Experiment and application of movable gel prepared by recycled produced water

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Abstract: Cations such as Ca$^{2+}$, Mg$^{2+}$, Fe$^{2+}$ etc. in recycled produced water seriously affect the viscosity and stability of movable gel. Four types of polymers were evaluated in laboratory including comb-shape polymer and hydrophobically associating polymer. By analyzing two types of polymers' molecular structures, it showed that comb-shape polymer was easier to improve its properties by cross-linking reaction, and the viscosity of the hydrophobically associating polymer mostly came from the viscosity of molecular structure. Cross-linking reaction contributed little to the viscosity of hydrophobically associating polymer. The movable gel was prepared in salt water of TDS=2.64× 10$^4$ mg/L by using comb-shape polymer B and modified phenolic resin prepolymer. By introducing rigid benzene ring structure, the salt tolerance and long-term stability were significantly improved. The viscosity of retain rate was more than 70% after 60d under 90°C. Field application of 3 wells showed that qualification rate of preparing movable gel was 100% and oil increment was 3020t.

1. Introduction
The weak gel flooding system is widely used in EOR and it has a good effect on EOR$^{[1-2]}$. Cations in water have a great influence on the properties of the gel. Gel is generally prepared with clear water in order to ensure the effect of gel flooding. However, with the increasingly serious environmental protection problems and scare water resources, the key point of development in the future is to use the recycled produced water on gel properties. One solution is to improve the salt resistance of the polymer by modifying its molecular structure. Acrylamide can be copolymerized with hydrophobic monomer to synthesize hydrophobically associating polymer$^{[4-5]}$, or Oil-wet monomer can be introduced on the polymer backbone, and the comb-shape polymer is formed by equidistant grafting on the polymer backbone. The second method is to increase the reactivity of the cross-linking agent to make the gel structure more stable$^{[6-8]}$. In this paper, the above two methods were discussed.

2. Experiment
2.1 Laboratory drugs and instruments
Drugs: comb-shape polymer A and B, Molecular weight: 25 million, hydrolysis degree 20-25%; hydrophobically associated polymer C and D, Molecular weight: 5-10 million, hydrolysis degree 20-27%. Modified phenolic resin pre-polymer as cross-linking agent, self-made in laboratory. 
Instruments: Anton Paar rheometer; electricity heat drum wind drying oven.
2.2 Water quality analysis
The water used was recycled produced water in one block of Huabei Oilfield. Water quality analysis was shown in Table 1, TDS=2.64×10^4 mg/L.

| Ion      | Concentration (mg/L) | Ion    | Concentration (mg/L) | Ion      | Concentration (mg/L) |
|----------|----------------------|--------|----------------------|----------|----------------------|
| Cl^-     | 15292.4              | Na^+   | 10067.2              | Total Fe | 5                    |
| F^-      | 24.3                 | K^+    | 66.2                 | TDS      | 26412.7              |
| HCO_3^-  | 818.5                | Ca^{2+} | 75.4                |          |                      |
| SO_4^{2-}| 3.2                  | Mg^{2+} | 17.2                |          |                      |

2.3 Gel preparation and viscosity test method
At room temperature, drugs were mixed in order and put into high temperature bottles. The cross-linking reaction took place in dryer at 90℃. The sample bottles were took out at specified time. When the temperature was reduced to room temperature, the viscosity was tested with rheometer. The viscosity of samples were measured by CP50-1 rotor at the shear rate of 7.34s⁻¹.

3. Results and discussions

3.1 Evaluation of salt resistant polymers

3.1.1 Viscosity comparison of different polymer solutions
The polymer solution of 3000mg/L was prepared and the solution viscosity was tested after 5 days at room temperature. The results were shown in Table 2.

| Polymer | Solution Viscosity (mPa·s) | Gel Viscosity (mPa·s) |
|---------|----------------------------|----------------------|
| A       | 57                         | 1099                 |
| B       | 78                         | 1227                 |
| C       | 385                        | 823                  |
| D       | 1576                       | 1550                 |

As seen in Table 2, the solution viscosity of hydrophobically associating polymer was obviously higher than that of comb-shape polymer. It depends on the molecular structure of the two polymers. The main chain of hydrophobically associating polymer contains several hydrophobic groups, which are associated with each other due to hydrophobic effect in water. Therefore, a three-dimensional network structure with certain strength and reversibility is formed among molecules. This network structure can be formed to wrap water molecules in it, and the viscosity of the solution can be greatly increased[9].

