Study on Optimization Application of Iron Ion Stabilizer in the Polymer Injection Process of Offshore Oilfield

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Abstract. A large amount of Fe2+/Fe3+ ions are produced by corrosion and fouling in the high-pressure polymer injection process of offshore platforms, which will affect the viscosity of the polymer solution, and is difficult to effectively control by the addition of stabilizers in the curing tank. In order to solve this problem, this paper has carried out related research and the results show that: 1) Fe2+ mainly generates free radicals (·OH) by oxidation catalysis, to destroy long chains of polymer molecules, causing irreversible fragment breakage, resulting in a significant decrease in polymer viscosity; 2) Fe3+ mainly binds to hydroxyl groups, resulting in flocculation and viscosity reduction of polymers; 3) Stabilizers with complexation can effectively control Fe3+ to form water-soluble complexes, while excess stabilizers increase salt content and reduce polymer viscosity by electrostatic shielding effect. In order to effectively control the influence of Fe2+/Fe3+ and the stabilizer on the polymer solution in the production process, an appropriate amount of complex stabilizer should be added to the diluent inlet of the mixture of the polymer mother liquor and the diluent.

1. Introduction
With the deepening of the development of oilfields and the application of polymer flooding technology, it is difficult to satisfy the needs of water for formulating polymer solutions simply by relying on fresh water/clean water. At the same time, environmental protection requires that the sewage generated in the oil field be re-injected into the oil layer/stratum. Most oilfields use a polymer injection process of “Preparing polymer mother liquor with clean water and then diluting and injecting the oil production wastewater” to meet the needs of oilfield production. Although the sewage is treated by ground equipment or process (such as filtration, exposure to oxygen, etc.), the salinity, bacterial content, dissolved oxygen content, reducing ions content, etc. of the treated sewage after treatment will still cause the viscosity of the polymer solution to decrease [1]. The effect of several metal ions on the viscosity of partially hydrolyzed polyacrylamide (HPAM) solution in the water preparation from large to small [2] is Fe2+ > Fe3+ > Mg2+ > Ca2+ > Sr2+ > Ba2+, where Fe2+ is the factor of a sharp decrease in the viscosity of the polymer solution, causing the viscosity of the polymer solution reaching the oil layer is only about 30% of the designed injection viscosity [3-5], and it is difficult to satisfy the performance requirements of the reservoir for the displacement agent. In order to maintain the viscosity of the polymer, different types of treatment agents and treatment techniques have been
developed [6, 7], which has greatly improved the viscosity of the polymer solution prepared by the sewage.

In the engineering application, the polymer injection process always has corrosion scale/fouling corrosion, even if it is treated by related techniques (such as oxygen exposure, adding water freshener and stabilizer), but a certain amount of iron ions (Fe²⁺ and Fe³⁺), still reduce the viscosity of the polymer solution after reaching the bottom of the well. Although the mechanism of the influence of Fe²⁺ and Fe³⁺ on the viscosity of the polymer solution is relatively clear, the influence of Fe²⁺ and Fe³⁺ on the viscosity is a function of time, and the degree of influence on the viscosity is different during the process. Iron ion stabilizers have different effects and even poor effects [8-10]. Therefore, the mechanism and process of Fe²⁺ and Fe³⁺ with polymer solution are studied in detail, and the mechanism of its effect on solution viscosity is further analyzed, which provides guidance and ideas for the screening and optimization of iron ion stabilizer.

2. Experimental conditions and methods

2.1. Experimental materials and instruments

Iron source: analytically pure FeCl₂, analytically pure Fe₂(SO₄)₃.

Polymer: Hydrophobically associating polymer (AP-P4), produced by Sichuan Guangya Company, with relative molecular mass of 6.6×10⁶, solid content of 88.9% and hydrolysis degree of 21.7%.

Stabilizer: PA-TL stabilizer, the main component is sodium nitrilotriacetate

Instruments: BROOKFIELD DV-III cloth viscometer, beaker, suspended agitator (IKA), FEI Quanta450 environmental scanning electron microscope

2.2. Experimental method

(1) Effect of ion concentration (Fe²⁺ and Fe³⁺) on viscosity of polymer solution with concentration of 1750mg/L: ① FeCl₂ and Fe₂(SO₄)₃ were prepared with Fe²⁺ and Fe³⁺ mother liquors with ion concentration of 5mg/L, respectively, and diluted to Fe²⁺(Fe³⁺) solution according to proportion of 0.5mg/L (0.5mg/L), 1.0mg/L (1.0mg/L), 1.5mg/L (5mg/L), 3.0mg/L (10mg/L); ② A polymer solution with a concentration of 1750mg/L was prepared by the above solution. After stirring and dissolving, the solution viscosity was measured by a cloth viscometer at a shear rate of 7.34 s⁻¹.

