Performance Evaluation and Adaptability Research of Flowing Gel System Prepared with Re-injected Waste Water

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Abstract: The crosslinking intensity and stability of flowing gel system prepared with re-injected waste water are seriously affected as the high salinity waste water contains a high concentration of Na+, Fe2+, S2-, Ca2+, etc. The influence of various ions on the flowing gel system can be reduced by increasing polymer concentration, adding new ferric ion stabilizing agent (MQ) and calcium ion eliminating agent (CW). The technique of profile controlling and oil-displacing is carried out in Chanan multi-purpose station, Chabei multi-purpose station and Chayi multi-purpose station of Huabei Oilfield. The flowing gel system is injected from 10 downflow wells and the 15 offsetting production wells have increased the yield by 1770 tons.

1. Introduction
The technique of profile controlling and oil-displacing for flowing gel which is referred to as Indepth Drive Fluid Diversion or Colloidal Dispersion Gel abroad is a new depth regulating and displaying technology and it is developed from a high concentration of identify gel system over the last decade\textsuperscript{1,2}. Mack and Smith were the first to discover and apply the gel technology\textsuperscript{3}. The crosslinking intensity and stability of flowing gel system prepared with re-injected waste water are seriously affected as the high salinity waste water contains a high concentration of Na\textsuperscript{+}, Fe\textsuperscript{2+}, S\textsuperscript{2-}, Ca\textsuperscript{2+}, etc\textsuperscript{4}, so the preparation method of the waste water system can not copy with the clear water system. The performance impacts evaluation experiments of water to phenolic resin flowing gel system which is carried out combining with the implementation of the flowing gel system prepared with re-injected waste water in Huabei Oilfield in 2014. The purpose of these laboratory tests is to optimize formula system and direct field conduct. The factors of the waste water that affect the performance of the phenolic resin flowing gel system are analyzed systematically for the first time.

2. Affecting Factors
Influence of the Na\textsuperscript{+}+K\textsuperscript{+} Concentration on the Gel. Na\textsuperscript{+} and K\textsuperscript{+} in the waste water have similar nature and the concentration of Na\textsuperscript{+} is much more than K\textsuperscript{+}, so different concentrations of NaCl is added to clear water system by converting the content of Na\textsuperscript{+} to investigate the influence of the Na\textsuperscript{+}+K\textsuperscript{+} concentration on the gel in laboratory experiment.

Experimental method: First, prepare flowing gel system in which the concentration of polymer is 1500mg/L and the phenolic resin crosslinking agent 2000mg/L. Second, add different concentration of
NaCl and stir evenly. Third, place the solution in the oven at 75°C and observe the crosslinking time. Finally, take the sample out after 3 days and measure the gel viscosity using Rheometer MARS at the shear rate of 7.34s⁻¹. The experimental results are presented in Table 1 and Fig.1. It shows that the viscosity retentivity declines faster in the early stage and then decreases slower as the concentration of Na⁺ rises to 1000mg/L. The stability of the gel is deteriorated when the Na⁺ concentration reaches 5000mg/L and starts to dissolve out water in 20 days. The gel becomes fragile as the concentration is 10000mg/L. The results indicate that the content of polymer in the flowing gel system should be higher than 1500mg/L when Na⁺ is more than 5000mg/L.

**Table 1** Influence of the concentration of Na⁺ on the gel

| concentration of Na⁺[mg/L] | 0    | 100  | 200  | 500  | 1000 | 5000 | 10000 |
|---------------------------|------|------|------|------|------|------|-------|
| crosslinking time[h]      | 24   | 24   | 24   | 24   | 24   | 30   | 30    |
| viscosity of gel[mPa·s]   | 1520 | 1350 | 1216 | 1140 | 1080 | 987  | 562(water-precipitated) |
| viscosity retention rate[%] | 100  | 88.82| 80.0 | 75.0 | 71.05| 64.93| 36.97 |

**Fig. 1** The curve of the change in gel viscosity retention rate with the concentration of Na⁺

Influence of the Ca²⁺⁺Mg²⁺ Concentration on the Gel. The concentration of Ca²⁺ is much more than Mg²⁺ in the waste water, so different concentrations of CaCl₂ is added to clear water system by converting the content of Ca²⁺ to investigate the influence of the Ca²⁺⁺Mg²⁺ concentration on the gel in laboratory experiment.

Experimental method: First, prepare flowing gel system in which the concentration of polymer is 1500mg/L and the phenolic resin crosslinking agent 2000mg/L. Second, add different concentration of CaCl₂ and stir evenly. Third, place the solution in the oven at 75°C and observe the crosslinking time. Finally, take the sample out after 3 days and measure the gel viscosity using Rheometer MARS at the shear rate of 7.34s⁻¹. The experimental results are presented in Table 2 and Fig.2. It indicates that the gel becomes fragile as the concentration of Ca²⁺ rises to 400mg/L. The stability of the system is deteriorated when the concentration reaches 200mg/L and starts to dissolve out water in 20 days. Therefore it needs to raise the content of polymer or add additives in the flowing gel system to weaken the influence of Ca²⁺⁺Mg²⁺.

