

Study on Movable gel Profiling/Flooding System Optimization at Boundary Temperature

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Abstract: 65-75°C is the boundary temperature of phenol-formaldehyde resin and organic chrome crosslink with HPAM to generate movable gel. Generally speaking, when the reservoir temperature is below 65-75°C, the crosslinking agent is Organic chrome. Phenol-formaldehyde resin is used when the temperature is above 65-75°C. In this paper the gelation properties of phenol-formaldehyde resin and organic chrome were compared at 70°C. The experiment results showed that the crosslinking time of phenol-formaldehyde resin gel was longer and more conducive to field injection. In addition the phenol-formaldehyde resin gel had greater viscosity, adhesion and shearing resistance compared with the organic chrome gel. So the phenol-formaldehyde resin was chosen for further optimization. The crosslinking time was shortened and the gel viscosity increased with the increase of the polymer concentration. As the polymer crosslinker proportion increased The crosslinking time was shortened and the gel viscosity increased first and then decreased. Reinforcer NC and stabilizer WG were added to improve the temperature and salt tolerance of the gel. The gel formula suitable for the boundary temperature was obtained. The optimum polymer concentration is 1200mg/L, the polymer crosslinker proportion is 1:1.1, the best reinforcer concentration is 400mg/L and the concentration of the stabilizer is 150mg/L. The crosslinking time is 31h, the gel viscosity is above 2100mPa·s. The gel did not shrink and no water separation was observed at 70°C for 150 days. The viscosity retention rate was more than 70%.

1. Introduction

At present, there are two kinds of movable gel crosslinking agents commonly used in oilfield. One is the organic chromium and the other is phenol-formaldehyde resin. The organic chromium crosslinking agent is generally used when the reservoir temperature is lower than 70°C, otherwise the phenol-formaldehyde resin is used^[1]. Thus, 65-75°C is the boundary temperature at which the two crosslinking agents react with HPAM to generate movable gel. There are 11 blocks whose reservoir temperature is in the range in Huabei Oilfield. The geological reserves are 4740×10⁴t. There is little research on the movable gel system at the boundary temperature currently. In this paper, the gelation properties of the two crosslinking agents were compared. Besides, the phenol-formaldehyde resin system with better crosslinking time strength was further optimized. The movable gel formula suitable for 65-75°C was obtained. This study is of great significance to the selection of profiling/flooding system in this temperature range.



2. The experiment

2.1 Experimental equipments and materials

2.1.1 Experimental equipments. analytical balance, magnetic stirring apparatus, constant temperature oven, HAAKE MARS rheometer.

2.1.2 Experimental materials. partially hydrolyzed polyacrylamide, the molecular weight is 25 million and the degree of hydrolysis is 25%~30% produced by Beijing Hengju Chemical Co.,Ltd., the crosslinking agents of water-soluble phenolic resin and organic chromium are both made in the laboratory, reinforcer NC is laboratory homemade; stabilizer WG is produced by Beijing chemical plant, chemical pure, water, clean water and formation water from Block Z.

Table 1 clean water and formation water quality analysis results of Block Z

	total salinity	Cl ⁻	HCO ₃ ⁻	CO ₃ ²⁻	Mg ²⁺	Ca ²⁺	SO ₄ ²⁻	Na ⁺	Total Fe	PH	water type
	mg/L										
Clean water	587.4	44.3	305.1	0.0	21.3	75.2	84.1	57.5	0.0	7.5	NaSO ₄
Formation water	6659.9	3323.4	823.5	30.0	18.2	50.1	12.0	2402.5	0.2	7.0	Cacl ₂

2.2 Experimental method

Phenol-formaldehyde resin gel and organic chrome gel were prepared according to the same recipe and placed in the oven of 70°C. The gel crosslinking time, viscosity, viscoelasticity and thermal stability were tested. Regularly observe the solution fluidity, when the fluidity is deteriorated and the solution is colloidal is the crosslinking time. Take out the gel after 5 days and then the gel viscosity was measured by using the Mars rheometer C60/27I L07024 rotor at a shear rate of 7.34s⁻¹. Appropriate oscillatory angular frequency and stress values are determined by the oscillatory measurement. According to the stress and frequency values oscillatory time is scanned to get the storage modulus (Elastic modulus G') and loss modulus (viscous modulus G'').

