has a certain pH sensitivity to the external environment, so when the external environment pH changes, it can break the bond under the action of the peroxide breaker and quickly degrade into small molecules.

Preparation. In total, 1 L of fresh water or sea water was weighed, and 0.03% sodium bisulfite, 0.6% sepiolite fiber, 3.5% polyvinyl alcohol and 0.35% xanthan gum were added under the condition of stirring at room temperature. After the polymer was fully dissolved, 1–2% dynamic covalent borate bond crosslinking agent was added while stirring to obtain the efficient degradable gel plugging system. After the system was heated to set temperature, the polymer molecules and the dynamic covalent borate ester bond crosslinking agent formed a degradable gel system with a high-efficiency plugging ability. Based on the amount of dynamic covalent borate ester bond crosslinking agent, the gelation time can be controlled.

2.4. Performance of Plugging Agent

2.4.1. Gelation Time

Gel formation time is very important to the result of gel plugging. If the glue formation time is too fast, then the glue formation in the surface preparation or in the pipe string will not only fail to plug the leak but also bring trouble to the drilling operation. If the gel formation time is too long, then the gel liquid will still not be in gel formation, and all loss-circulation in the loss-circulation layer will lead to the failure of the plugging operation. Due to the difference of the loss-circulation zone in different wells, the time of gel flow into the leak zone is not fixed, and the effect of pump speed on loss-circulation is relatively small and limited. Therefore, the control gel system gel formation time, after flowing into the loss-circulation layer and quickly crosslinking glue, has a profound impact on the success of the plugging operation. Many leak plugging gel systems control the gel formation time by changing the crosslinking ratio. Although this method is effective, it also affects the gel strength and reduces the plugging pressure.

The gelation time can be determined by observing the gelation state of gel. Gelation time generally refers to the time it takes for the system to change from non-detectable gel (the viscosity of the system is equivalent to that of polymer, and gel formation cannot be observed) to fluid gel (most of the gel can flow to the other end of the bottle when the bottle is turned over). The final gelation time generally refers to the time it takes for the system to reach the final gel-forming strength from non-detectable gel. Sydansk et al. divided Gel Strength Codes (GSC for short) in 10 grades according to visual results [7].

2.4.2. Evaluation of Pressure-Bearing Capacity

A high-temperature and high-pressure plugging apparatus (200 °C, 150 Pa) was used to test the pressure-bearing plugging capability of the efficient degradable gel system. Artificial cores with different fracture widths were selected, and the cores were placed into the high-temperature and high-pressure pressure plugging apparatus. The plugging agent was added into a container, the pipeline was connected and the temperature was set. After the gel plugging material solidified, the drilling fluid was added, the pressurized air valve and lower liquid outlet were opened and a measuring cylinder was placed directly below liquid outlet. Then, the cores were left to slowly pressurize and stabilize for a period of time, and the volume of the discharge liquid was measured.

2.4.3. Test of Rheology

Flow performance determines whether the gel system can be successfully pumped into the ground and into the loss-circulation layer. Due to deep burial or other reasons in some reservoirs, the density of the drilling fluid is high, so the plugging gel should have an appropriate density to avoid complicated situations. At this time, the rheological property evaluation of the gel is more important.

An HAAKE rheometer was used to test the rheology of the efficient degradable gel plugging system. The pumpability and shear resistance of gel system were evaluated by the shear viscosity test. The shear rate range was 0.01~600 s^{-1}. The stress, strain and viscoelastic modulus of gel system were measured by the steady shear method.

2.4.4. Evaluation of Degradation Performance and Reservoir Protection Performance

The gel was broken by oxidant potassium persulfate. Oxidant solutions with different concentrations and different pH values were prepared. After the gel was aged at different temperatures for 72 h, it was fully crosslinked to form a high-strength gel. Then, it was soaked in an oxidant solution to observe the gel breaking effect. In the end, the viscosity of the residual liquid was measured by an HAAKE rheometer.

