The compatibility evaluation of Cr\textsuperscript{3+} Gel system and polymer/surfactant system with alternating injection mode

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Abstract. Alternately injecting the slug of the gel and polymer/surfactant compound system is a new way to further enhance oil recovery after polymer flooding. The displacement system needs to produce an ultra low interfacial tension to oil and to enlarge swept volume significantly. Based on experimental analysis, the influence factors of Cr\textsuperscript{3+} gel system viscosity and the compatibility of gel with two types of surfactant compared with composite ion gel system has been studied. The experimental result shows that it has well stability, and the compatibility of gel with RMA-1 type surfactant is very well. It can produce an ultra low interfacial tension to oil so that enhanced oil recovery has been reached more than 10 percent by using the gel system to displace residual oil after polymer flooding in artificial large flat-panel model.

1. Introduction
Polymer Flooding has been applied in the Daqing Oilfield since 1996, its scale expands unceasingly and has become the leading technology for the development of Daqing Oilfield. Although the polymer flooding can enhance recovery more than 10% higher than that of water flooding, there are still some problems, such as polymer will be held up in channel and injection profile will reverse after injecting a certain amount of polymer solution, which lead to about 50% crude oil still can not be produced after polymer flooding [1-4]. Water breakthrough and water out degree is being aggravated by the more serious reservoir heterogeneity after polymer flooding. In the existing various kinds of deep profile control and flooding technology, it’s economically feasible to use the crosslinked polymer as profile control and displacement agent. Although certain effects are obtained in pilot tests, its antiscour performance is weaker because of many influential factors in the reservoir after polymer flooding [5-6]. When gel is injected into the inhomogeneous formation, it will take the lead into the high permeable layers where the filtrational resistance is smaller and the permeability is higher [7]. The gel can plug the high permeability layers temporarily with its gel forming properties, which makes the subsequent injection of binary complex system turn and into the low permeability layers that are unswept [8-9].

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the displacement technology, alternately injecting the slug of the gel and polymer/surfactant compound system, is presented to improve development effect [10].

Gel is the decentralized system, formed by the crosslinking reaction between crosslinking agent (such as chromium ion crosslinking agent) and polyacrylamide molecular functional groups. And the gelling process is the phenomenon that many individual growth clusters of substance form infinite network structure by the crosslinking. The concentration of crosslinker agent (chromium ion) will affect the relaxation time of the gel system [11]. Although the gel can reduce the oil flow rate well, the condition of high temperature can make the oil displacement performance reduced greatly [12].

The compatibility of gel with polymer/surfactant compound system is unclear; therefore the performance of Cr\(^{3+}\) gel system and its compatibility is studied, comparing with composite ion gel system.

2. Experimental condition

Laboratory chemicals & reagents includes polymer (molecular weight is 2.5×10\(^7\)), Cr\(^{3+}\) crosslinking agent, composite ion crosslinking agent, RMA-1 type surfactant, Heavy alkylbenzene sulfonate. The water used in experimental solutions is advanced treated sewage that degree of mineralization is 6495.15mg/L. Experiment equipment includes interfacial tensiometer, Brookfield viscometer, multi-start magnetic stirring apparatus, electronic balance, thermostat, etc. The experimental temperature is of 45ºC.

3. Results and Discussion

3.1. Influence factors of viscosity of gel system

3.1.1. Mass concentration of polymer.

Using Brookfield viscometer, the viscosity of Cr\(^{3+}\) gel system (the concentration ratio of polymer to crosslinking agent is 10:1) at the initial time and 24 h is measured under different mass concentrations. The relation curves of viscosity with mass concentration are plotted in Figure 1. The regularity can be seen that the viscosity of gel system increases with the increase of mass concentration. This is due to the greater the mass concentration of polymer solution, the higher the carboxyl content of the solution, and the higher the probability of collision between Carboxyl and Cr\(^{3+}\) released from crosslinking agent, which accelerate the complexation between carboxyl and Cr\(^{3+}\). Molecular chains of polymer solutions get entangled with each other and form an irregular mesh structure. With the increase of solution concentration, the entanglement among molecular chains becomes more closely, the relative intermolecular distance becomes smaller, and the arrangement becomes more closely, which results in the increase of gel strength. When the mass concentration of polymer is 1800 mg/L, the viscosity of the system is more than 16000mPa.s after preparing 24h. And then with the increase of mass concentration the rising range of the viscosity decreases. So it’s best to prepare the gel system with polymer of which mass concentration is 1800mg/L from the perspective of economy.