3. Experimental results and discussion

3.1 Comparison of the two gel systems performance

3.1.1 Crosslinking time. The gel was prepared with the two crosslinking agents and the HPAM concentration was 1000mg/L-1800mg/L, the polymer crosslinker proportion was 1:1-1:1.3. The experimental results indicated that the crosslinking time of organic chromium system is 4-7h, and the phenolic resin system is 28-33h. The phenolic resin system is more conducive to field injection and deep into the formation because of longer crosslinking time.

3.1.2 Gel viscosity. The viscosity of the two gel systems were compared after 5 days (Figure 1). The results indicated that when the HPAM concentration was less than 1500mg/L, the chromium system did not form the gel. While the phenolic resin gel viscosity was more than 1000mPa•s when the HPAM concentration was 1000mg/L. The viscosity of the phenolic resin gel was always greater than that of the organic chrome gel, regardless of the polymer crosslinker proportion. This may be related to the crosslinking mechanism of the two systems. Cr³⁺ and the carboxyl group of HPAM are linked by coordinate bond in organic chromium system. While the aldehyde base of phenolic resin is linked to the amide group by covalence bond^[2]. The bonding energy of coordination bond is smaller than covalent bond. Moreover, as the temperature increases, the coordination bond gradually weakens and can not be effectively crosslinked at a certain temperature^[3].

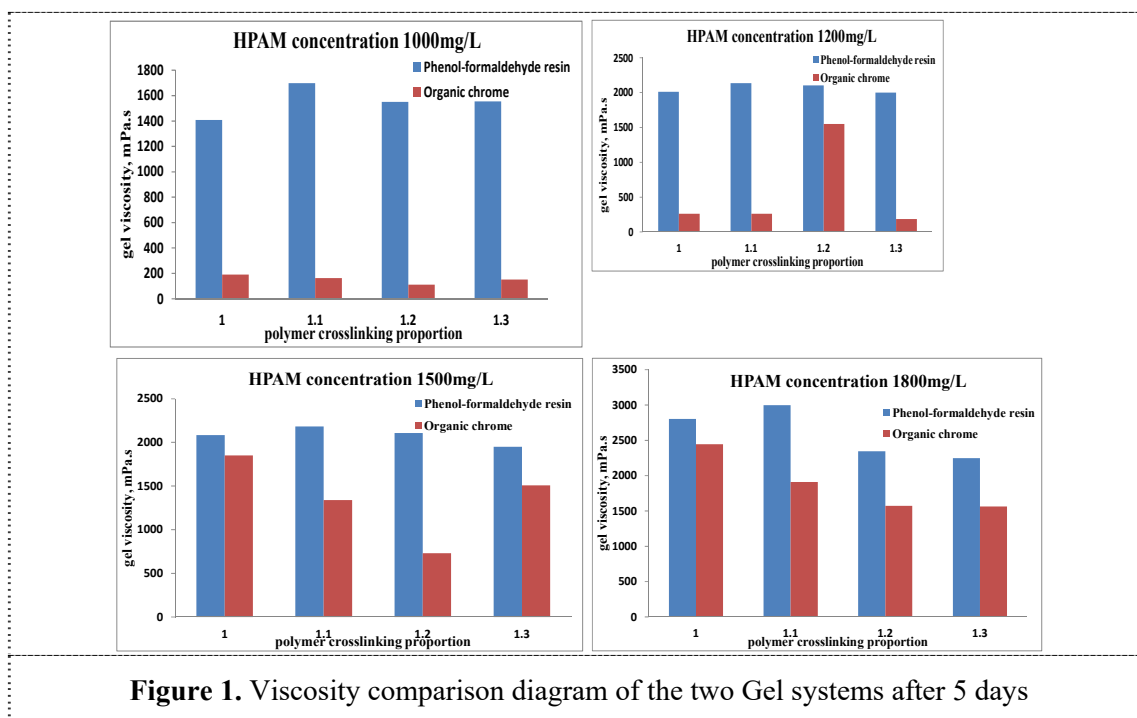


Figure 1. Viscosity comparison diagram of the two Gel systems after 5 days

3.1.3 Gel viscoelasticity. The storage modulus is also called the elastic modulus (G'). The greater the elastic modulus is, the stronger the shear resistance is. The loss modulus is also named the viscous modulus (G''). The larger the viscous modulus is, the stronger the adsorptive capacity of the gel on the rock surface. The modulus test results showed that the phenolic resin gel has stronger shear resistance and adhesion than the organic chrome gel.

