The Study on Double Cross-linking Gel Plugging System

Ting Liang, Zhenzhong Fan, Qingwang Liu, Jigang Wang, Jianjun Xu *
Department of Petroleum Engineering, Northeast Petroleum University, 163318, China
*Corresponding Author: 123939274@qq.com

Abstract. In this paper, double cross-linked gel system was first screened. Organic chromium cross-linking agent was selected as primary cross-linking gel system, hyperbranched polyacrylamide as primary cross-linking system main polymer, phenolic resin system as a cross-linking agent for secondary cross-linked gel system, cationic polyacrylamide as a cross-linking agent for secondary cross-linked gel systems. Through the experiment ,the formula of the double cross-linked gel system was that the amount of fixed hyperbranched polyacrylamide was 2000mg/L, the amount of internal network cross-linking agent was 300mg/L, the amount of stabilizer was 800mg/L, the amount of cationic polyacrylamide was 2000mg/L, the amount of enhancer was 150mg/L and the system performance was evaluated.

1. Introduction
The main difference between double cross-linked gels and other types of water blocking agent is the secondary gelation process of the gel, even though using a small amount of more active internal network cross-linking agent, under the ground conditions, organic chromium cross-linking agent and hyperbranched polymer slightly cross-linked to form a flow, a certain network structure and a certain viscosity of the weak cross-linked gel[1-3].When primary cross-linked gel is injected into the formation cracks, due to the polymer macromolecules have a certain viscosity and molecular size is large, almost do not enter the tiny cracks, only along the medium or large cracks in the forward flow and fluid loss hardly occurs in the fracture face[4,5].In the reservoir under high temperature conditions, external network cross-linking agent begin to play a role gradually, external network cross-linking agent reacts with the hyperbranched polymer and cationic polymer in the gel system again and eventually forms a high viscosity double cross-linked gel [6].

Double cross-linked gel have the characteristics as follows [7]. (1) Under low temperature conditions of the ground, weak cross-linking occurs, fast gelation time, shear resistance, low filtration loss and good injection property. (2) Under high temperature conditions of the ground, gelation strength is high, strong adhesion and less penetrability.

2. Experimental section
The hyperbranched polyester Bolton H20 as a branching agent for the polymerization reaction, cerium ammonium nitrate as initiator and DMC (methacryloyloxyethyl trim ethyl ammonium chloride) as monomer react with acrylamide in an aqueous solution by free radical polymerization to prepare hyperbranched polyacrylamide.
3. Results and discussion

3.1. Determination of primary cross-linked gel system

The gelation strength of the primary cross-linked gel system is neither too high nor too low, because the primary cross-linked gel system is completed in the ground conditions, the aim is to prevent the loss of the polymer solution in the formation matrix, to reduce the damage to the formation, and to have a good pump ability. If the gelation strength is too high, it will cause the polymer system injection pressure becoming too high or the gelation strength is too low, it will cause the filtration loss of the polymer becoming too large. So we choose the gelation strength of the primary crosslinked gel system between 100mPa·s and 300mPa·s.

3.1.1. Determination of the concentration of the polymer networks. Under the condition, the amount of immobilized cross-linking agent was 300mg/L, the amount of stabilizer was 800mg/L, the degree of mineralization was 10000mg/L, the reaction temperature was 20℃ and the pH of the system was 6.5. Then the effect of the amount of hyperbranched polyacrylamide on the adhesive properties of primary cross-linked gel system was studied. The experimental results were shown in Table 1.

| Table 1. Effect of different polymer concentration on primary crosslinked gel system |
|---------------------------------|-------|-------|-------|-------|-------|-------|-------|-------|
| Polymer concentration (mg/L)    | 250   | 500   | 750   | 1000  | 1250  | 1500  | 1750  | 2000  |
| Gelation time (h)               | 8.5   | 5.5   | 3     | 2     | 1.5   | 1.2   | 1     | 1     |
| Viscosity (mPa·s)               | 65    | 100   | 190   | 300   | 390   | 500   | 570   | 610   |
| Gelation strength (level)       | A     | B     | B     | B     | B     | B     | C     |       |

As can be seen from Table 1, with the increasing concentration of hyperbranched polymer, the viscosity of the primary cross-linked gel system gradually increased, and the gelation rate gradually accelerated. When the concentration of polymer was less than 750mg/L, the gelation rate was slow and the viscosity of the formation of weak gel is very small, which cannot meet the requirement of the blocking agent in the low loss in the cracks. When the polymer concentration is more than 1250mg/L, the cross-linking time is so fast and the viscosity of the system is more than 500mPa·s, which is not advantageous to inject the blocking agent. According to the requirement of the oilfield, the ideal adhesive time of the gel system is about 2h, the range of the primary cross-linked gel viscosity is 300~500mPa·s and the concentration of the polymer is between 750mg/L and 1250mg/L. So we choose the optimal concentration of the polymer is 1000mg/L.