The reservoir protection ability of the gel plugging material was tested by a high-temperature and high-pressure pressure plugging apparatus. Cores were selected with different permeabilities and placed into the high-temperature and high-pressure pressure-bearing plugging apparatus. The plugging agent was added into apparatus container, and after the gel plugging material solidifies, the cores were removed, and the core permeability was measured by gas measurement. Then, the blocked core was soaked in 8.0% oxidant potassium persulfate solution, a small amount of dilute hydrochloric acid was dropped to adjust the pH value of the solution and the core was removed from the solution after soaking for a certain time. The permeability recovery rate was calculated according to following formula:

$$\omega = K_1 / K_2 \times 100 \quad (1)$$

where K_1, permeability after plugging (μm^2); K_2, permeability before plugging (μm^2).

3. Results

3.1. Gel Gelation Time

In accordance with the temperature field of ultra-deepwater granite reservoir in Yongle block, the temperature of its main reservoir layer can be estimated to be about 80~106.5 °C. According to the characteristics of ultra-deepwater drilling technology, in order to ensure drilling safety, the gelation of the crosslinked polymer gel at 60~110 °C was evaluated. In the experiment, the traditional organic chromium crosslinking agent was used instead of the dynamic covalent borate ester bond crosslinking agent as a control experiment, and the crosslinking effect of the dynamic covalent borate ester bond crosslinking agent was compared and evaluated. The gel plugging system formula was: water +0.03%

sodium bisulfite +0.6% sepiolite fiber +3.5% polyvinyl alcohol +0.35% xanthan gum +1–2% crosslinking agent. The results are listed in Table 1.

Table 1. Effect of Different Factors on Gelation Time.

Crosslinking Agent	Density (g/cm^3)	Temperature/°C	Gelation Time/min
1% dynamic covalent	1.03	60	108
borate ester bond	1.03	80	105
crosslinking agent	1.03	110	72
2% dynamic covalent	1.03	60	104
borate ester bond	1.03	80	71
crosslinking agent	1.03	110	65
1% chromium crosslinking agent	1.02	80	72
2% chromium crosslinking agent	1.04	80	63

It can be concluded that the gelation time of gel system will decrease with the increase of temperature. This is because the increase of gel viscosity after crosslinking is mainly due to the formation of the network structure, and the increase of temperature strengthens the hydrogen bond with lower bond energy or some chemical bonds in the network structure. However, with the increase of the amount of the crosslinking agent, the gelation time also clearly decreases, which is due to the increase of the amount of the crosslinking agent, the increase of crosslinking with the active groups in the polymer liquid molecules and the faster formation of the gelation structure. This shows that the gelation time of the gel plugging system can be effectively controlled by adjusting the amount of the crosslinking agent. In the temperature range of 60–110 °C, the gel plugging system with the dynamic covalent borate ester bond crosslinking agent was adopted, and the gelation time could be controlled between 65–108 min. However, the gelation time of the gel system using the traditional organic chromium crosslinking agent at 80 °C was between 63 and 72 min. Compared with the dynamic covalent borate ester bond crosslinking agent, it can be found that the latter agent can appropriately delay the crosslinking reaction rate, which can smoothly pump the gel to plugging target layer during the drilling plugging operation. When reaching the target layer, the gel will be further crosslinked to generate high-strength gel to achieve the plugging purpose.

In the literature [4], the gelation rate increased rapidly with increasing temperature, which means that the gelation time decreased with increasing temperature. In the literature [18], with the increase of the amount of crosslinking agent, the gelation time was gradually shortened. At a higher temperature, the gelation time was generally shorter.

3.2. Plugging Performance

The plugging performance of gel plugging materials for micron-sized fractures was analyzed using a plugging evaluation apparatus. The fracture width of the core was selected by referring to the data analysis of imaging logging data of granite reservoir in the Yongle block of South China Sea, which was set to 1 mm, 2 mm, 3 mm and 3.5 mm, respectively, and the loss-circulation situation corresponding to different fracture width was analyzed. The gel plugging system formula was: water +0.03% sodium bisulfite +0.6% sepiolite fiber +3.5% polyvinyl alcohol +0.35% xanthan gum +1.5% dynamic covalent borate bond crosslinking agent (the same below), and the experiment temperature was 110 °C.

