Study on a new composite gel system

Sun Yi¹, Gao Wei¹, Zhang Ding-Xue*²

¹College of Petroleum Engineering, Yangtze University, Wuhan, 43100, China;
²Changqing Oilfield No. 1 Gas Production Plant, Yulin, Shaanxi, 75001, China

Author: 2540456412@qq.com; * Corresponding author: zdx7773@163.com

Abstract. A composite gel system was developed to solve the problems of low gel forming viscosity, gel forming and high salinity resistance in pH range of 6~8. The viscosity of the gel was determined by rotary viscometer, and the performance of the composite gel was analyzed. The pH of the composite gel, the gelation property of the mineralized degree and the plugging test of the sand filling pipe and the oil displacement experiment were carried out. The results showed that the gel performance of the composite gel was better than that of the conventional gel system at 60 degrees Celsius. The viscosity of the composite gel reached 10000 mPa S, at 0.1% polyacrylamide concentration, the gel forming range of pH was 6~12, and the viscosity of 20000 mg/L NaCl solution reached 15000 mPa / s, which had better salt resistance. The plugging test of sand filling pipe showed that the plugging rate of the gel to permeation layer was close to 90%, and the plugging ability was better. After 18% 0.2pv injection, the recovery rate increased by about 18%, which can meet the requirements of profile control in most oilfields.

1. Introduction

At present, China's oilfield development has entered the late stage of high water cut, the conventional control and water injection methods gradually can not meet the needs of field development, so the treatment of deeper formation is particularly important. Among them, water injection well profile control technology is one of the effective solutions. The dispersed gel deep profile control technology is a new technology of enhanced oil recovery. It can simultaneously perform profile control and oil displacement. It is one of the efficient displacement methods for low permeability old oilfields to exploit remaining oil and continue to enhance oil recovery[1-4]. At present, the dispersed gel systems commonly used at home and abroad are intermolecular crosslinked polyacrylamide / organic chromium system, polyacrylamide / phenolic resin system and intramolecular crosslinked polyacrylamide / aluminum citrate system. In the application of these gel systems, pH has a narrow scope of application and poor salt resistance. It fails to gel before reaching the depth of the formation or fails to reach the depth of the formation, resulting in failure of construction. The existing gel systems seldom analyze the effect of crosslinking on their gel properties[5-7]. In this paper, the gelation properties of gel systems with different crosslinking methods were studied. Through theoretical analysis, it was proved that the intermolecular and intramolecular crosslinking could make the gel system better in gel performance, and the plugging performance of the composite system of aluminum citrate and phenolic resin was also studied.
2. Experimental Part

2.1 main reagents and instruments
Polyacrylamide (HPAM), industrial grade, hydrolysis degree 22%, molecular weight 10-12 million; Urotropine (hexamethylenetetramine, molecular formula: C6H12N4), citric acid (C6H8O7), thiourea (CH4N2S), ammonia (NH3·H2O), hydrochloric acid (HCl), aluminum chloride (AlCl3), sodium chloride (NaCl), calcium chloride (CaCl2), ammonium chloride (NH4Cl), magnesium chloride (MgCl2), resorcinol were all analytically pure; Quartz sand. Rotary viscometer, constant temperature oven, sand filling tube, magnetic stirrer, etc.

2.2 experimental methods
(1) Preparation of polymer. According to the maximum concentration of the solution, the polymer is called, the magnetic stirrer is started, the polymer solid particles are slowly and slowly added (no more than 1 min), stirring at a certain speed until the gel solution has "climbing rod phenomenon", immediately stop stirring (about 0.5~1 h), swelling at room temperature for at least 24 h.

(2) Preparation of crosslinking agent. Crosslinking agent phenolic resin (self-made in laboratory); Crosslinking agent aluminum citrate (self-made in laboratory).

(3) preparation of dispersive gel. The prepared polyacrylamide mother liquor and stabilizer were mixed evenly in a certain proportion, stirring with a crosslinking agent, placed at constant temperature at 60 degree water bath, and the gel was obtained after gluing.

(4) Performance test. The viscosity of the gel system was characterized by measuring the viscosity of the gel system. The viscosity was measured by rotational viscometer and the rotational speed was 6 r/min.