(2) Effect of time of action of iron ion and ferrous ion on viscosity of polymer diluent: In order to reduce the experimental error, 5.0mg/L (100mg/L), 10 mg/L (300 mg/L) of higher Fe²⁺(Fe³⁺) content was prepared in 1750mg/L polymer solution, the solution viscosity was measured every 8 min.

(3) Effect of pure stabilizer concentration on polymer solution: polymer mother liquor prepared by using distilled water, the ratio of the actual stabilizer to polymer solution concentration is 1:40, the amount of stabilizer added and the concentration of polymer mother liquor ratios are 1/20, 1/25, 1/30, 1/40, 1/50, 1/61.5, 1/99, 1/124, 1/165.6, 1/249, 1/499, 1/999.

(4) Explore the control effect of stabilizers on iron ions and ferrous ions: Select a solution of Fe²⁺ and Fe³⁺ ions with concentrations of 0.5mg/L and 1.5mg/L respectively as solvent to prepare 5000mg/L polymer mother liquor, and determine the solution every 8 min. Viscosity, after the viscosity is stable, the actual application ratio of 1:40 and the 1:99 ratio of the double reduction are studied separately to study the viscosity change.

(5) Environmental scanning electron microscopy was used to analyze the microscopic morphology of polymer solution under different conditions: ① the morphology of 5000mg/L polymer mother liquor prepared by solvent solution with Fe²⁺(Fe³⁺) ion concentration of 0.5mg/L and 1.5mg/L, separately added stabilizer ratios 1/40 and 1/99; ② step (4) separately; ③ step (4) prepared in the system solution method. The scanning electron microscope can be used as follows: 1) Sample preparation: take a drop of the polymer solution from the configured polymer solution and place it on the metal sample bench and fix it. Quickly solidify the solution with liquid nitrogen to freeze the solution, and lock the structural form of polymer solution; then the water molecules are sublimed in a freeze vacuum dryer to maintain the original structure and form of the polymer. 2) Coating gold film: A special device is used to
evaporate gold with a small resistivity and cover the surface of the sample. After the gold film is applied on sample, there is not only a path for incident electrons is provided, but also the charge phenomenon of charge accumulation is eliminated, which can also improve the secondary electron emission rate, increase the signal-to-noise ratio, and obtain images with rich details and high resolution. In addition, after the sample is coated, it can also improve the mechanical strength of the sample surface and enhance the bombardment ability of the electron beam. 3) The microstructure of the polymer solution was observed by scanning electron microscopy.

3. Results

3.1. Effect of Fe\textsuperscript{2+}/Fe\textsuperscript{3+} on viscosity of polymer solution

The long-term production and development of the oilfield has caused the composition of the liquid water to become complex, and the process corrosion and scaling phenomenon has increased. Fe\textsuperscript{2+} and Fe\textsuperscript{3+} will inevitably appear in the injection polymerization process, which will have certain influence on the preparation of the polymer solution. In order to avoid the influence of other ions in the aqueous solution on the polymer, different concentrations of Fe\textsuperscript{2+} and Fe\textsuperscript{3+} were prepared by using distilled water to study the effect of the polymer on the viscosity of the polymer solution.

3.1.1. Effect of concentration on viscosity of polymer solution

The effect of different ion concentration on the viscosity of polymer solution with a concentration of 1750mg/L is shown in the following Figure 1:

\[
y = -28.869x + 332.88 \quad R^2 = 0.9905
\]

\[
y = -2.3736x + 341.82 \quad R^2 = 0.949
\]

![Fig.1 Effect of different Fe\textsuperscript{2+}/Fe\textsuperscript{3+} concentration on polymer solution](image)

It can be seen from Figure 1 that the polymer solution in the Fe\textsuperscript{2+} solution increases linearly with the increase of Fe\textsuperscript{2+} content, and the fitting degree is as high as 99.05%. According to the fitting function, for each increase of 1mg/L Fe\textsuperscript{2+}, the viscosity of the solution decreased by 28.9mPa·s. It can be seen that the effect of Fe\textsuperscript{2+} concentration on the polymer solution is very significant; while in Fe\textsuperscript{3+} solution, the content of Fe\textsuperscript{3+} is increased by 1mg. The viscosity of the solution was only reduced by 2mPa·s. Therefore, compared with Fe\textsuperscript{3+}, Fe\textsuperscript{2+} has a 14-fold increase in the influence on the solution, which indicates that the effect of Fe\textsuperscript{2+} with oxidation catalysis on the polymer solution is much greater than that of Fe\textsuperscript{3+}. The damage of Fe\textsuperscript{2+} in the solution is huge.