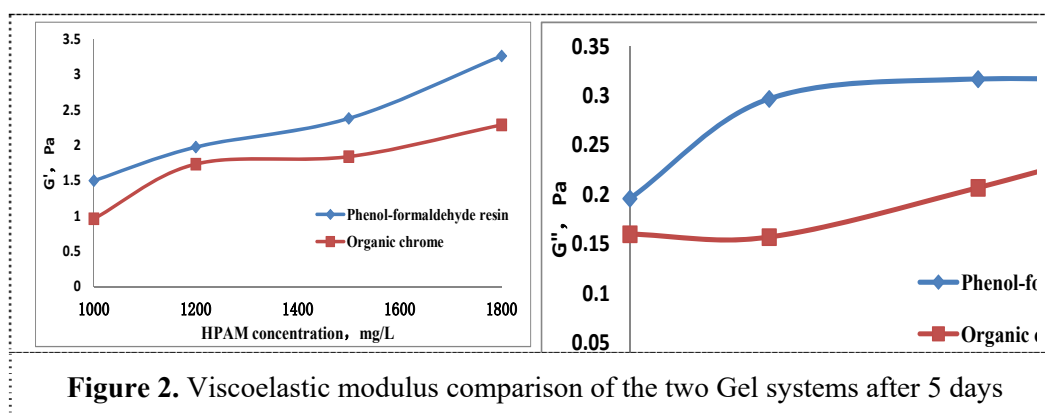


Figure 2. Viscoelastic modulus comparison of the two Gel systems after 5 days

The phenolic resin system was more suitable for the condition of boundary temperature according to the comparison of gel properties. The next step the phenolic resin system should be further optimized.

3.2 Optimization of the phenolic resin system

3.2.1 The effect of HPAM concentration. The gel viscosity was tested when the HPAM concentration was 800mg/L to 2000mg/L and the polymer crosslinker proportion was 1:1.1 to 1:1.2. The results showed that with the HPAM concentration increased, the crosslinking time was shortened, gel

viscosity increased significantly. This is because the chance of polymer intermolecular collision and banding increases with the increase of HPAM concentration. Besides, the amount of polymer molecule reacting with the crosslinking agent increases. So the gelling speed becomes faster and the viscosity increases^[4]. When the HPAM concentration was 1200mg/L, the gel viscosity reached above 2000mPa·s and the crosslinking time was about 30h. The gel viscosity increased slowly when the HPAM viscosity was more than 1200mg/L. Based on the results, the optimum HPAM concentration is 1200 mg/L.

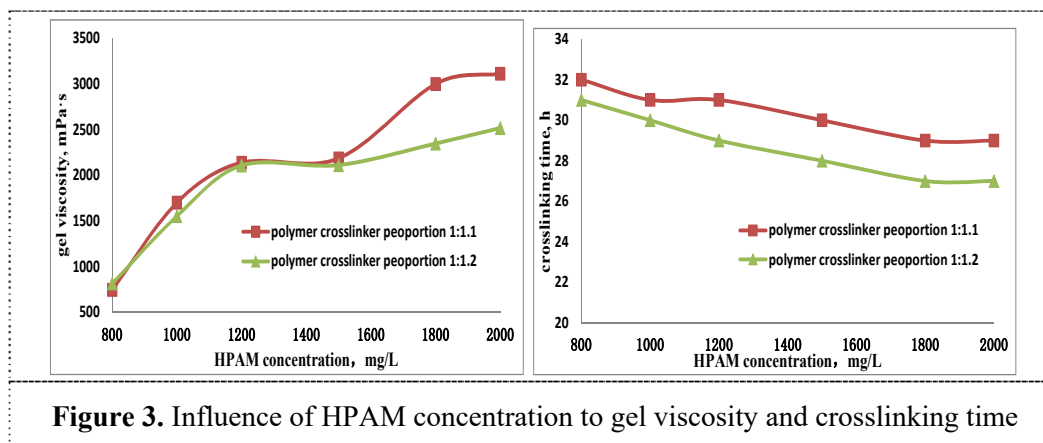


Figure 3. Influence of HPAM concentration to gel viscosity and crosslinking time

3.2.2 The effect of polymer crosslinking proportion. The gel viscosity was tested when the HPAM concentration was 1200mg/L and the polymer crosslinking proportion was 1:1.1 to 1:1.3. The results indicated that with the decrease of the polymer crosslinking proportion (the increase of the crosslinking agent concentration), the crosslinking time was shortened and the gel viscosity increased first and then decreased. This is because the crosslinking agent reacts with the polymer molecules more easily when the crosslinking agent concentration increases. The crosslinking speed and the gel viscosity both increase. However, when the crosslinking agent concentration exceeds 1:1.1, the gel would crosslink excessively. The water would be separated out from the gel causing the gel brittle. As a result, the gel viscosity decreases and the stability becomes poor^[5]. Therefore, the best polymer crosslinking proportion is 1:1.1.