3. results and discussion

3.1 gel formula optimization

3.1.1 optimization of phenolic resin concentration
A certain amount of swelling polyacrylamide mother solution was diluted and crosslinked with phenolic resin cross-linking agent of different concentrations. The polyacrylamide in the fixed formula was 1000 mg/L, the stabilizer concentration was 150 mg/L, pH was 6~7, and the temperature was 60 degrees. Gel was prepared. The influence of different concentration of phenolic resin system on CDG viscosity and gelation time was studied, as shown in Figure 1. It can be seen from Fig. 1 that with the increase of phenolic resin concentration, the gelling viscosity will gradually increase, and the gelation time is between 41 h and 24 h. When the phenolic resin concentration exceeds 0.12%, the gel viscosity will no longer increase, and the gelation time will remain stable. Therefore, the optimum concentration of phenolic resin is 0.1%.

Fig.1. The relationship between the mass fraction of phenolic resin and gelling time and viscosity
3.1.2 effect of polyacrylamide concentration
Crosslinking phenolic resin can crosslink with HPAM under certain temperature and form weak gel. Different concentrations of polyacrylamide and crosslinking agent were used in the gelation experiment. The experimental conditions were: pH = 6～7, temperature 60 ℃. The viscosity of the gel is measured by rotary viscometer. The result is shown in Figure 2. It can be seen from Fig. 2 that with the increase of time, when the concentration of polyacrylamide is 300 mg / L, the viscosity decreases continuously, resulting in dehydration and no gelation; When the polymer concentration is greater than 300 mg/L, the viscosity of the gel system increases with time, and at the same time, the viscosity tends to a stable value after a period of reaction. This is because when the polymer concentration increases, the probability of intermolecular contact and collision increases, and cross-linking is more likely to occur. In terms of gelation viscosity and time, the gelation time of 1000 mg / L polyacrylamide was about 30 h, and the gelation viscosity was 2386.34 mPa · s after gelation, the viscosity continued to increase to more than 3000 mPa · s, and the viscosity remained stable for 60 h.

3.1.3 influence of aluminum citrate addition
Take a certain amount of swelling polyacrylamide mother liquor diluted to a certain concentration, and then cross-linked with different concentrations of aluminum citrate cross-linking agent. The polyacrylamide in the fixed formula was 1000 mg/L, phenolic resin 0.1%, stabilizer 150 mg/L, PH 7, and temperature 60 degrees. Gel was prepared. The CDG viscosity and gelation time were measured at different concentrations of citrate aluminum crosslinking agent, as shown in Fig. 3. It can be seen from Figure 3 that with the increase of aluminum citrate concentration, the gelation time first increases, then has a weakening period, and finally keeps increasing continuously. The gelation viscosity reaches above 8000 mPa · s when the concentration is 0.1% ~ 0.16%, which can meet the requirements of profile control and water shutoff operation. When the concentration of aluminum citrate increases, the citric acid gradually increases, which makes the solution maintain a better acidic condition, so that the phenolic resin can be better formed. When the concentration is too high, the pH of the solution is too low, which hinders the formation of phenolic resin. From the gelation viscosity and gelation time, the composite gel system has better performance than the phenolic resin system, and can meet the requirements of profile control and water plugging. Therefore, the optimum concentration of aluminum citrate is 0.1%. 

![Fig.2.Viscosity changes of different concentrations of polyacrylamide](image)
3.2 Evaluation of gel forming properties

3.2.1 Effect of pH

In order to study the acid-base properties of the composite gel system, pH gel was used to adjust the composite gel system. In the process of adjustment, the pH value was observed with a wide range of pH test paper contrast colorimetric card. The experimental results are shown in Figure 4. It can be seen from Fig. 4 that when the pH value is between 0 and 4, the system cannot gel. This is because the H⁺ content in the solution is too high in the strong acid environment, resulting in the protonation of the carboxyl group on the polyacrylamide, so that the carboxyl group and the polynuclear hydroxyl group cannot form polar bonds and coordination bonds for cross-linking [9]. When the pH is greater than 0~4, the pH gel range of the composite gel is wider and can reach more than 10, which indicates that the synergistic effect of the aluminum citrate and phenolic resin can make the gel gelling better.