![Figure 1. The relationship between concentration and viscosity of Cr\(^{3+}\) gel system.](image-url)
3.1.2. Gel time of Cr\(^{3+}\) gel system.
Using Brookfield viscometer under the condition of 45°C, the viscosity of Cr\(^{3+}\) gel system which mass concentration is 1800mg/L and the concentration ratio of polymer to crosslinking agent is 10:1 at certain time interval is measured. The change of gel viscosity with time is observed, and the curve of Cr\(^{3+}\) gel stability is plotted in figure 2.

![Figure 2. Curve of Cr\(^{3+}\) gel stability.](image)

The gel viscosity increases rapidly at first. There’re gels after preparing 11h, which the gel viscosity has risen to 2639mPa·s, and then the gel viscosity has risen to more than 15000mPa·s after 24h. It has risen to 25000mPa·s after 7d, and then remain stable at more than 20000mPa·s, which shows that gel performance is very good under the condition of 45°C.

3.1.3. Concentration ratio of polymer to crosslinking agent.
The influence of the concentration ratio to the viscosity relates to the gel time. The polymer solution whose mass concentration is 1800 mg/L is sheared into a dilute solution that viscosity is about 20mPa·s. The gel solutions are prepared according to the concentration ratio is 10:1, 20:1, 30:1, 40:1, 50:1, 60:1 respectively. Then their viscosities are measured when the time is 0h, 6h, 12h, 24h and 48h. The relationship between the concentration ratio and the viscosity can be known after measuring experiment, and it is shown in table 1.

**Table 1.** Viscosity (mPa·s) data tables of Cr\(^{3+}\) gel system of different concentration ratios.

| concentration ratios | 0    | 6    | 12   | 24   | 48   |
|----------------------|------|------|------|------|------|
| 10:1                 | 18   | 163.94 | 2963.28 | 7248.45 | 7222.39 |
| 20:1                 | 17   | 141.95 | 2409.49 | 6318.65 | 6639.01 |
| 30:1                 | 19.5 | 119.43 | 335.93  | 4479.04 | 4569.23 |
| 40:1                 | 21.5 | 101.95 | 209.46  | 2819.32 | 3196.23 |
| 50:1                 | 21.5 | 96.97  | 194.46  | 1986.23 | 2569.38 |
| 55:1                 | 20.5 | 55.99  | 83.98   | 1789.45 | 2389.36 |
The regularity can be seen that the greater the concentration ratio of polymer to crosslinking agent, the longer the gel time, and the weaker the gel strength. When the concentration ratio is relatively small, such as 10:1, the gel time is shorter and the gel viscosity has been more than 2000 mPa.s after 10h. If the gel system which concentration ratio is equal to 10:1 is used to displace oil, it may lead to gel in the near wellbore zone and even block, and the injection pressure may rise sharply, which is bad for deep profile control and flooding. Therefore, choosing the appropriate concentration ratio of polymer to crosslinking agent can generate gel in the depth of high permeability layers to be effective for the deep profile control and flooding. So that the subsequent injection of binary complex system could sweep more residual oil and further enhance oil recovery.

3.2. Compatibility of gel with surfactant

3.2.1. Compatibility of Cr³⁺ gel system with surfactant.

The first solution formula: the concentration of polymer (molecular weight is $2.5 \times 10^7$) is 1800mg/L, the concentration of Cr³⁺ crosslinking agent is 180mg/L.

The second solution formula: the concentration of polymer (molecular weight is $2.5 \times 10^7$) is 1800mg/L, the concentration of Cr³⁺ crosslinking agent is 180mg/L, the concentration of heavy alkylbenzene sulfonate is 0.3 percent.

The third solution formula: the concentration of polymer (molecular weight is $2.5 \times 10^7$) is 1800mg/L, the concentration of Cr³⁺ crosslinking agent is 180mg/L, the concentration of RMA-1 type surfactant is 0.3 percent.

