Research Article

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A self-breaking supramolecular plugging system as lost circulation material in oilfield

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Abstract: Lost circulation is a frequently encountered problem during workover operations of a low-pressure reservoir. Many lost circulation materials (LCM) have been used to solve the problem, but various disadvantages still exist, for example, oil-soluble materials are easy to get stuck in the pipe string as the temperature drops and gel time and gel strength of the cross-linking gel systems are difficult to control in the occasion of inadequate stirring. A self-breaking supramolecular plugging system used to control lost circulation of workover operations is developed, and it can encounter the aforementioned disadvantages of the traditional LCM. The system forms a space grid structure by non-covalent bonds between the molecules without adding a cross-linking agent. Sand beds plugged with the supramolecular plugging system had a pressure bearing capacity of 4.5 MPa. The self-breaking rate of the supramolecular system was 100% after 7 days at a temperature of 120°C. The core permeability recovery of the self-breaking liquid was 91.9%, indicated that the plugging system is compatible of the reservoir. The supramolecular plugging system has been used in four wells in the Jidong oilfield of East China. Field practice showed that the supramolecular LCM can effectively control lost circulation at different rates during workover operations. The increase in the daily fluid after operations indicated that the slurry has not damaged the reservoir.

Keywords: supramolecular plugging system, lost circulation material, lost circulation, self-breaking, temporary plugging operation

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1 Introduction

With the development of oilfield exploration and development, the formation pressure decreases rapidly and circulation loss of the workover fluid is serious [1-4]. Previously, many plugging methods were used to prevent the plug leaks, such as oil-soluble resin [5,6], composite shielding temporary plugging [7–10], gel plugging agent [11], and microbubble workover fluid [12]. However, oil-soluble materials are greatly affected by temperature, so they are easy to get stuck in the pipe string due to equipment failure, temporary stop of workover operation, and other reasons, and the recovery time of oil output of most wells is very long. Cross-linking gel systems are composed of a polymer and a cross-linking agent, which are connected by covalent bond to form a network structure. Gel time and gel strength of the cross-linking gel systems are difficult to control with inadequate stirring. Microbubble workover fluid is foamed with surfactant, and the stable time is short under high temperature. The working fluid density can be adjusted to achieve the effect of reducing the column pressure and controlling the circulation loss only in a short time.

To overcome the shortcomings of the above leakage prevention and plugging technology, a supramolecular plugging system is developed, which is based on the supramolecular chemistry theory [13,14]. The system forms a complex and ordered molecular aggregate through the weak interaction of non-covalent bonds between molecules. It has the following characteristics: no need to add crosslinking agent, high temperature resistance, simple preparation, and low cost. The initial phase of the solution is a low viscosity fluid, which is easy to pump into wellbore. At 90–120°C, the viscosity increases and the leakage layer is sealed. After the operation, the supramolecular plugging gel can break automatically without adding a gel breaker [1,14].

2 Materials and methods

2.1 Experiment equipment

The following equipment was used in the experiments: (1) FANN 35SA coaxial cylinder rotational viscometer,

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(2) Hakke RS6000 high pressure and high temperature (HPHT) rheometer, (3) HPHT Filter Press with a 175 ml slurry cup, (4) America Core Company formation damage system 800 for permeability recovery test, and (5) JY2004 precision balance with a readability of 0.01 g.

2.2 Materials

Supramolecular plugging mixtures are composed of four additives: distilled water, polypentadienamide (PPDA), polydiethyl diallyl ammonium chloride (PDAC), and sodium chloride (NaCl). PPDA is the main agent of the supramolecular gel. During the gel breaking performance determination, a gel breaking agent, ammonium persulfate, was introduced to the plugging mixtures.

2.3 Plugging solution preparation

Supramolecular plugging solutions were prepared by the following procedure:

- (1) Place the beaker on the precision balance.
- (2) Add the required amount of distilled water.
- (3) Add the required amount of PDAC and stir the solution with an electric stirrer at 600 rpm for at least 1h at room conditions.
- (4) Add the required amount of NaCl and stir the solution with an electric stirrer at 200 rpm for 20 min at room conditions.
- (5) Add the required amount of PPDA and stir the solution with an electric stirrer at 200 rpm for 40 min at room conditions.