Table 2 shows the plugging performance of the gel plugging materials. It can be concluded that the efficient degradable gel system could effectively block the fractures with different widths. When the fracture width was 1 mm, the bearing capacity could reach 7.2 MPa. When the fracture width increased to 2 mm, the pressure bearing capacity decreased slightly to 7.1 MPa. For the 3 mm and 3.5 mm cracks, the bearing capacity was reduced to 6.5 MPa and 5.8 MPa, respectively, which still represents good bearing capacity. This shows that under the action of the dynamic covalent borate ester bond crosslinking agent, the gel with a network structure and certain pressure-bearing capacity can be crosslinked in fractures with different widths. Based on this, it can be concluded that the high-efficiency degradable gel material has fine fracture plugging performance and adaptability and can effectively plug the fractured reservoirs with width of 1.0~3.5 mm.

Table 2. Plugging Performance of Efficient Degradable Gel Plugging Material for Fractures with Different Widths.

Fracture Width/mm	Pressurization Time/min	Maximum Pressure/MPa	Plugging Performance
1.0	20	7.2	Plugging Success
2.0	15	7.1	Pressure bearing of 6.7 MPa
3.0	16	6.5	Pressure bearing of 6.2 MPa
3.5	18	5.8 (Broken)	Pressure bearing of 5.8 MPa

According to the characteristics of ultra-deepwater drilling technology and the distribution of the temperature field, the influence of the ultra-deepwater drilling temperature field on the gel system was analyzed. An artificial core with a fracture width of 1.5 mm was selected to test the plugging performance of the highly efficient degradable gel material at 60~110 °C. The results are shown in Table 3. It can be concluded that the plugging pressure-bearing capacity of the efficient degradable gel plugging material was above 7.1 MPa at different temperatures, and the pressure-bearing capacity at 110 °C was 7.1 MPa, which indicates that the high-efficiency degradable gel plugging material has good temperature resistance and can meet the plugging requirements of granite in Yongle block.

Table 3. Plugging Performance of Efficient Degradable Gel Plugging Materials under Different Temperatures.

Temperature/°C	Fracture Width/mm	Pressurization Time/min	Maximum Pressure/MPa	Plugging Performance
60	1.5	15	8 (Broken)	Pressure bearing of 8 MPa
80	1.5	13	8 (Broken)	Pressure bearing of 8 MPa
85	1.5	19	7.2	Plugging Success
95	1.5	20	7.2	Plugging Success
110	1.5	15	7.1	Plugging Success

3.3. Rheology Test

The plugging agent needs to have fine rheology in the process of pumping. Therefore, in this experiment, the rheology of the gel plugging material at different temperatures and cooling time after preparation was tested so as to simulate the situation that polymer gel encountered different formation temperatures in actual pumping. It was found that, although the viscosity of the gel material tended to increase with the increase of cooling time, the rheological variation of the gel plugging material was not significant within 1 h, and fine rheology was maintained. Moreover, with the increase of shear rate, the shear viscosity decreased continuously, showing the characteristics of pseudoplastic fluid, which indicates that the gel had fine shear dilution and thixotropy. The above characteristics are beneficial to the proper pumpability of gel plugging materials. It was found that low temperatures will slightly increase the initial viscosity of the gel, but with the increase of shear rate, the viscosity decreases rapidly, which is close to that of the gel at 40 °C at a higher shear rate. However, the viscosity of gel material increases more obviously at high temperatures, but it still has strong shear dilution and fine thixotropy. All of these findings are beneficial to the pumping of gel plugging materials.

3.4. Evaluation of Anti-Contamination Performance

After the gel is injected into the formation fracture, it will make contact with the drilling fluid from the downhole, resulting in the formation water or oil from the inside of the formation before and after gelling. Therefore, it is necessary to investigate the influence of the drilling fluid, the formation water or oil on the gelling performance and the bearing strength of the gel so as to analyze the capability of the gel system to resist the contamination of drilling fluid, formation water and oil.

The drilling fluid was added on the top of the gel system, and the volume ratio of the gel system to the drilling fluid was 1:1. The drilling fluid used was from the ultra-deepwater block of the South China Sea: fresh water + 15% NaCl + 6% KCl + 1.0% filtration reducer PF-FLOTROL + 0.3% PF-PLUS + 0.3% PF-XC + 0.7% anti-bit balling lubricant PF-HLUB + 0.7% PF-UHIB + 0.7% coating agent. After preparation, the drilling fluid was placed into an aging tank and put it in an oven at 80 °C for aging. Then, its stress variation curve and elastic modulus were tested after fully aging for 24 h. The results showed that the gel system still had good shaping after 24 h of drilling fluid contact and immersion. The elastic modulus was about 9000 Pa, indicating that the gel system has a fine anti-drilling fluid contamination capability, which can ensure the downhole gel-forming effect and pressure-bearing capacity.