According to the above three formulas, solutions were prepared, then were sealed and put in a thermostat set at 45º C. Changes of viscosity within a certain time can be observed, and correlation curve can be made a graph (Figure 3).

![Figure 3. Correlation curve of viscosity with three compounded solutions of Cr³⁺ gel system.](image)

By the three curves of figure 3, the growth trend of viscosity can be seen that increase rapidly at first and then remain stable at more than 20000mPa·s, which shows that the gel stability is very good.
By contrast with three solutions of viscosity, the compatibility of Cr\(^{3+}\) gel system with RMA-1 type surfactant is better than with heavy alkylbenzene sulfonate. Different forms of three formulas before and after the gelling process were shown in figure 4.

![Figure 4. (a) Before](image1)
![Figure 4. (b) After](image2)

**Figure 4.** Before and after the gelling process about three formulas.

### 3.2.2 Compatibility of composite ion gel system with surfactant.

The first solution formula: the concentration of polymer (molecular weight is \(2.5 \times 10^7\)) is 1800mg/L, the concentration of Cr\(^{3+}\) crosslinking agent is 180mg/L.

The second solution formula: the concentration of polymer (molecular weight is \(1.9 \times 10^7\)) is 3500mg/L, the concentration of organic resin crosslinking agent A is 200mg/L, the concentration of organic resin crosslinking agent B is 1300mg/L, the concentration of heavy alkylbenzene sulfonate is 0.3 percent.

The third solution formula: the concentration of polymer (molecular weight is \(1.9 \times 10^7\)) is 3500mg/L, the concentration of organic resin crosslinking agent A is 200mg/L, the concentration of organic resin crosslinking agent B is 1300mg/L, the concentration of RMA-1 type surfactant is 0.3 percent.

According to the above three formulas, solutions were prepared, then were sealed and put in a thermostat set at 45ºC. Changes of viscosity within a certain time can be observed, and correlation curve can be made a graph (Figure 5).

![Figure 5. Correlation curve of viscosity with three compounded solutions of composite ion gel system](image3)
The curves shown in figure 5 indicates that there’re not gels until three days later and their viscosity increase to more than 2000 mPa·s. By contrast with three solutions of viscosity, the compatibility of composite ion gel system with RMA-1 type surfactant is better than with heavy alkylbenzene sulfonate. But from the viscosity variation tendency of composite ion gel it will be gel breaking. Compared with Cr\textsuperscript{3+} gel system, its stability is worse and its gel viscosity is less. It shows that gel performance of Cr\textsuperscript{3+} gel system is better than composite ion gel system.

3.2.3. The interface compatibility between gel system and surfactant.
The interfacial tension was measured by using interfacial tensiometer for two kinds of surfactants solution and the combination solutions of surfactants solution and gel system. The measuring results are shown in table 2.

| Sample                                      | Interfacial tension mN/m |
|---------------------------------------------|--------------------------|
| RMA-1 surfactant                            | 1.43×10\textsuperscript{-3} |
| heavy alkylbenzene sulfonate                | 1.39×10\textsuperscript{-1} |
| Cr\textsuperscript{3+} gel + heavy alkylbenzene sulfonate | 1.58 |
| Cr\textsuperscript{3+} gel + RMA-1 surfactant | 6.91×10\textsuperscript{-3} |
| composite ion gel + heavy alkylbenzene sulfonate | 1.76 |
| composite ion gel + RMA-1 surfactant        | 7.52×10\textsuperscript{-3} |

The interfacial tension of RMA-1 surfactant has reached 10\textsuperscript{-3} mN/m, but the interfacial tension of alkylbenzene sulfonate surfactants is only 10\textsuperscript{-1} mN/m. The heavy alkylbenzene sulfonate solution is added into prepared solution of Cr\textsuperscript{3+} gel system, and its interfacial tension is measured equal to 1.58 mN/m, but the interfacial tension of solution that added RMA-1 surfactant has reached 6.91×10\textsuperscript{-3} mN/m. This shows that compared with heavy alkylbenzene sulfonate, RMA-1 surfactant has better interface compatibility with Cr\textsuperscript{3+} gel system, which can form ultra-low interfacial tension.

Similarly, heavy alkylbenzene sulfonate and RMA-1 surfactant solution is respectively added into prepared solution of composite ion gel system. The interfacial tension sequence is the same as that of Cr\textsuperscript{3+} gel system. It also shows that gel system has better compatibility with the RMA-1 type surfactant than heavy alkylbenzene sulfonate.