3.2.2 influence of salinity

In order to study the salt resistance of the composite gel, different gel systems were prepared by using simulated mineralized water respectively. The specific ionic content was shown in Table 1. The salt resistance of the solution was studied by adding NaCl solution of 20005000100002000030000 mg/L in the solution. The gel was evenly distributed in a constant temperature drying oven at 60 degrees centigrade, and the viscosity of the gel was measured by rotary viscometer and glass rod respectively. The experimental results are shown in Figure 5.
Table 1. Composition of simulated formation water in Changqing

| Ion type         | Content (mg/L) |
|------------------|----------------|
| K⁺+Na⁺          | 452.21         |
| Mg²⁺            | 0.65           |
| Ca²⁺            | 127.02         |
| Cl⁻             | 384.66         |
| SO₄²⁻           | 479.78         |
| HCO₃⁻           | 250.72         |
| Mineralization degree | 1695.04       |

Fig. 5. Gelation time and gelation viscosity of gel system under different salinity

From the experimental results, it was found that the gelation viscosity increased with the increase of NaCl concentration within a certain salinity range. However, the gel gelling range of the composite gel was wider and the highest reached 25000 mg/L, but the gel was not gel when it exceeded the gel range. The reason is that a certain amount of electrolyte will make the polymer molecular chain in a semi curly state, which makes the polymer molecular chain closer to each other, and is conducive to the crosslinking with the crosslinking agent; When the electrolyte content is too high, the molecular chains of polymers will produce excessive curl, and the network structure formed by crosslinking reaction of polymer and crosslinking agent will be more compact, and the amount of water that can be wrapped will be reduced, so the viscosity of weak gel will decrease by [11]. It can be seen from the gel viscosity that the salt resistance of the composite gel system is good.

3.2.3 Plugging test

Three kinds of gels were tested by sand filling model. After gelatin injection, the gelatin time is placed in the oven at 60 degrees, and then gelatin is formed. The experimental water is the pseudo water of the model formation in a block of Ji Yuan, and the salinity is 1695.04 mg/L. The injection rate was 0.4 ml/min. The experimental results are shown in Fig 6. The results showed that the plugging rate of phenolic resin and composite gel system increased with the increase of PV, but when the PV was over 0.2, the plugging rate increased little. The plugging rate of composite gel system is the best from the aspect of plugging rate. The plugging rate of composite gel reached 87.18% when 0.2PV was injected, and the plugging rate of phenolic resin was 79.67%.
3.2.4 Oil displacement experiment
In order to further study the profile control performance of composite gel, an oil displacement experiment was carried out on the basis of plugging test. The injection rate was 0.4 mL/min, the viscosity of crude oil was 7.1 mPa·S, the experimental temperature was 60°C, and the experimental results were shown.

It can be seen from Fig. 7 that in the initial stage of water injection, because the viscosity of simulated oil is higher than that of water, the injected fluid needs to overcome the larger seepage resistance when entering the sand filling pipe, so the injection pressure rises sharply. With the deepening of water drive process, the water saturation in the pore medium increases, the injection pressure begins to decrease, and finally remains stable. Before the breakthrough, water flooding mainly plays the role of oil displacement and forms water flow channel. When 2PV water is injected, the overall water cut is 85%, and the water cut of sand filling pipe B is 96%, which indicates that most of the water flows away in high permeability layers, which makes it difficult to water drive the oil in low permeability layers; After injection pressure was stabilized, 0.2PV composite gel was injected, and 30h was coagulated. Then water flooding was continued. From the change of moisture content curve, it was found that the water content decreased significantly after injection, and the recovery rate increased with the increase of pressure, and the recovery increased to 18% when the moisture content increased to 98%.

3.3 Gelation mechanism of aluminum citrate/phenolic resin composite gel
The carboxyl and aluminum ions in polymer polyacrylamide are easy to crosslink and form gel. The effect of aluminum citrate is to slow down and control the gel speed. The crosslinking process of gelling is realized by the exchange of complexes. When gluing in gel solution, aluminum citrate will release

Fig. 6. plugging rate of aluminum citrate, phenolic resin and composite gel system under different PV injection