3.1.2 Viscosity comparison of gels prepared by different polymers
The gel with polymer 1500mg/L was prepared and reacted in the dryer at 90℃. After 5 days, the gel was taken out. Viscosity of the gel was tested and investigated. The results were shown in Table 2.

It was shown in Table 2 that the gel viscosity of the two hydrophobically associating polymers was not significantly higher than that of the polymer solution. The viscosity of the comb-shape polymer increased greatly after gelatinization. There are two groups on the comb-shape polymer chain, which repel each other in aqueous solution, and the molecular chain is more stretched. This structure makes the amide groups involved in the cross-linking reaction more exposed and easier to react. Because of steric hindrance effect of hydrophobic groups, it is difficult for amides on the chain to react. The contribution of chemical cross-linking to viscosity is much smaller than that of molecular structure.
Although the associative force of hydrophobic groups is larger than that of van der Waals force and hydrogen bond energy, it is much smaller than that of chemical bonds. A polar covalent bond is formed after the dehydration of the amide group and hydroxymethyl, so the bond energy can be bigger, the structure can be more stable.

3.1.3 Long-term stability of gels prepared with different polymers
The gel solution of polymer with different concentration were prepared and viscosity was tested. The results were shown in Table 3.

| concentration (mg/L) | test time (d) | gel viscosity (mPa·s) |
|---------------------|--------------|----------------------|
|                     | A  | B  | C          | D            |
| 1200                | 5  | 759| 980        | 712          | 1300        |
|                     | 30 | 523| 650        | breaking     | 940         |
| 1500                | 5  | 1099| 1527      | 823          | 1550        |
|                     | 30 | 814| 1343      | 709          | 1069        |
| 1800                | 5  | 1350| 2070      | 1493         | 1707        |
|                     | 30 | 1007| 1702     | 898          | 1434        |
| 2000                | 5  | 1750| 2302      | 1520         | 1991        |
|                     | 30 | 1423| 1918     | 1192         | 1466        |

It was shown in Table 3 that, the gel viscosity of polymer D did not change much with the change of polymer concentration. This indicated that, for hydrophobically associating polymer, the contribution to viscosity was mainly due to the structural viscosity of molecular association, while the contribution of cross-linking reaction to gel viscosity was small. But The contribution of comb-shape polymer gel viscosity was mainly due to cross-linking reaction. According to the long-term stability of the gel, the stability of gel prepared by polymer C was poor. The gel prepared by polymer B had better long-term stability than the gel prepared by A. By analyzing the molecular structure of the two polymers, we could see that the alkyl side chain of polymer B was longer, which made it more difficult for the double ionspheres to be compressed and more difficult for chains to curl, so salt resistance was better. So polymer B was selected to optimize the formula concentration.

3.2 Effect of cross-linking agent concentration on gel properties
The modified phenolic resin pre-polymer was synthesized by a new method\textsuperscript{[10]}. The product was a completely water-soluble brown-red solution. Polymer B concentration 2000mg/L and cross-linking agent concentration 2000mg/L were selected to investigate the effect of different cross-linking agent concentrations on gel properties. The results were shown in Figure 1.
According to the experiment results, with the increase of cross-linking agent concentration, the viscosity of gel increased. The two parameters had positive correlation. When the concentration of cross-linking agent increased to a certain value, the corresponding increase of gel viscosity became slowly. The gel will dehydrate due to the overreaction of cross-linking. Gel had poor elasticity, easy to break. According to the experiment results, the optimal cross-linking agent concentration was 2200-2600mg/L.

3.3 Effect of cross-linking promoter concentration on gel properties
The polymer B concentration of 2000mg/L and cross-linking promoter concentration of 2200mg/L were selected to analyze the effect of different cross-linking agent concentrations on the gel properties. The results were shown in Figure 2.

The promoter was a compound of inorganic salts. It played main role to adjust the pH value of the solution in order to affect the gelation time and it had less effect on the viscosity of gel. When the concentration of the cross-linking promoter was 1800-2200mg/L, the pH value of the solution was between 7-9, and the gelation time was 40-50h. The time of gelation met the requirements of site construction.
3.4 long-term stability of gel

Three gels of different concentrations of polymer B were prepared and were taken out at a certain time to test the viscosity. The results were shown in Figure 3.

![Curves of gel viscosity vs. time.](image)

Figure 3. Curves of gel viscosity vs. time.