3.1.2. Effect of action time on viscosity of polymer solution

The effects of different action times of Fe\textsuperscript{2+} and Fe\textsuperscript{3+} on the viscosity of the solution were further studied. For the Fe\textsuperscript{2+}, three ion concentrations of 1mg/L, 5mg/L and 10mg/L were selected, and Fe\textsuperscript{3+} was selected as 10mg/L and 100mg/L to prepare the polymer solution. 1750mg / L) see Figure 2 and Figure 3:
It can be seen from Figure 2 that different concentrations of Fe$^{2+}$ exhibit different influence characteristics, and have a better linear decreasing relationship under lower concentration conditions (<5mg/L); the concentration decreases at 10mg/L. This indicates that Fe$^{2+}$ will destroy the polymer in a short period of contact, resulting in a large viscosity loss. It can be seen from Figure 3 that the influence of Fe$^{3+}$ is relatively small, and the concentration is enlarged to 100 mg/L, which is equivalent to the viscosity loss of Fe$^{2+}$ concentration of 5 mg/L. It can also be seen from the figure that as the action time of Fe$^{2+}$ and polymer solution is prolonged, the viscosity loss of the polymer solution gradually increases, and finally stabilizes, which means that the Fe$^{2+}$ of the polymer solution is prepared, the earlier the treatment is better.

3.1.3. Microscopic morphology analysis of ion-pair polymer solution

The surface morphology of the polymer solution was further analyzed by environmental scanning electron microscopy. The influence of Fe$^{2+}$/Fe$^{3+}$ on the polymer solution was analyzed, as shown in Figure 4:
It can be seen from Figure 4 that: 1) the blank polymer mother liquor forms a compact spatial
network structure under the association; 2) the microscopic topography of the polymer solution with
Fe\(^{2+}\) concentration of 0.5 mg/L. There are obvious fracture chains in some regional structures. On the
more concentrated chain, the polymer is denser than the blank, because the catalytic oxidation causes
the molecular chain to break. 3) The Fe\(^{3+}\) concentration is 0.5 mg/L. Without destroying the polymer
molecular chain, only the polymer molecular chain is aggregated by complexation, which shows a
phenomenon of concentrated chain bunch aggregation.

The reason that Fe\(^{2+}\) ions have a great influence on the viscosity of the polymer solution is that Fe\(^{2+}\)
ions have strong reducibility and are prone to redox reactions, resulting in the formation of free
radicals. Active radicals easily cause the polymer skeleton to break, making the polymer The
molecular weight is reduced, which ultimately results in a substantial loss of polymer viscosity. In
addition, the oxidation of Fe\(^{2+}\) ions to Fe\(^{3+}\) ions also has a viscosity-reducing effect on the polymer
solution. Therefore, Fe\(^{2+}\) ions can significantly reduce the viscosity of polymer solutions by catalytic
oxidation [10].

3.1.4. Mechanism of action of Fe\(^{2+}\) and Fe\(^{3+}\) on polymers
The mechanism analysis of the influence of iron ions and ferrous ions on the performance of polymer
solution: Fe\(^{2+}\) is different from Fe\(^{3+}\), which is a reducing substance, which is easy to undergo redox
reaction to form Fe\(^{3+}\); in solution, O\(_2\) oxidizes Fe\(^{2+}\) to generate free radicals (·OH) is extremely
unstable and quickly captures electrons from adjacent molecules (long chains of polyacrylamide
molecules), leaving itself in a stable state, causing the polymer to break long chains, showing a
viscosity rapid decline phenomenon of the polymer shown in Fig. 2, the mechanism is as shown in
formula (1)-(8).

\[
\begin{align}
O_2+H_2O+2e & \rightarrow \cdot OH+HO_2^- \\
\cdot HO_2^-+H_2O+2e & \rightarrow 3OH^- \\
HO_2^- + H^+ & \xrightarrow{Fe^{2+}} 2 \cdot OH \\
\cdot OH+PH & \rightarrow P+H_2O(P:HPAM) \\
P+O_2 & \rightarrow P-O-O^- \\
P-O-O^-+PH & \rightarrow P-O-O^-H+P \\
P-O-O-H+Fe^{2+} & \rightarrow P-O^-+Fe^{3+}+OH^- \\
\end{align}
\]

The damage of Fe\(^{2+}\) to the polymer can be manifested by the physical form (spatial geometric
factor) of the polymer molecule in the aqueous solution and the change of the chemical structure. It
mainly means that the "body shape becomes thinner" and the viscosity of the polymer solution
becomes smaller; the polymer in the aqueous solution Molecular degradation, its molecular weight
becomes smaller, the main mechanism refers to "chain becomes shorter" [5]. On the other hand, Fe$^{2+}$ is oxidized to Fe$^{3+}$, and Fe$^{3+}$ is easily bonded to a carboxyl group (-COOH) bond in the polymer molecule to form a coordination bond compound (complex), which destroys the structural characteristics of the polymer molecule and further leads to polymer viscosity reduce.