**Table 2** Influence of the concentration of Ca²⁺ on the gel

| concentration of Ca²⁺[mg/L] | 0    | 50   | 100  | 200  | 300  | 400  | 500  |
|-----------------------------|------|------|------|------|------|------|------|
| crosslinking time[h]        | 24   | 24   | 24   | 24   | 30   | 36   | 36   |
Influence of the Fe\textsuperscript{2+} Concentration on the Gel. Fe\textsuperscript{2+} can affect the gel property and is mainly derived from the iron corrosion products which exist in the form of ferric iron precipitation and Fe\textsuperscript{2+} in the waste water\textsuperscript{[5]}. FeSO\textsubscript{4} is added to the gel system to investigate the influence of Fe\textsuperscript{2+} concentration and oxygen scavenger is also added to prevent Fe\textsuperscript{2+} being oxidized.

Experimental method: First, prepare flowing gel system in which the concentration of polymer is 1500mg/L and the phenolic resin crosslinking agent 2000mg/L. Second, add different concentration of FeSO\textsubscript{4} and a small amount of oxygen scavenger. Third, place the solution in the oven at 75\textdegree C and observe the crosslinking time. Finally, take the sample out after 3 days and measure the gel viscosity using Rheometer MARS at the shear rate of 7.34s\textsuperscript{-1}. The experimental results are presented in Table 3 and Fig.3. It shows that the gel viscosity decreases significantly with the increase of Fe\textsuperscript{2+} content. When the Fe\textsuperscript{2+} concentration reaches 0.5mg/L the gel viscosity declines 12.5% comparing with the clear water system. The stability of the system is deteriorated when the concentration reaches 2mg/L and starts gelout in 15 days. The results indicate that the Fe\textsuperscript{2+} has great effect on the gel. So it needs to strengthen the waste water treatment and slow down the corrosion to reduce the Fe\textsuperscript{2+} concentration. Furthermore, shielding agents which can cause complexation reaction or precipitation should also be added to eliminate the influence of Fe\textsuperscript{2+}.

**Table 3** Influence of the concentration of Fe\textsuperscript{2+} on the gel

| concentration of Fe\textsuperscript{2+} [mg/L] | 0   | 0.5 | 1.0 | 2.0 | 5.0 | 10.0 | 20.0 |
|---------------------------------------------|-----|-----|-----|-----|-----|------|------|
| crosslinking time[h]                       | 24  | 24  | 36  | 40  | 60  | 60   | 60   |
| viscosity of gel[mPa·s]                    | 1520| 1330| 1156| 970 | 736 | 505  | 460  |
| viscosity retention rate[%]                | 100 | 87.50| 76.05| 63.82| 48.42| 33.22| 30.26|

**Fig. 2** The curve of the change in gel viscosity retention rate with the concentration of Ca\textsuperscript{2+}
Influence of the $S^{2-}$ Concentration on the Gel. $S^{2-}$ content is an important indicator of waste water and also the reason of stink.

Experimental method: First, prepare flowing gel system in which the concentration of polymer is 1500mg/L and the phenolic resin crosslinking agent 2000mg/L. Second, add different concentration of Na$_2$S to convert the content of $S^{2-}$. Third, place the solution in the oven at 75$^\circ$C and observe the crosslinking time. Finally, take the sample out after 3 days and measure the gel viscosity using Rheometer MARS at the shear rate of 7.34s$^{-1}$. The experimental results are presented in Table 4 and Fig.4. It shows that the crosslinking time extends with the increase of $S^{2-}$ concentration, but the impact is not so significant. The $S^{2-}$ content in the re-injected waste water of Huabei Oilfield is less than 5mg/L, so the $S^{2-}$ can be viewed as a secondary factor.

**Table 4 Influence of the concentration of $S^{2-}$ on the gel**

| concentration of $S^{2-}$[mg/L] | 0     | 0.1   | 0.2   | 0.5   | 1     | 2     | 5     | 10    |
|---------------------------------|-------|-------|-------|-------|-------|-------|-------|-------|
| crosslinking time[h]            | 24    | 24    | 24    | 36    | 36    | 40    | 40    | 48    |
| viscosity of gel[mPa·s]         | 1520  | 1495  | 1490  | 1475  | 1430  | 1380  | 1320  | 1200  |
| viscosity retention rate[%]     | 100   | 98.36 | 98.03 | 97.04 | 94.08 | 90.79 | 86.84 | 78.95 |

**Fig. 3** The curve of the change in gel viscosity retention rate with the concentration of Fe$^{2+}$

**Fig. 4** The curve of the change in gel viscosity retention rate with the concentration of $S^{2-}$
3. Solution

Countermeasure of Na\(^{+}\)K\(^{+}\). The concentration of Na\(^{+}\)K\(^{+}\) in Huabei Oilfield is 1500mg/L~10000mg/L. This is quite high and the span is extremely great. Additionally, Na\(^{+}\)K\(^{+}\) is not easy to generate precipitation and be screened by other substances. So it is very difficult to remove these two ions and the cost must be quite high. The simplest method is to increase the polymer concentration.