2.4 Rheological determination

Gel rheological characteristic is an important parameter while selecting gel compositions for specific operations. The gel mixtures were prepared by the aforementioned steps. Then, the mixtures were poured into the viscometer cup and the cup was placed on the viscometer. The rotational speed was adjusted in the order of 600, 300, 200, 100, 6, and 3 rpm, then the readings were recorded.

2.5 Yield stress determination

The gel mixtures were prepared according to the procedure given in Section 2.3. Then, the supramolecular

plugging system was put into an aging tank for different time (0, 4, 8, 12, 16 and 32 h) at 120°C. Yield stresses were measured by Hakke RS6000 HPHT rheometer.

2.6 HPHT plugging performance determination

The gel mixtures were prepared according to the procedure given in Section 2.3. The HPHT Filter Press apparatus was used to evaluate the plugging performance of the supramolecular system. The sand-filled pipe was filled with 100 g sand of 40-70 mesh. The plugging solution was injected into the cup and aged for 4 h, then the plugging experiment was conducted at 120°C.

2.7 Gel breaking performance determination

2.7.1 Gel breaking efficiency test

The plugging mixtures without gel breaker were prepared according to the procedure given in Section 2.3. In addition, the solutions adding a gel breaker with the concentration of 10% main agent are prepared. The gel solutions were aged at 120°C for 16 h, then the gel qualities were tested once a day for 7 days until gels were completely disappeared. The gel breaking efficiency was calculated according to the mass change rate.

2.7.2 Core permeability recovery test of gel breaking liquid

The core permeability recovery test was conducted to assess the degree of damage. First, the reservoir core was displaced by the gel liquid after complete breaking for 10 PV. Then, the core was displaced by standard brine for 5 PV. The permeability recovery was calculated according to the permeability change rate.

Ethical approval: The research conducted is not related to either human or animal use.

3 Results and discussion

3.1 Rheological analysis

3.1.1 Effect of PPDA concentration on the rheology

The rheological experiments were performed by changing the PPDA concentrations in the order of 1.5%, 2%, and 2.5%,

Table 1: Rheological data of the gels with different PPDA concentrations

Concentration (%)	FL _{API} (ml)	AV (mPa s)	PV (mPa s)	YP (mPa s)	YP/PV (mPa s)	Gel (Pa)
1.5	20	45	15	28.80	1.92	4.60
2.0	5	57.5	25	31.20	1.25	11.75
2.5	1.5	92.5	15	74.40	4.96	18.40

FL, filter loss; AV, apparent viscosity; PV, plastic viscosity; YP, yield point.

while the concentration of PDAC was kept constant as 0.09% and NaCl 5%. As shown in Table 1, with the increase in the PPDA concentration, the viscosity of the gels increased and the American Petroleum Institute (API) filtration loss decreased. The PPDA concentration of 2.0% and 2.5% can meet the needs of plugging operation.

3.1.2 Effect of PDAC concentration on the rheology

The rheological experiments were performed by changing the PDAC concentrations in the order of 0.06%, 0.09%, and 0.12%, while the concentration of PPDA was kept constant as 2% and NaCl 5%. As shown in Table 2, the PDAC concentration has little effect on the rheological behavior of the gels.

3.1.3 Effect of NaCl concentration on the rheology

The rheological experiments were performed by changing the NaCl concentrations in the order of 3%, 5%, and 10%, while the concentration of PPDA was kept constant as 2% and PDAC 0.09%. As shown in Table 3, the API filtration loss was minimum, while the NaCl concentration was 5%.

According to the above experimental results, the recommended formula for field applications is 2.0% PPDA, 0.09% PDAC, and 5% NaCl, and this formula is followed in the rest of the study. The initial viscosity of the gel system is 1,650 mPas, and it appears as a fluid that flows easily. The gelatinizing viscosity is 17,750 mPas, and it appears as a semisolid gel with high viscoelasticity.