Fig. 7. variation curve of water cut, recovery degree and injection pressure of heterogeneous model
Al$^{3+}$ and a certain amount of citric acid (CA), and Al$^{3+}$ will form the polynuclear hydroxyl bridging ions of aluminum through complexation, hydrolysis and hydroxyl bridging. Among them, different molar ratio of Al$^{3+}$ and CA will have different effects on the complexation process. When the molar ratio is 3:1, the polynuclear hydroxyl bridged complex ion of aluminum can be formed and cross-linked with -CONH$_2$, -COO$^-$ in polymer polyacrylamide. The gelation effect is good when the pH of gelation solution is neutral or weak acid or base$^{[9-10]}$. In the crosslinking process of polymer polyacrylamide and phenolic resin, firstly, formaldehyde is produced from Urotropine under acidic heating conditions, and then formaldehyde and resorcinol form different linear structures in different pH environments. The acid is linear, and the alkaline is linear. Finally, it is polycondensated with HPAM$^{[11-12]}$. In the complex crosslinking system of aluminum citrate and phenol formaldehyde ressin, the citric acid aluminum gel system with intermolecular crosslinking will produce certain citric acid slowly, and create a favorable acidic condition for the crosslinking agent of phenolic resin. The gel system can be prepared by intermolecular crosslinking of phenolic resin system and aluminum citrate system.

4. conclusion
The water-soluble composite gel system is composed of polyacrylamide, phenolic resin and aluminum citrate. At low concentration of polyacrylamide (1000 mg/L), the gel with viscosity of 10000 mPa·s was formed. The pH range of the system is 6 ~ 12, and the viscosity is more than 15000 mPa·s when the salinity is 20000 mg/L. The system has good alkali resistance and salt resistance. The plugging experiment shows that the plugging rate of the plugging agent can reach 90%, and it has good plugging performance; Injection of 0.2pv gel can increase oil recovery by 18%. It can provide reference for low permeability oilfield.

References
[1] Fu Guoqiang. Research on the influencing factors and profile control effect of polyacrylamide/Cr(III) gel system[D]. Northeast Petroleum University, 2016.
[2] Wang Keliang, Kong Hui, Fu Guoqiang, Li Weiliang. Research on the gel forming characteristics of partially hydrolyzed polyacrylamide/chromium lactate under the conditions of oilfield sewage[J]. Oilfield Chemistry, 2016, 33(02): 240-243.
[3] Liu Ximing, Tian Yuqin, Liu Weiwei, Tang Yanyan, Zhang Donghui, Hou Wanguo. Rheology of partially hydrolyzed polyacrylamide and polyvinyl alcohol mixed solution[J]. Oilfield Chemistry, 2020, 37(01): 115-120.
[4] Yao Puyong. Performance evaluation of high concentration, high molecular weight partially hydrolyzed polyacrylamide and low viscosity cellulose blending plugging system[J]. Oilfield Chemistry, 2017, 34(03): 412-416.
[5] Jin Yanxin, Wang Lushan, Wang Tao, Zheng Xin, Yan Youguo, Liu Bing. Experimental and theoretical study on the effect of inorganic salt on the viscosity of partially hydrolyzed polyacrylamide solution[J]. Journal of China University of Petroleum (Natural Science Edition), 2016,40(04):165-170.
[6] Hao Yufei, Chen Yanling, Dong Bingyang. Synthesis and application of A-C composite crosslinking agent[J]. Geological Science and Technology Information, 2010, 29(01): 131-136.
[7] Chen Gang, Tang Ying, Zhang Jie, Xu Jiaye. The synthesis of aluminum citrate and the preparation of HPAM/aluminum citrate weak gel system[J]. Drilling Technology, 2010, 33(05): 89-92+141.
[8] Jia H, Pu W F, Zhao J Z, et al. Research on the Gelation Performance of Low Toxic PEI Cross-Linking PHPAM Gel Systems as Water Shutoff Agents in Low Temperature Reservoirs[J]. Ind.eng.chem.res, 2010, 49(20):9618-9624.
[9] Shi Zheng, Tian Yunji, Wan Wenjie, Xu Yiyi, Lin Xi. Laboratory study on organic polymer crosslinking weak gel[J]. Modern Engineering, 2019, 39(01): 167-170.
[10] Liu Li, Guo Xuan, Sun Ning. Feasibility analysis of weak gel control and flooding after binary
combination flooding in offshore oilfields[J]. Science Technology and Engineering, 2020, 20(14): 5610-5614.

[11] Guo Rui, Wang Ning, Han Shuang, Gao Wanwan, Zhang Yao. Modification of polyacrylamide weak gel by sodium hydroxymethyl lignosulfonate[J]. Applied Chemical Industry, 2019, 48(04) :870-873+887.

[12] Luo Wenli, Wu Zhaoliang, Niu Yabin. New progress in the research of colloidal dispersion gels[J]. Oilfield Chemistry, 1999(02):188-193.