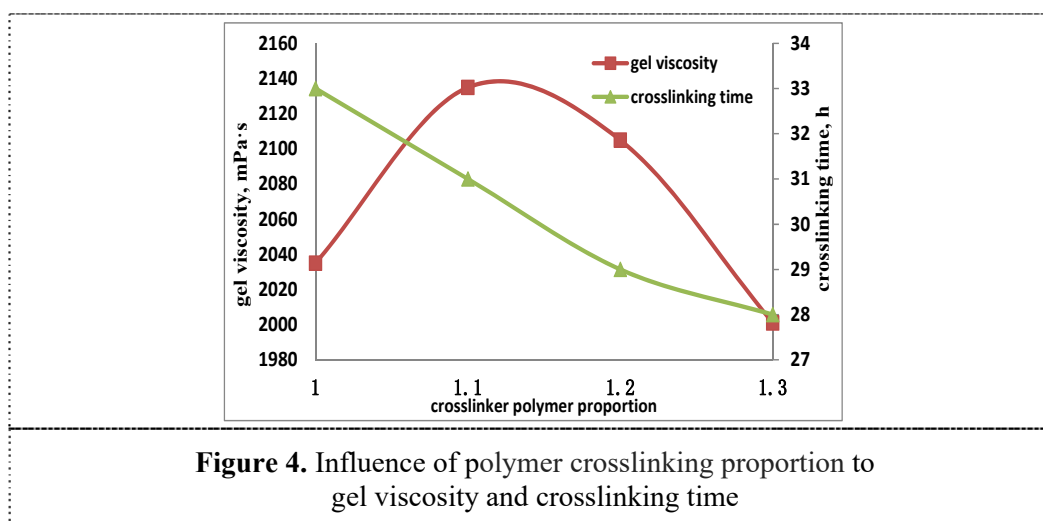


Figure 4. Influence of polymer crosslinking proportion to gel viscosity and crosslinking time

3.2.3 The effect of additives. It can be seen from Table 1, when the gel enters the information it would contact with positive ions, oxidizer, bacteria and so on in the lease water at high temperatures for a

long time. The gel viscosity reduced to 900mPa·s at 70°C after 60 days which can not meet the requirement of blanking off high permeability channel. The gel also shrunk and had water separation^[6]. The reason may be the double electrode layer of polymer molecules was compressed when it contacted with cations in formation water for a long time. The polymer molecular chain curled excessively. The network structure formed by intermolecular crosslinking would be tighter. Thus the amount of water infolded in the molecular network reduced. As a result, the amount of free water increased and gel viscosity decreased^[2]. In addition, long-term high temperature will promote hydration groups such as amide group CONH₂, carboxyl COOH condensation with hydroxyl OH. It will also lead to water retention capacity declining and gel shrinkage^[7].