3.2.4. Compatibility of gel system and surfactant after gelling.
The equal amount solution of RMA-1 surfactant or heavy alkylbenzene sulfonate surfactants is respectively added into the gelled solutions, and then the changes of interface between gel and surfactant solution are observed regularly whether gel breaking or not. The observed result indicate that there is no obvious change on the interface between gel and surfactant, and no turbid matter and surfactant have better compatibility in static situation.

The author and others use the slug of the gel system (molecular weight of polymer is 2.5×10\textsuperscript{7}, mass concentration is 1800mg/L, the concentration ratio of polymer to crosslinking agent is 40:1) and polymer/surfactant compound system (molecular weight of polymer is 2.5×10\textsuperscript{7}, RMA-1 surfactant) to displace residual oil after polymer flooding in artificial large flat-panel model, and achieve success that enhanced oil recovery has been reached more than 10 percent after polymer flooding\textsuperscript{[13]}. It can be a technical reserve after polymer flooding which can further enhance oil recovery.

4. Conclusions
- The influence factors of Cr\textsuperscript{3+} gel system viscosity are analyzed by experiment. The result shows that the viscosity of gel system increases with the increase of mass concentration, increases firstly and then remain stable with time, and the greater the concentration ratio of polymer to crosslinking agent, the longer the gel time, and the weaker the gel strength.
Based on experimental analysis, the compatibility of gel with two types of surfactant compared with composite ion gel system has been studied. The experimental result shows that the compatibility of gel with RMA-1 type surfactant is very well. It can produce an ultra low interfacial tension to oil so that enhanced oil recovery has been reached more than 10 percent by using the gel system to displace residual oil after polymer flooding in artificial large flat-panel model.

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References
[1] Xia H F, Jiang Y and Wang G 2010 Study on improving residual oil recovery of polymer/surfactant system after polymer flooding J. Journal of Xi’an Shiyou University (Natural Science) 25 45-9
[2] Zhao F L, Wang Y F and Dai C L 2006 Study on technology of improving oil recovery after polymer flooding J. Journal of China University of Petroleum 30 86-8
[3] Wang D M, Lu H and Nu J G 1998 Application results and understanding of several problems of industrial scale polymer flooding in Daqing oil field
[4] Yang Puhua 1999 Study on present situation of improving recovery and its development direction in the near future J. Petroleum Geology and Recovery Efficiency 6 4-5
[5] Liu Y J and Wang X Z 1999 Technology of profile control and water plugging M. Petroleum Industry Press 127
[6] Liu X G 1998 Technical proceedings of water plugging used in oilfield M. Petroleum Industry Press 94
[7] Zhang J H, Liu M J and Zhang G 2008 Study of the rheological property of low temperature gelatinous plugging agent solution J. Journal of Daqing Petroleum Institute 32 60-2
[8] Zheng B, Hou J R and Zhang M 2016 Research on oil displacement mechanism of crosslinked polymer using CT technique J. Xinjiang Petroleum Geology 1 97-101
[9] Niu L W, Lu X G and Wang X Y 2014 Differences in molecular configuration and seepage properties among polymer, active polymer and Cr$^{3+}$ polymer gel J. Journal of China University of Petroleum 6 186-91
[10] Zhang J H, Dong X and Ye Y Z 2010 Effect of the gel and surfactant alternating injection after polymer flooding J. Daqing Petroleum Institute 34 85-8
[11] Vargas-Vasquez S M, Romero-Zerón L B and Macmillan Bryce 2007 1H NMR characterization of HPAM/Cr(III) acetate Polymer Gel Components International Journal of Polymer Analysis and Characterization 12 115-29
[12] G.X. Shen, J.H. Lee and K.S.Lee 2013 Performance of silicate gel and polymer/Cr(III) gel treatments in high temperature reservoirs Applied Mechanics and Materials 316-317 782-5
[13] Wang Zhongguo, Zhang Jihong and Zhang Zhiming 2012 Oil Displacement by Alternately Injecting Slug of Gel and Polymer/Surfactant Compound System after Polymer Flooding J. Northeast Petroleum University 36 49-53