3.1.2. Determination of the concentration of the cross-linked networks. In the experiment, the amount of immobilized hyperbranched polyacrylamide was 1000mg/L, the amount of stabilizer was 800mg/L, the degree of mineralization was 10000mg/L, the reaction temperature of cross-linking was 20℃, the pH of the system was 6.5. The results of the experimental results were shown in Table 2.

| Table 2. Effect of different cross-linking agent’s concentration on primary cross-linked gel system |
|-----------------------------------------------|-------|-------|-------|-------|-------|-------|-------|-------|
| Cross liner concentration (mg/L)               | 0     | 50    | 100   | 150   | 200   | 250   | 300   | 350   |
| Gelation time (h)                              | -     | -     | 12    | 6     | 4     | 2.5   | 2     | 1.5   | 1     |
| Viscosity (mPa·s)                              | 30    | 31    | 90    | 130   | 150   | 210   | 300   | 450   | 580   | 620   |
| Gelation strength (level)                      | -     | -     | A     | B     | B     | B     | B     | B     |       |

ps:- means cannot form gel.

It can be seen from Table 2 that when the concentration of the hyperbranched polymer was fixed, with the increase of the concentration of the cross-linker networks, the gelation rate of primary cross-linked gel system became faster. When the amount of cross-linking agent was in the range of 100~450mg/L, with the increase of the concentration of the cross-linked networks, the viscosity of the
gel system became larger. When the concentration of the cross-linking agent was a constant, the gelation rate of primary cross-linked gel system was too fast and the stability of the weak gel was too poor. Due to the concentration of the cross-linking agent was too large, excessive cross-linking occurred between the cross-linking agent and the polymer, causing gel dehydration to shrink. So when the concentration of polymer was 2000mg/L, the best amount of cross-linking agent in the range of 200mg/L~350mg/L.

The gelation principle of the primary cross-linked gel system was as follows:

$$\text{organic chromium solution , } \text{Cr}^{3+}\text{+organic acid radical}$$

We can know from Le Chatelier's principle, when the concentration of organic chromium cross-linking agent increased, the concentration of Cr$^{3+}$ also increased and the rate of cross-linking reaction was proportional to the concentration of Cr$^{3+}$. Therefore, with the increase of the concentration of cross-linking agent, the cross-linking speed of the system became faster, the gelation time was shortened and the gelation strength became larger. When the concentration of cross-linking agent was greater than a constant, the release rate of Cr$^{3+}$ became faster, causing the reaction rate was so fast that appeared gel dehydration phenomenon.

3.1.3. Effect of the concentration of the stabilizer on adhesive properties. Cr$^{3+}$ was selected as the central ion in the primary cross-linked gel system, the addition of stabilizers is mainly through the addition of a certain amount of complex ligands to achieve the purpose of improving the stability of the complex. In the experiment, the amount of the fixed hyperbranched polyacrylamide was 1000mg/L, the amount of network cross-linking agent was 300mg/L, mineralization degree was 10000mg/L, the cross-linking reaction temperature was controlled at 20℃, the pH of the system was 6.5, and the effect of stabilizer addition on the gelation properties of primary cross-linked weak gel system was studied. The experimental results were shown in Table 3.

| Stabilizer concentration (mg/L) | 0   | 200 | 400 | 600 | 800 | 1000 | 1200 | 1400 | 1600 |
|-------------------------------|-----|-----|-----|-----|-----|------|------|------|------|
| Gelation time (h)             | 0.8 | 1   | 1.5 | 2.5 | 2   | 2.5  | 2.5  | -    | -    |
| Viscosity (mPa·s)             | 800 | 700 | 400 | 340 | 300 | 285  | 280  | -    | -    |
| Gelation strength (level)     | B   | B   | B   | B   | B   | B    | B    | B    | -    |
| 3 days later                  | dehydration | dehydration | no change | no change | no change | no change | no change | no change | no change |

ps:: means cannot form gel.

It can be seen from Table 3 that in the absence of the addition of stabilizer, the rate of the primary cross-linked gel system was so fast, but 3 days later, the gel appeared dehydration phenomenon and the stability of gel was so poor that cannot play a very good role in delayed cross-linked interaction. When the concentration of the stability was more than 1200mg/L, the gelation time became long or cannot form gel. Taking into the consideration of the gelation time and gelation strength, the best concentration of stabilizer was 800mg/L.

