Effect of polymerized sewage on viscosity of polymer solution and countermeasures

W T Dong¹,³, K L Wang¹, Y Qiu¹ and W Peng²

¹Key Laboratory of Enhanced Oil Recovery, Northeast Petroleum University, Ministry of Education, Daqing, Heilongjiang, 163318, China
²Bohai Petroleum Research Institute, Tianjin Branch, CNOOC, Tianjin, 300450, China

E-mail: dongwenting@cnooc.com.cn

Abstract. In order to better analyze the influence of sewage on the viscosity of polymer solution, this paper uses BROOKFIELD viscometer to determine the viscosity value of solution. The results show that the viscosity decreases rapidly with the increase of the polymer solution concentration of metal cations. Especially, the concentration of Mg²⁺ and Ca²⁺ have a great influence on the viscosity and the small increase of the concentration of Mg²⁺ and Ca²⁺ can lead to the decrease of the viscosity of HPAM solution. Na₂CO₃ was chosen as the complexing agent to improve the viscosity of HPAM solution, and the viscosity increasing rate of HPAM solution with the concentration of 1500 mg/L reached 33.2%.

1. Introduction

Polymer solutions are widely used in major oil fields in China due to their good viscosity. The mechanism of enhanced oil recovery of polymer solutions is mainly through improving the oil-water mobility ratio and expanding the sweep volume [1-3]. Therefore, the viscosity is directly related to the oil displacement effect. The higher the viscosity of the polymer, the greater the recovery of crude oil [4,5]. At present, Daqing Oilfield mainly uses partially hydrolyzed polyacrylamide (HPAM) as a polymer agent for polymer flooding. The HPAM solution has a good viscosity-increasing effect, but its temperature and salt resistance is poor. In the field construction process of the oil field, sewage is usually used as the water for formulating the polymer, and the composition of the inorganic salt in the oil field sewage is very complicated, and ion concentration has a serious effect on the viscosity of polymer [6,7]. In order to investigate the effect of the polymerization wastewater on the viscosity of the polymer solution [8-10], the method of increasing the viscosity of HPAM solution by sewage polymerization method was studied. The experiment of measuring the viscosity of polymer solution by different sewage was carried out.

2. Experimental conditions

2.1. Experimental materials

Polymer: Partially hydrolyzed polyacrylamide (HPAM for short), solid content of 90%, relative molecular mass of 2500 × 10⁴; Experimental water: 1 on-site sewage in Daqing Oilfield; 2 simulated sewage in Daqing Oilfield, mineralization and ion composition; see text; Inorganic salts: NaCl,
KCl, MgCl₂ and CaCl₂ are all produced from Yangxing Dongxing Reagent Factory, and the content is ≥ 96.0%.

2.2. **Experimental instruments**

BROOKFIELD viscometer (DVII+ type), electronic analytical balance, JJ-1 six-electromechanical stirrer, constant temperature oscillating water bath, 500 mL beaker.

2.3. **Experimental methods**

According to the national standard SY/T6576-2003, the vector process is to add 200 mL of simulated sewage to a 500 mL beaker, and the polymer dry powder required for mass concentration of 5 000 mg/L polymer solution is weighed with a precision balance. At a higher speed mechanical agitator, the polymer dry powder was slowly added to the simulated sewage. After the polymer dry powder was completely added to the simulated sewage for 30 s, the rotation speed was lowered to 100r/min, and stirring was continued for 3 hours. The prepared polymer solution with a mass concentration of 5000 mg/L can be used as mother liquor, which can be diluted into any concentration target solution after completely aging after sealing. Finally, the polymer solution was placed in an oven at 45°C for 12h. The BROOKFIELD viscometer was used to measure the viscosity of the target solution at a rotating speed of 6r/min.

3. **Experimental results and analysis**

3.1. **Effect of monovalent ion concentration on viscosity of polymer**

In order to eliminate the influence of other ions and conditions in the sewage on the polymer solution, this paper first uses distilled water to prepare the polymer mother liquor. The polymer solution was diluted to the desired solution by separately adding a salt solution containing different concentrations of sodium chloride and potassium chloride. The mass concentrations of Na⁺ and K⁺ in the sample to be tested are 0, 500, 1000, 1500, 2000, 2500, 3000, 3500, 4000, 4500, 5000, 5500, 6000 mg/L and the polymer solution is 1500 mg/L. The results of measuring the viscosity of the polymer solution at different monovalent ion concentrations are shown in Figure 1.

