Study on ammonium-promoted phenol-formaldehyde-based gel for enhanced oil recovery and its seepage characteristics in porous media

Hongshen Wang[1], *Jinlin* Wang[1], *Duansheng* Shi[1], *Lei* Yang[1], *Ruoshui* Han[1], *Fujian* Yin [1], *Yimin* Han[1], and *Siqi* Liu[2*]

[1]CNOOC Ener Tech-Drilling & Production Co., Tianjin, 300452, China;
[2] Petroleum Engineering School, Southwest Petroleum University, Chengdu, Sichuan, 610500, China.

Abstract. The phenol-formaldehyde crosslinker has low reactivity at low temperature, and is not easy to occur crosslinking reaction. In order to solve this problem, a kind of ammonium-promoted phenol-formaldehyde-based gel profile control agent was constructed which has the reactivity at low temperature. The basic formula is 0.30%~0.60%polymer, 0.01%resorcinol, 0.60% phenol-formaldehyde crosslinker and 0.10% ammonium salt. The results showed that the final gelling time was 6 days at 65℃, and the final gelling strength could reach G grade. In response to the problem that the plugging characteristics of ammonium-promoted phenol-formaldehyde-based gel are still unclear, the seepage characteristics of the phenol-formaldehyde-based gel in porous media are revealed by physical simulation of sand-pack. The research shows that the plugging rate of porous media with permeability of 2000 mD reaches 98%, the breakthrough pressure gradient is greater than 1.35 MPa/m.
Keywords: Polymer Gel; Ammonium-promoted; Enhanced Oil Recovery; Porous Media.

1 Introduction

Polymer gel is one of the most commonly used profile control agents in oilfield, mainly obtained by cross-linking reaction between polyacrylamide and cross-linking agent. The cross-linking agent controls the gel-forming performance and application temperature range of the polymer gel[1-3]. At present, the commonly used crosslinking agents are mainly divided into organic crosslinking agents and inorganic crosslinking agents. Inorganic polyvalent metal ion crosslinking system has been gradually withdrawn from application, replaced by organic crosslinking agent with less environmental pollution. Phenol-formaldehyde crosslinker is widely used in high-temperature reservoir dissection and water plugging because of the characteristics of temperature and salt resistance[4]. However, the

* Corresponding author: 297047698@qq.com

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crosslinking mechanism between phenol-formaldehyde crosslinker and polyacrylamide is covalent bonding, which requires high activation energy for reaction. At low temperature (30℃~80℃), the cross-linking between phenol-formaldehyde crosslinker and polyacrylamide is slow, and even the reaction cannot occur[5-6]. In this paper, we introduce a low-temperature reactive coagulant to promote the rapid gelation of phenol-formaldehyde crosslinker and polyacrylamide under low temperature conditions[7].

2 Experimental studies

2.1 Materials and Equipment

The effective content of the phenol-formaldehyde crosslinker is greater than 20%. The relative molecular weight of polymer is 300~500×10^4**,** and the degree of hydrolysis is 80%.The effective contents of ammonium coagulant and resorcinol were greater than 99%.High temperature and high pressure rheometer and multi-functional core displacement device were used in the experiment.

2.2 Experimental methods

2.2.1 Preparation of gel system

Firstly, the polymer mother liquor was stirred for 40 min under an electric stirrer at 400 r/min to ensure its full dissolution. Subsequently, resorcinol and coagulant were added to the phenol-formaldehyde crosslinker master solution according to the mass percentage, stirred with a glass rod to dissolve them fully, and then poured them into the polymer mother liquor and continued to stir 20 min to prepare the gel system. The relationship between gel formation time and gel formation strength was observed according to the Sydansk code.

Table 1. Composition of gel system.

Number	Polymer (%)	Resorcinol (%)	Crosslinker (%)	Coagulant (%)
1	0.3	0.05	0.6	0.1
2	0.4	0.05	0.6	0.1
3	0.5	0.05	0.6	0.1
4	0.6	0.05	0.6	0.1

As shown in Fig 1, the hydroxylmethyl functional group (-CH2OH) on the phenolic resin crosslinking agent reacts with the amino group (-CONH2) on the polymer molecular chain to generate phenolic gel with three-dimensional structure. By adding coagulants with reactive activity at low temperature, such as ammonium salt coagulants used in this paper, among which ammonium cation (NH^{4}_{+}) promotes the occurrence of cross-linking reaction in the form of ion adsorption and increasing active reaction groups.