3.2. Determination of double cross-linked gel system

Based on the composition of primary cross-linked gel system, taking into the consideration of the influence of polymer concentration, cross-linked concentration, and concentration of enhancer and environment factors on the properties of secondary cross-linked gel system to determine the composition of the secondary cross-linked gel system.
In the experiment, under the conditions that the amount of fixed hyper branched polyacrylamide was 1000mg/L, the amount of internal network crosslinking agent was 300mg/L, the amount of stabilizer was 800mg/L, the amount of external network cross-linking agent was 2000mg/L, the amount of enhancer was 150mg/Mineralization degree was 10000mg/L, the cross-linking reaction temperature was controlled at 70℃ and the pH of the system was 5.5.

3.2.1. Determination of the concentration of external network polymer. The effects of addition of external polymer (cationic polyacrylamide) on adhesive properties of double cross-linked gel system were studied. The experimental results were shown in Table 4.

| Polymer concentration (mg/L) | 500 | 1000 | 1500 | 2000 | 2500 | 3000 | 3500 | 4000 |
|------------------------------|-----|------|------|------|------|------|------|------|
| Gelation time (h)            | 72  | 56   | 24   | 20   | 18   | 16   | 15   | 12   |
| Viscosity (mPa·s)            | 450000 | 600000 | 120000 | 135000 | 139000 | 140000 | 151000 | 158000 |
| Gelation strength (level)    | G   | G    | H    | H    | H    | H    | I    | I    |

Experimental results showed that when the concentration of external network polymer was between 500mg/L and 4000mg/L, the gelation strength reached above the G level that can form a better stability of the double cross-linked gel. With the increase in the concentration of external network polymer, the rate of double cross-linked gel system was fast and the formation of the gelation strength also increased. Due to the polymer is subjected to two cross-linking, the double cross-linked gel system has a higher gelation strength than a single phenolic system or an organic chrome system.

3.2.2. Determination of concentration of external network cross-linking agent. The effects of external cross-linking agent on the gelation properties of double cross-linked gel system were studied. The experimental results were shown in Table 5.

| Cross linker concentration (mg/L) | 500 | 1000 | 1500 | 2000 | 2500 | 3000 | 3500 | 4000 |
|-----------------------------------|-----|------|------|------|------|------|------|------|
| Gelation time (h)                 | 84  | 48   | 26   | 20   | 17   | 11   | 8    | 6    |
| Viscosity (mPa·s)                 | 18000 | 50000 | 120000 | 135000 | 145000 | 150000 | 155000 | 160000 |
| Gelation strength (level)         | F   | G    | H    | H    | H    | I    | I    | I    |

It can be seen from Table 5 that with the increase of the concentration of the network cross-linking agent, the gelation time became shortened and the viscosity became large. When the concentration of the external network cross-linking agent was between 500mg/L and 1000mg/L, the gelation strength was below H, when the concentration of the external network cross-linking agent was more than 2500mg/L, the rate of gel system was so fast that caused the stability of the double cross-linked gel was poor. It may be the excessive concentration of the external network cross-linking agent, and cross-linking agent and the polymer over reacted causing gel dehydration shrinkage. Taking into account the gelation time and gelatinization viscosity, the best concentration of the external network cross-linking agent was 2000mg/L.

3.2.3. Long-term stability of water plugging the physical and chemical structure of the double cross-linking agent and the poor formation conditions of its injection determine the problem of its inevitable failure, especially water plugging agent og polyacrylamide gel. After high temperature, shear
degradation and high mineralization degree and thermal oxygen degradation, gel molecular chain will appear oxidation chain directly leading to gel cracking failure and other issues [8].

Taking the same proportion of the gel system into the same two reaction bottles, respectively were placed in 70℃ and 80℃ incubator and the viscosity was measured regularly. The experimental results were shown in Figure 1.

![Figure 1. Relationship between gelation strength and maintenance time](image)

It can be seen from Figure 1 that double cross-linked gel-type plugging agent at 70℃ and 80℃ can be stable for more than a year and did not occur dehydration. At the beginning of the gel formation, the strength of blocking agent gradually increased and the intensity was slightly lower after reaching the extreme value. It is able to meet the requirements of more than one year of the plugging requirements.

4. Conclusion

(1). Through the indoor experiment, the formula of the primary cross-linked gel system was that hyper branched polyacrylamide was 1000mg/L, the internal network of cross-linking agent was 300mg/L and the concentration of stabilizer was 800mg/L.

(2). The formula of the double cross-linked gel system was that the amount of fixed hyper branched polyacrylamide was 2000mg/L, the amount of internal network cross-linking agent was 300mg/L, the amount of stabilizer was 800mg/L, the amount of cationic polyacrylamide was 2000mg/L, the amount of enhancer was 150mg/L.

(3). Indoor experiments showed that the rate of gelation and strength can be controlled. In the temperature of 60~100℃, mineralization degree of 1000~40000mg/L, pH in the range of 4~9, the effect of the gelation was good, the plugging agent at 70℃ and 80℃ had a long-term stability.

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