3.2 Yield stress analysis

Figure 1 shows that the yield stress of the supramolecular plugging system increased as the aging time increased at 120°C. The yield stress was maximum at 16 h, and there was no obvious yield at 300 Pa. Figure 2 indicates that the gel after aging 16 h has the maximum gelatinizing strength. The yield occurred after 32h, indicating that the gelatinizing strength began to decline after 32 h but still had a high yield stress.

Table 2: Rheological data of the gels with different PDAC concentrations

Concentration (%)	FL _{API} (ml)	AV (mPa s)	PV (mPa s)	YP (mPa s)	YP/PV (mPa s)	Gel (Pa)
0.06	6	60.5	33	26.40	0.80	7.15
0.09	5	57.5	25	31.20	1.25	11.75
0.12	5	63.5	33	29.28	0.89	7.67

FL, filter loss; AV, apparent viscosity; PV, plastic viscosity; YP, yield point.

Table 3: Rheological data of the gels with different NaCl concentrations

Compositions (%)	FL _{API} (ml)	AV (mPa s)	PV (mPa s)	YP (mPa s)	YP/PV (mPa s)	Gel (Pa)
3	11	55	28	25.92	0.93	13.29
5	5	57.5	25	31.20	1.25	11.75
10	15	61	37	23.04	0.62	9.20

FL, filter loss; AV, apparent viscosity; PV, plastic viscosity; YP, yield point.

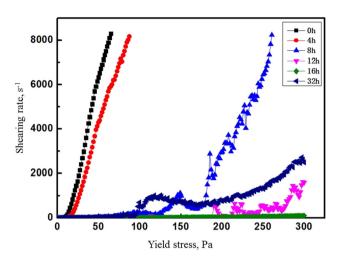


Figure 1: Yield stress curve at different time.

3.3 HPHT plugging performance evaluation

The results of HPHT plugging performance are shown in Table 4. It is obvious that the gel mixtures can withstand

Table 4: Results of plugging performance evaluation of the supramolecular plugging agent under 120°C

Pressure (MPa)	Stand-up pressure time (min)	Water loss (ml)	
2	10	13.5	
2.5	10	14	
3	10	15.5	
3.5	10	17	
4	10	17.5	
4.5	10	18	

pressure up to 4.5 MPa. The water loss of the plugging agent was 18 ml when the pressure was 4.5 MPa. The filtration liquid was nonviscous, that is, to say the water within the system was extruded. After the tests, the sand beds were taken out and examined. It was found that the gels were evenly attached to the upper part of the sand body with strong wall adhesion and no gel inside the sand body (Figure 3). This indicates that the supramolecular plugging agent has good plugging performance.

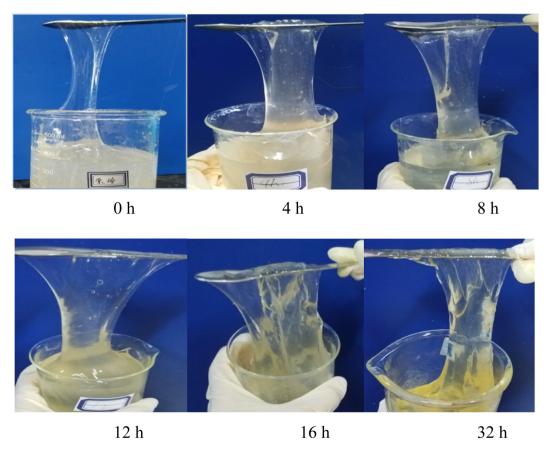


Figure 2: Appearance of the supramolecular plugging system at different aging time.







Figure 3: Appearance of the gel and cross section of the sand bed after HPHT filter press experiment.