Countermeasure of Ca\(^{2+}\)Mg\(^{2+}\). Ca\(^{2+}\)Mg\(^{2+}\) affect both the polymer and the phenolic resin crosslinking agent. The approach of complexation shielding or generating precipitation can reduce the impact. Therefore, the first stage is to screen appropriate additives.

The thiocarbamide concentration of 50mg/L~100mg/L can stabilize the gel system according to literatures. A new type of organic acid salt (CW) which can reduce the effects of Ca\(^{2+}\)Mg\(^{2+}\) effectively has been developed on the basis of chelating mechanism and initial screening experiments. So the second stage is to optimize the concentration.

Experimental method: First, prepare flowing gel system in which the concentration of polymer is 1500mg/L, the phenolic resin crosslinking agent 2000mg/L and Ca\(^{2+}\) 200mg/L. Second, add thiocarbamide 100mg/L and different concentration of CW. Third, place the solution in the oven at 75\(^{\circ}\)C and observe the crosslinking time. Finally, take the sample out after 3 days and measure the gel viscosity using Rheometer MARS at the shear rate of 7.34s\(^{-1}\). The experimental results are presented in Table 5. The results indicate that the combination of CW and thiocarbamide can increase the gel viscosity effectively and the optimal concentration is 200mg/L~300mg/L.

| Table 5 | Influence of the concentration of CW on the gel |
|---|---|
| concentration of CW[mg/L] | 0 | 50 | 100 | 150 | 200 | 500 |
| crosslinking time[h] | 60 | 50 | 48 | 40 | 40 | 40 |
| viscosity of gel[mPa·s] | 1030 | 1270 | 1360 | 1380 | 1380 | 1350 |

Countermeasure of Fe\(^{2+}\). Fe\(^{2+}\) is a main factor that affects the gel property. Converting Fe\(^{2+}\) into Fe\(^{3+}\) or Fe(OH)\(_{3}\) through adding oxidizing agent can reduce the impact significantly. The oxidizing agent can cause the polymer oxidative degradation easily, so it is not available. Stirring to cause the re-injected water aeration can convert Fe\(^{2+}\) into Fe\(^{3+}\) and generate precipitation when the Fe\(^{2+}\) content is low. Moreover, new ferric ion stabilizing agent (MQ) has been developed and the concentration has been optimized.

Experimental method: First, prepare flowing gel system in which the concentration of polymer is 1500mg/L, the phenolic resin crosslinking agent 2000mg/L and Fe\(^{2+}\) 2mg/L. Second, add MQ and stir evenly. Third, place the solution in the oven at 75\(^{\circ}\)C and observe the crosslinking time. Finally, take the sample out after 3 days and measure the gel viscosity using Rheometer MARS at the shear rate of 7.34s\(^{-1}\). The experimental results are presented in Table 6. The results show that MQ can increase the gel viscosity effectively and the optimal concentration is 20mg/L~50mg/L.

| Table 6 | Influence of the concentration of MQ on the gel |
|---|---|
| concentration of MQ[mg/L] | 0 | 10 | 20 | 50 | 80 |
| crosslinking time[h] | 60 | 50 | 48 | 40 | 40 |
| viscosity of gel[mPa·s] | 950 | 1270 | 1340 | 1320 | 1310 |

4. Application in the Field

The technique of profile controlling and oil-displacing is carried out in Chanan multi-purpose station, Chabei multi-purpose station and Chayi multi-purpose station of Huabei Oilfield in December 2013. New ferric ion stabilizing agent (MQ) and calcium ion eliminating agent (CW) is added to the gel system. The gel is injected from 10 downflow wells. The injection pressure rises steadily and the 15 offsetting production wells have increased the yield by 1770 tons.
5. Conclusion

1) The ions in the waste water including Na\(^+\), Ca\(^{2+}\) and Fe\(^{2+}\) have strong influence on the gel intensity, especially Ca\(^{2+}\) and Fe\(^{2+}\). The stability of the gel are weakened on condition that the concentration of Ca\(^{2+}\) is more than 200mg/L or Fe\(^{2+}\) more than 2mg/L, thus stabilizer is needed.

2) Due to the complexity of the impact factors of the re-injected waste water and superimposed effect of the factors, it is necessary to run experiments to verify and evaluate the formula of flowing gel which is prepared with re-injected waste water. Field application shows that adding new ferric ion stabilizing agent (MQ) and calcium ion eliminating agent (CW) to the profile controlling and oil-displacing system can promote the performance of the gel effectively.

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