The results show that the viscosity of polymer solution decreases with the increase of Na⁺ and K⁺ concentration. Especially when the sodium and potassium ions in the sewage are increased from 0 mg/L to 1000 mg/L, the viscosity of the polymer solution is greatly reduced. Taking the Na⁺ solution as an example, when the viscosity of the solution containing no ionic component in the polycondensation water is 210.6mPa•s, the viscosity of the solution drops to 74mPa•s when the concentration of the monovalent ion is increased to 1000 mg/L, and then further increases by one. The valence ion concentration polymer solution viscosity decreases slowly. However, compared with the low concentration of Na⁺ solution, the viscosity of the polymer with a monovalent ion concentration of 8000 mg/L is only 33.5mPa•s, and the oil displacement effect of the polymer solution will be greatly affected. The main reason for the above phenomenon is that the negative charge of -COO⁻ on the polymer molecule decreases with the increase of the concentration of Na⁺ and K⁺, the electrostatic attraction between the molecules and the molecules decreases, and the friction between molecules decreases. It becomes curled, so the viscosity drops. Because of the small radius of Na⁺ and the same charge, Na⁺ is easier to enter the polymer molecular chain than K⁺ to neutralize the negative charge, and Na⁺ has greater influence on the viscosity of polymer solution than K⁺.

3.2. **Effect of divalent ion concentration on viscosity of polymer solution**

The polymer solution was prepared in the same manner as above, and the mass concentrations of Ca²⁺ and Mg²⁺ in the sample to be tested were 0, 25, 50, 75, 100, 200, 300, and 400 mg/L, respectively. The results of measuring the viscosity of the polymer solution at different divalent ion concentrations are shown in Figure 2.
The higher the concentration of Ca$^{2+}$ and Mg$^{2+}$, the higher the polymer solution also shows a tendency to decrease rapidly and then gradually decrease. This rule has the same effect as the influence of monovalent ions on the viscosity of the polymer solution. Unlike monovalent ions, Ca$^{2+}$ and Mg$^{2+}$ have a large effect on the viscosity of the polymer at a small mass concentration change. When the Ca$^{2+}$ concentration in the solution increased from 0mg/L to 75mg/L, the solution viscosity decreased from 210.6mPa•s to 39.9mPa•s. This is mainly because the Ca$^{2+}$ and Mg$^{2+}$ charge numbers are larger than Na$^+$ and K$^+$, and the ability of the -COO- to carry a negative charge on the polymer molecule is stronger, so that the polymer molecules are polycondensed, the molecular chain shrinks, and dehydration occurs. Therefore, the viscosity is reduced to a greater extent.

3.3. Effect of oilfield wastewater with different ion composition on polymer viscosity
The effects of Na$^+$, K$^+$, Ca$^{2+}$ and Mg$^{2+}$ on the viscosity of the solution were studied by preparing a polymer solution from a single component of simulated sewage. The composition of inorganic salts in oilfield wastewater is very complicated. In this paper, several oilfield wastewaters were used to prepare polymer solutions, and viscosity tests were carried out. The ionic composition of the sewage is shown in Table 1, and viscosities of polymer solutions with a mass concentration of 1500mg/L dissolved in wastewater are shown in Figure 3.
Table 1. Ion composition of sewage.

| Total salinity (mg·L⁻¹) | K⁺ and Na⁺ | Ca²⁺ | Mg²⁺ | Cl⁻ | HCO₃⁻ | SO₄²⁻ | CO₃²⁻ |
|------------------------|-----------|------|------|-----|-------|-------|-------|
| 388                    | 85.8      | 10.9 | 24.1 | 53.2| 122.0 | 62.4  | 30.0  |
| 3261                   | 1178.5    | 13.0 | 28.0 | 1408.9| 323.3 | 278.4 | 60.6  |
| 8930                   | 3130.8    | 27.8 | 64.9 | 4047.3| 891.8 | 696.0 | 71.4  |