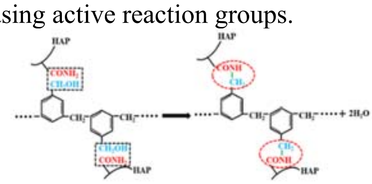


Fig. 1. Schematic diagram of gel reaction mechanism.

2.2.2 Gel modulus of elasticity determination

The variation of the elastic modulus of the gel samples with shear frequency at 0~15.8 Hz was tested, and the test temperature was 25°C.

2.2.3 Porous-media-seepage characteristics

The sand-pack was compressed by 60 quartz sand at 10MPa pressure. Firstly, the sand-pack was saturated with water at a rate of 1.0ml/min.

Table 2. Basic parameters of sand-pack.

Number	Dry weight (g)	Wet weight (g)	Pore volume (cm^3)	Porosity (%)
1	3053.6	3118.4	64.8	33.01
2	3049.5	3121.2	71.7	36.52
3	3011.6	3077.9	66.3	33.77
4	3028.5	3102.4	73.9	37.64

Secondly, the gel systems were injected into the sand-pack until 0.30 pore volume at the same rate of 1ml/min. Then, the sand pack with gel system was aged at 65℃. After aging for 6 days, the injection water was used to carry out water flooding at 1ml/min. The pressure difference between the two ends of the sand pack was recorded when the first drop of liquid flows from the outlet end of the sand pack, which is the breakthrough pressure (P_b) of the gel.

3 Experimental results and analysis

3.1 Performance evaluation of coagulant phenolic gels

It can be seen that the modulus of elasticity of phenolic gels gradually increases with increasing polymer concentration at the same shear frequency[8]. At the shear frequency of 15.8 Hz, the elastic modulus of this gel is in the range of 15~50 Pa.

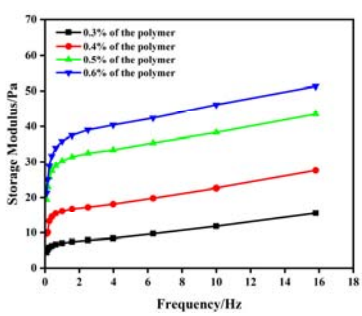


Fig. 2. Elastic modulus test curves for different polymer concentration systems.

3.2 Seepage characteristics analysis of coagulant phenolic gel

As shown in Table 3, it can be seen that as the polymer concentration increases, the blocking rate of the gel also increases. And the blocking rate can reach 98% for all the gel systems with different polymer concentrations.

Table 3. Gel blocking rates for different polymer concentrations.

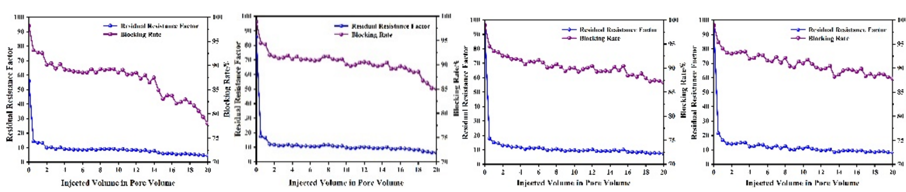
Number	k_a (mD)	k_b (mD)	η (%)
1	2064.3	37.7	98.17
2	2118.7	28.29	98.67
3	2091.5	23.69	98.87
4	2050.8	23.10	98.88

In the case of comparable permeability of porous media, the breakthrough pressure of the gel in porous media mainly depends on the strength of the gel.

Table 4. Breakthrough pressure gradients for different concentration gel systems.

Number	System concentration (%)	Breakthrough pressure (MPa)	Breakthrough pressure gradient (MPa/m)
1	0.3	0.54	1.35
2	0.4	0.86	2.15
3	0.5	0.92	2.30
4	0.6	0.96	2.40

After continuous 20 PV water flooding, the plugging rate of different polymer gels is still maintained at 78%, among which the plugging rate of gels with 0.60% polymer concentration is still 87%, showing very good scouring resistance. The higher the polymer concentration, the tighter the gel structure, the less likely it is to be broken by water flow shear.



（a）0.3%Polymer (b) 0.4%Polymer (c) 0.5%Polymer (d) 0.6%Polymer

Fig. 3. Scour resistance curves of gels with different polymer concentrations.

4 Conclusion

(1) The final gelling time was 6 days at 65℃, and the final gelling strength could reach G grade, and the modulus of elasticity is greater than 15 Pa.

(2) The plugging rate of porous media with permeability of 2000 mD reaches 98%

(3) The gel breakthrough pressure gradient is greater than 1.35 MPa/m in sand-pack with permeability of 2000 mD.

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