Table 5: Results of gel breaking performance evaluation experiment at 120°C

Time (h)	Without gel	breaker	With gel breaker		
	Gel weight (g)	Gel breaking efficiency	Gel weight (g)	Gel breaking efficiency	
0	362	0	376	0	
24	360	2.17%	62	83.15%	
48	320	13.04%	8	97.83%	
72	265	27.99%	0	100.00%	
96	167	54.62%	_	_	
120	87	76.36%	_	_	
144	28	92.39%	_	_	
168	0	100.00%	_	_	

3.4 Gel breaking performance evaluation

3.4.1 Gel breaking efficiency analysis

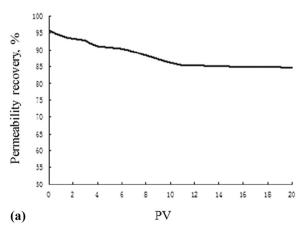
Table 5 indicates that the self-breaking efficiency of the gel was 92.39% after 6 days, and the gel completely broke 7 days later. The addition of a gel breaker with a concentration of 10% of the main agent can accelerate the breaking process, and the gel breaking efficiency was 97.83% after 2 days. Therefore, operation period in 5—7 days of various operations can be conducted without breaking agent.

3.4.2 Core permeability recovery analysis

The permeability recovery of the self-breaking solution reached 84.7% after 10 PV displacement (Figure 4(a)). The permeability recovery of the standard brine reached 91.9% after 5 PV displacement (Figure 4(b)). Therefore, the gel breaking solution has caused little damage to the reservoir and can protect the reservoir very well.

4 Field application

Supramolecular plugging agent was applied in four pump checkout wells with low pressure and leakiness formation (Table 6). Circulation loss was completely eliminated by injecting 5–10 m³ plugging solution into each oil well. The



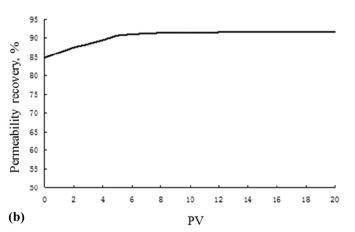


Figure 4: Permeability recovery curve of the gel breaking solution to reservoir core. (a) Displacement of self-breaking solution. (b) Displacement of standard brine.

Table 6: Field application effect of the supramolecular plugging agent on pump checko	out wells
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Oil well	Operation date	Injecting volume (m ³)	Before operation		After operation	
			Fluid output (m ³ /d)	Oil output (t/d)	Fluid output (m ³ /d)	Oil output, (t/d)
G15-12	2017/12/27	10	1.1	0.01	3.4	0.03
G66-28	2018/1/25	10	1.1	0.01	21.5	0.21
G62-40	2018/3/17	12	1	0.06	13.11	0.07
G66-32	2018/5/9	8	2.4	0.04	18.1	2.99

gel broke automatically after pump checkout operation and flowed out of wellbore. The average daily fluid output increased to 12.6 m³, and the average daily oil output increased to 0.8t, indicating that the supramolecular plugging agent did not pollute the reservoir.

5 Conclusions

- (1) The supramolecular plugging agent forms a spatial network structure by non-covalent bonds between the molecules. The gel has low initial viscosity and is easy to flow and easy to pump into wellbore.
- (2) After gelling, the supramolecular plugging agent appears a semisolid gel with high viscoelasticity and high strength. The supramolecular gel can effectively seal sand contact surface. At 120°C, the sand bed bearing capacity of the gel can reach 4.5 MPa. It can effectively plug 90-120°C low-pressure and leaky formation.
- (3) The supramolecular plugging agent can break itself after 6 days at 120°C. The addition of a gel breaker with a concentration of 10% as the main agent, the breaking time declines to 3 days, and the gel breaking liquid has caused little damage to the reservoir.
- (4) The agent was used for pump checkout wells of low pressure and leakiness formation in field application. After temporary plugging operation, wellbore circulation can be established and fluid and oil output increased after the operation. The technological ideas and innovation of the self-breaking supramolecular plugging agent can be a valuable reference and demonstration effect for the exploration and development of low pressure and leakiness reservoirs in China and around the world.

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Conflicts of interest: The authors declare that they have no conflicts of interest.

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