The reservoir water and oil were injected into the upper part of the fully solidified gel system to simulate the contact process between gel and the reservoir water and oil during operation, and then the stress variation was tested after aging in an oven at 80 °C for 48 h. The composition of formation water and oil refer to the South China Sea deepwater block, in which the formula of formation water is: fresh water + 6% NaCl + 3% KCl + 0.12% $MgCl_2$ + 0.8% $CaCl_2$; Oil is taken from Well Y in South China Sea. The experiment results indicate that under different test conditions, the gel systems have good gel-forming properties and thermal stability; moreover, the elastic characteristics and mechanical properties of the solidified gel system were still at a high level after long-term contact with formation water.

3.5. Evaluation of Degradation Performance of Gel Materials

For the completion operation of the fractured reservoir, the gel plugging material needs to be broken after temporary plugging and loss-circulation prevention. The high-efficiency degradation gel system can be broken by the chemical method. The gel breaking time and residual viscosity of different gel systems at different temperatures and pH values were tested. In the experiment, the traditional organic chromium crosslinking agent was used instead of the dynamic covalent borate ester bond crosslinking agent as a control. It can be seen that the gel breaking time of the high-efficiency degradation gel system at different temperatures was lower than that of the gel material with organic chromium as the crosslinking agent, which indicates that the high-efficiency degradation gel system has higher gel breaking rate and efficiency. As the gel breaking time of the system decreases with the solution pH, the gel breaking rate and efficiency of the system will be further accelerated, showing fine pH sensitivity. In 6% peroxide solution with a pH of 4.0, the gel was completely broken at 6.1 h, indicating that the gel system formed by the dynamic covalent borate ester bond crosslinking agent could effectively degrade under weak acid conditions, reduce the damage to fractured oil and gas reservoirs and realize the reservoir protection in the process of plugging fractured oil and gas reservoirs.

3.6. Evaluation of Gel Material Reservoir Protection Performance

To test the reservoir protection effect of the gel system, permeability recovery before and after plugging was tested, and the results are shown in Table 4. From the experimental results, it can be concluded that the efficient degradation gel system had a higher permeability recovery rate than the gel system prepared by organic chromium as the crosslinking agent. For the core with a fracture width greater than 1 mm, the permeability recovery rate could reach more than 88%, while for the core with a fracture width of 0.75 mm, the permeability recovery rate was 84.53%. This could be attributed to the small micro-cracks.

In addition, the contact surface between the gel invaded by the core and the gel breaker was small, and a small amount of gel material after gel breaking remained in the tiny micro-cracks, but it still had a high permeability recovery rate. With the same fracture width and the same temperature, the permeability recovery rate of the dynamic covalent borate ester bond crosslinking agent was significantly higher than that of the chromium crosslinking agent. The experiment results show that the highly effective degradation gel system had a better reservoir protection effect.

Table 4. Recovery of Permeability.

Crosslinking Agent	Fracture Width/mm	Temperature/°C	Soaking Time/h	Permeability before Plugging/10^{-3} μm^2	Permeability after Plugging/10^{-3} μm^2	Permeability Recovery Rate/%
Dynamic covalent borate ester bond crosslinking agent	1.6	80	8	7025.342	6345.213	90.32
	1.4	80	8	6324.159	5626.564	88.96
	1.2	100	8	5964.325	5436.258	91.14
	0.75	80	8	1725.323	1458.351	84.53
Chromium crosslinking agent	1.6	80	12	7055.125	4203.426	59.58
	0.75	80	12	1720.545	785.346	45.65

4. Field Deployment

The fractured granite formations in the deep and ultradeep water wells of Yongle block in the South China Sea led to loss-circulation during the drilling process. In the early stage, the conventional plugging gel was not effective during drilling of the target formation in three wells, resulting in a large amount of drilling fluid loss-circulation, which not only seriously restricted the drilling efficiency but also increased the drilling cost. Well YL-5 was taken as an example to illustrate the optimized plugging effect.