The experimental results revealed that the viscosity of the polymer solution prepared using different salinities and ionic compositions varied greatly. The viscosity of HPAM decreases drastically as the degree of mineralization in the solution increases. For a wastewater with a salinity of 388.5mg/L, the viscosity of a polymer with a concentration of 1500mg/L is 88.3mPa·s; when the salinity of the sewage reaches 5176.6mg/L, the polymer solution of the same mass concentration The viscosity is 53.5mPa·s. HPAM exhibits poor salt tolerance, which is mainly due to the negative charge of COO⁻ on the molecular chain of the polymer. The cations in the solution migrate to the vicinity of the negatively charged polymer group under the action of the opposite phase. The number of cations in the adsorption layer is increased, and the number of corresponding diffusion layer cations is reduced. The electrostatic repulsion between the polymer molecules is continuously weakened, and the polymer molecules gradually recover from the stretched state. When the molecular chain is curled, the water molecules around the cation are squeezed out. At this time, the volume of the polymer molecules in the curled state is the smallest, the contact area between the molecules is reduced, the internal friction between the molecules is minimized, and the viscosity of the solution is minimized. Reduce to the lowest value.

3.4. Increase viscosity measures
The above results indicate that the cation in the sewage is the main factor affecting the viscosity of the polymer. Therefore, the method of adding Na₂C₂O₄ as a metal complexing agent is used as a method for increasing the viscosity. The viscosity of the polymer solution is compared with the non-complexing agent and the addition of 210 mg/L of Na₂C₂O₄ as a metal complexing agent under the same sewage conditions and the same polymer mass concentration. The results are shown in Figure 4.
It can be seen from the viscosity results of Figure 4 that Na$_2$C$_2$O$_4$ as a metal complexing agent can effectively reduce the influence of Na$^+$, K$^+$, Ca$^{2+}$ and Mg$^{2+}$ on the viscosity of the solution. After adding 210 mg/L Na$_2$C$_2$O$_4$, the viscosity of HPAM with mass concentration of 1500 mg/L increased from 53.9mPa·s to 71.8mPa·s, and viscosity growth rate reached 33.2%.

4. Conclusions

(1) The concentration of metal cations in the wastewater has a great influence on the viscosity of the polymer, and the viscosity decreases as the concentration of the metal cation increases. In particular, Ca$^{2+}$ and Mg$^{2+}$ have a large influence on the viscosity of the polymer solution at a small change in mass concentration.

(2) Na$_2$C$_2$O$_4$ as a metal complexing agent can effectively improve the viscosity of polymer solution prepared from sewage. After adding 210 mg/L Na$_2$C$_2$O$_4$, the viscosity increasing rate of HPAM with concentration of 1500 mg/L reached 33.2%.

References

[1] Yang C Z and Han D K 1991 Present status of EOR in the Chinese Petroleum industry and its future *J Petrol Sci Eng* 6 175-89
[2] Sevic S and Solesa M 1999 Application, efficiency, and optimisation of chemical for injection water treatment *J Petrol Sci Eng* 15 695-8
[3] Lü X 2010 Study on the influencing factors of preparing polymer solution by using sewage *J Southwest Petrol Univ* 32 162-6
[4] Fernandez I J 2005 Evaluation of cationic water-soluble polymer with improved thermal stability *J Petrol Sci Eng* 9 93-103
[5] Zhang J G 2005 Analysis of the main influencing factors of polymer solution viscosity *Fault Block Oil Gas Field* 12 57-9
[6] Yu D S 2003 Mechanism of polyacrylamide flooding *Oil Gas Field Surf Eng* 8
[7] He S S and Zhang X J 2002 A novel complexing agent for non-pure water polymer flooding polymer solution *Drilling Fluids Completion Fluids* 13 13-5
[8] Ren J W, Zhou X S and Zhang D 2016 Analysis of influencing factors and viscosity effect of polymer solution in sewage *Contemp Chem Indus* 2 272-5
[9] Luo F and Sun G 2016 Study on stability and improvement of polymer solution in sewage *Contemp Chem Indus* 4: 661-4+692
[10] Lin C Y, Xue X S, Zhu W, Zhang X S, Sun F J and Liu H Q 2012 Study on aging law of polymer solution under reservoir flow conditions *Contemp Chem Indus* 8 771-3