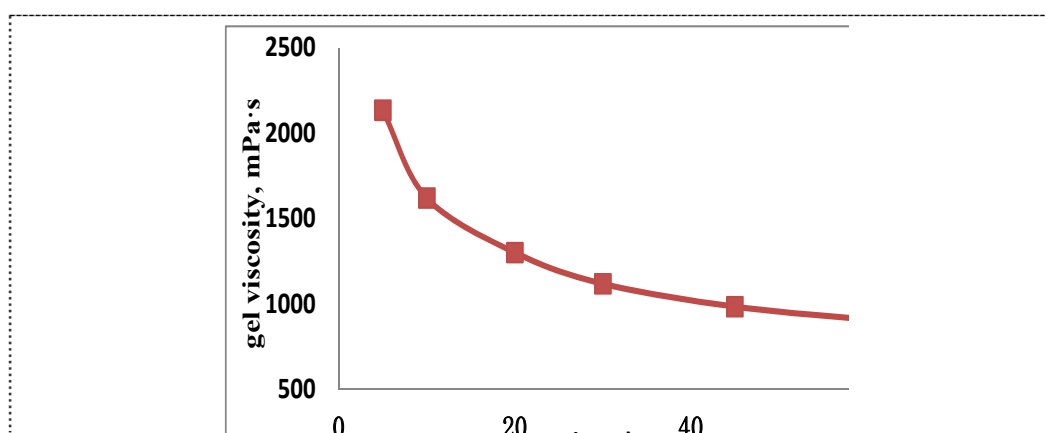


Figure 5. Schematic of gel viscosity varied with time at 70°C

Based on the mechanism of gel instability, two additives were screened. The reinforcer NC can chelate cations in the water, remove oxygen and destroy harmful microorganisms. It can weaken the affection of formation water on the gel. The stabilizer WG reacts with the reactive groups such as the amide group, the carboxyl group and the hydroxyl group by introducing the ether bond. Therefore, the chance of condensation reaction between the active groups is reduced and the gel stability at the formation temperature is improved.

Two different concentrations of additives were added into the system. The gel viscosity varied with time was tested when HPAM concentration was 1200mg/L and polymer crosslinking proportion was 1:1.1. It can be seen from the figure that the rate of gel viscosity decline slowed down significantly after adding the reinforcer NC and stabilizer WG. With the increase of the of NC concentration, the gel viscosity and stability increased. With the increase of WG concentration, the gel viscosity increased first and then decreased. According to the experimental results, the optimum NC concentration was 400mg/L and WG was 150mg/L. The optimized system was not gelout and the viscosity retention rate was above 70% after being placed at 70°C for 150 days.

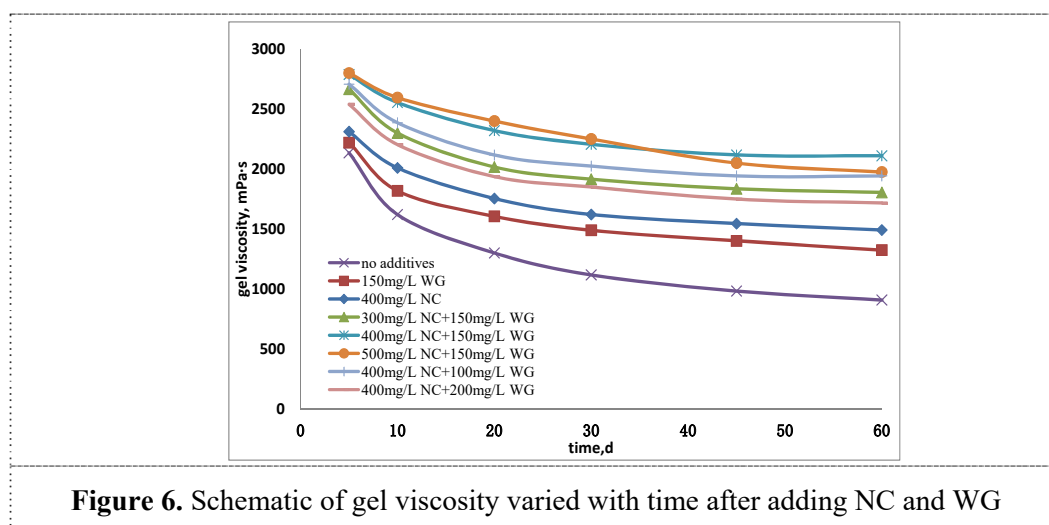


Figure 6. Schematic of gel viscosity varied with time after adding NC and WG

4. Conclusions

i. The gel performance of phenol-formaldehyde resin and organic chromium crosslinking systems was compared. The crosslinking time of organic chromium system was 4-7h and the phenol-formaldehyde resin system was 28-33h. The lower limit HPAM concentration of the chromium system was 1500mg/L, while the phenol-formaldehyde resin system was 1000mg/L. The viscosity of the phenolic resin gel was always larger than that of the organic chrome gel. Moreover, the viscoelastic modulus of the phenolic resin gel was also greater indicating that it has a stronger shear resistance and adhesion.

ii. The phenol-formaldehyde resin system was further optimized. Two kinds of additives were screened to solve the problem of gel instability at the formation temperature. One was the reinforcer NC and the other was the stabilizer WG. The optimal movable gel formula was that HPAM concentration is 1200mg/L, the polymer crosslinking proportion is 1:1.1, reinforcer NC concentration is 400mg/L and stabilizer WG concentration is 150mg/L. The system was not gelout and the viscosity retention rate was above 70% after being placed at 70°C for 150 days.

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Acknowledgements

The study was supported by PetroChina Science and Technology Major Project “Study and application of key technologies for production stable and increase to 8 million tons in Huabei oilfield” under Grant No.2014E-3507.

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