The plugging gel was prepared in the mud pit in advance, and its formula was: water + 0.03% sodium bisulfite + 0.6% sepiolite fiber + 3.5% polyvinyl alcohol + 0.35% xanthan gum + 1–2% crosslinking agent. Its properties were: density 1.06 g/cm^3, plastic viscosity 16 MPa·s and dynamic shear force 16 Pa. During the drilling of the granite reservoir in the 311.15 mm hole of Well YL-5, downhole loss-circulation occurred, and the maximum loss-circulation rate monitored by the trip tank was 90 m^3/h. Then, 20 m^3 of efficient degradable plugging gel was pumped into the annulus through the standpipe and drill pipe. After tripping out 200 m, the pump pressure of the circulating drilling fluid increased, and the pump pressure increased from 6.2 MPa to 9.6 MPa. There was no continuous loss-circulation of drilling fluid, and the plugging was successful. In the process of plugging, 2 tons of inhibitor PF-UHIB and 4 tons of lubricant PF-HLUB were added simultaneously to the active pit to improve the inhibition and lubrication of the drilling fluid in the circulating system. At the same time, a solution with the same concentration as the plugging material of drilling fluid in the circulating system was added to the active pool in a few cycles, which played a role in maintaining the stability of drilling fluid performance.

5. Conclusions

1. A dynamic covalent borate ester bond crosslinking agent was developed, which can be physically and chemically crosslinked with polyvinyl alcohol and xanthan gum in a controllable time by means of dynamic covalent bond crosslinking, resulting in a high-efficiency degradable gel with certain strength, which can be used for plugging fractured formations.
2. The efficient degradable gel had fine rheology at room temperature, as well as a rheological property, shear dilution property and thixotropy at 25 °C for 1.0 h, which is prone to perform pump injection.
3. The gelation time is related to the type of crosslinking agent, the amount of crosslinking agent and the temperature. With the increase of temperature, the gelation time of gel system decreased. With the increase of the amount of the agent, the gelation time of gel system decreased. The gelation time was 105 min when using the 1%

dynamic covalent borate ester bond crosslinking agent at 80 °C; the gelation time was 72 min when using the 1% dynamic covalent borate ester bond crosslinking agent at 110 °C; the gelation time was 71 min when using the 2% dynamic covalent borate ester bond crosslinking agent at 80 °C; the gelation time was 65 min when using the 2% dynamic covalent borate ester bond crosslinking agent at 110 °C; the gelation time was 72 min when using the 1% chromium crosslinking agent at 80 °C; the gelation time was 63 min when using the 2% chromium crosslinking agent at 80 °C.

4. The efficient degradable gel system had a fine plugging effect on artificial cores with different widths (1.0–3.5 mm). For cores with fracture widths of 3.5 mm, the pressure bearing could reach 5.8 MPa below 110 °C. The gel system had pH sensitivity. In a gel breaker solution with a pH of 4 and oxidant potassium persulfate concentration of 6%, the gel material was completely broken after 6.1 h, and the viscosity of the residual liquid was low. After high-efficiency degradation, the permeability recovery rate could reach 91%.
5. The gel system had good reservoir protection performance. The permeability recovery rate was introduced to evaluate reservoir protection performance. The permeability recovery rate of using the dynamic covalent borate ester bond crosslinking agent was superior to that of using the chromium crosslinking agent.

Using the dynamic covalent borate ester bond crosslinking agent, when the fracture width was 1.6 mm, the temperature was 80 °C and the soaking time was 8 h, the permeability recovery rate was 90.32%; when the fracture width was 0.75 mm, the temperature was 80 °C and the soaking time was 8 h, the permeability recovery rate was 84.53%.

Using the chromium crosslinking agent, when the fracture width was 1.6 mm, the temperature was 80 °C and the soaking time was 12 h, the permeability recovery rate was 59.58%; when the fracture width was 0.75 mm, the temperature was 80 °C and the soaking time was 12 h, the permeability recovery rate was 45.65%.

The gel system using the dynamic covalent borate ester bond crosslinking agent can better solve the plugging problem of fractured granite reservoir in Yongle deepwater block. There are some differences between the laboratory simulation experiment and the real leak zone, and the specific well conditions are also different. According to the actual downhole situation, the best plugging effect can be achieved by adjusting the gel formula. The gelation time was optimized by adjusting the amount of crosslinking agent. Further strengthening the field application research is suggested.

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