Small amount of cations in recycled produced water will compress the polymer's double ionospheres. The modified phenolic resin cross-linking agent had less free formaldehyde content and more methylated benzene rings. All of that would accelerate the cross-linking and could form three-dimensional network structure in a short time. More benzene ring structures could be introduced into network structure by more hydroxymethyls taking part in the cross-linking reaction. Because the benzene ring is a rigid molecular structure, the structure can enhance the stability of the gel three-dimensional network. With the increase of reaction time, and cations will compress the polymer double ionospheres more and more[11]. Because of this, polymer chains would get closer together. As a result, the gel would over crosslink and took the water molecules out of the network structure. A three-dimensional network of gels made from modified phenolic prepolymers and polymers would introduce more benzene rings. The introduction of benzene ring structures would play a role in supporting the network structure, thus preventing the polymer main chains from getting close to each other, thus enhancing the salt resistance and long-term stability of the weak gel. It was shown in Figure 3, the viscosity retention rate of gel system for 60 days was 70%.

4. Field application

According to the comprehensive performance of the gel system, three injection Wells in one block of Huabei Oilfield were selected for field test. The water injection profile of the injection well showed the prominent contradiction between layers. Fingering of Water absorption in the bottom was obvious. The thickness of the waterflood sweep became smaller. The water cut was 97%. The movable gel flooding system was applied in this block in June, 2018. The total injection volume was 17600m³. After the implementation, the injection well pressure steadily climbed 4-8MPa. The daily oil increment was 19.7t at the peak. The water cut of the wells decreased by 7.5%. The cumulative amount of oil added in this block was 3020t.

5. Conclusions

(1) Comb-shape polymers are more likely to increase the viscosity of the gel by cross-linking than hydrophobically associating polymers. The three-dimensional network structure formed by chemical cross-linking reaction will be more stable, which can ensure the gel maintaining the viscosity energy and the elasticity energy for a long time.
(2) Cross-linking reaction sites can be increased by using modified phenolic resin prepolymer made in laboratory. Therefore, more benzene ring structures can be introduced into the network structure of the gel. This structure can reduce the compression of the polymer double ionospheres by various kinds of cations in recycled produced water. Thus, the salt resistance and long-term stability of the gel were enhanced.

(3) The concentration of cross-linking agent and promoter was optimized by experiment. The gelation time was 40-50h. The viscosity retention rate of the gel system for 60d was above 70%. Oilfield application showed that This gel system can improve the heterogeneity of oil layers and reduce water cut in oil well and increase oil addition.

References
[1] He E. J. Du Y. H. Luo C. J., et al. (2003) Field test on movable gel as profile control and flooding in Huabei Oilfield. J. Acta Petrolei Sinica, 46(2): 64-68.
[2] Ye Y. Z., Wu X. C., Yu Z. B., et al. (2010) Development of movable gel system and mechanism analysis. J. Petroleum Geology and Engineering, 24(3): 73-76.
[3] Yang G., Zhang J., Xie S., et al. (2013) Development and evaluation of salt-resisting polymer gel profile control agent. J. Advanced Materials Research, 781-784: 426-430.
[4] Jia W. F., Chen Z., Gui S. Y., et al. (2017) Thickening mechanism of amphoteric hydrophobically associating polymer by experimental study and simulation. J. Science Technology and Engineering, 17(3): 213-217.
[5] Peng T. J., Liu J. X., Zhao Z. C., et al. (2016) Effect of micro-block length on rheological performance of hydrophobically associating polymer. J. Oilfield Chemistry, 33(4): 670-674.
[6] Guo H., Yang C. H., Fan J., et al. (2010) Study and application on heat resistant and salts tolerant flooding system in high-temperature low permeability reservoir. J. Oilfield Chemistry, 27(2): 183-186.
[7] Wang F. G., Zhao F. L., Hou J. R., et al. (2015) Performance comparison of comb Polymer gel and ordinary polymer gel. J. Oilfield Chemistry, 32(2): 209-212.
[8] Shi L., Cui Y. J., Wang Z. Q., et al. (2014) Application in WEN120 block with new profile-control flooding. J. Journal of Yangtze University(Natural Science Edition), 32(11): 104-107.
[9] Jiang K. Y., Ren K., Xu C. M., et al. (2003) Synthesis technology and property evaluation of hydrophobical association polymer solution. J. Journal of the University of Petroleum, China, 27(6): 80-83.
[10] Qiu L., Pu W. F., Zhang J., (2011) Synthesis and gelling performance evaluation of an improved phenolic resin crosslinker. J. Advances in Fine Petrochemicals, 12(8): 15-18.
[11] Chen T. L., Zhou X. J., Tang F. P., et al. (2006) Weak gel flooding in EOR, Petroleum Industry Press, Beijing, China.