Therefore, the effect of Fe$^{3+}$ on Fe$^{2+}$ on polymer molecules lacks rapid and strong oxidative degradation, and the viscosity reduction rate and extent are significantly weaker than Fe$^{2+}$, which confirms the experimental phenomena in Fig. 2 and Fig. 3.

3.2. Effect of stabilizer on viscosity of polymer solution

In view of the serious influence of Fe$^{2+}$/Fe$^{3+}$ on the viscosity of polymer solution, the mine uses iron ion stabilizer to control the addition in the polymer preparation process, but the effect is not obvious. Therefore, the effect of the iron ion stabilizer on the polymer solution and the solution containing Fe$^{2+}$/Fe$^{3+}$ polymer was investigated under distilled water conditions.

### 3.2.1. Effect of stabilizer on polymer solution

The effect of stabilizer content on the apparent viscosity of the polymer solution is shown in Figure 5:

![Fig.5 Effect of stabilizers with different content on polymer solution](image)

It can be seen from Figure 5 that as the specific gravity of the stabilizer increases, the viscosity of the polymer mother liquor gradually decreases; in the range of ratio 61.5:1-499:1, the stabilizer has less damage to the polymer mother liquor, and relatively stable (viscosity loss is around 20%); in the range of ratio 40:1 and 50:1, the loss of mother liquor viscosity is further increased to 40%; and the ratio further increase, the viscosity loss increases rapidly. Since the polymer solution is prepared by using distilled water, the influence of other substances on the polymer is excluded in the aqueous solution, and only the presence of the stabilizer affects the viscosity of the polymer solution.

In order to more clearly understand the effect of the stabilizer on the solution, the analysis was compared by scanning electron microscopy, as shown in Figure 6:
Comparing the blank morphology of the blank sample of Figure 4 with the different amount of stabilizer in the polymer matrix of Figure 6, it can be found that the spatial structure of the polymer molecular chain in the blank sample is stretched; and the polymer solution space of the 1/99 stabilizer is added. The structure is deteriorated, the entanglement between the chains is weakened, and the viscosity of the polymer solution is decreased. As the amount of stabilizer increases (1/40), the spatial structure of the polymer solution is forced to deteriorate further, and part of the network structure “collapses”. The influence of the stabilizer mainly composed of sodium nitrilotriacetate on the polymer is chemically analyzed as the polymer prepared by distilled water. Through the electrostatic shielding effect of Na+ salt brought by the stabilizer on the polymer, the viscosity of the polymer solution decreases [11].

3.2.2. Analysis of the Effect of Stabilizer on Fe²⁺/Fe³⁺
The polymer mother liquor was prepared by dissolving Fe²⁺ water. After being dissolved for a certain period of time, a stabilizer was added to determine the viscosity change of the solution, wherein the time of 1/99 addition was 72 min, and the time of 1/40 addition was 84 min. The results are shown in Figure 7:

It can be seen from Figure 7 that: 1) With the stirring time, the viscosity of the solution is gradually decreased by the influence of Fe²⁺. After adding the stabilizer, the viscosity of the polymer mother liquor is not recovered, indicating that the damage caused by Fe³⁺ to the polymer solution is irreversible; 2) Comparing different amounts of stabilizers, the stabilizer with a low adding ratio of
1/99 has little effect on the viscosity of the polymer mother liquor, while the stabilizer with a higher adding ratio of 1/40 ratio controls the Fe\textsuperscript{3+}, and the excess stabilizer further damage to the polymer solution, so the viscosity of the solution is further reduced.

The experimental results of the influence of Fe\textsuperscript{3+} and stabilizer on the viscosity of polymer solution are shown in Figure 8:

It can be seen from Figure 8 that the 1/40 ratio addition of the stabilizer further deepens the damage to the viscosity of the polymer solution, and the experimental phenomenon of the 1/99 ratio addition of the stabilizer shows the opposite state. The analysis considers that the stabilizer complexes Fe\textsuperscript{3+}, which reduces the adverse effect of Fe\textsuperscript{3+} on the polymer solution; while 0.5mg/L and 1.5mg/L appear opposite, the analysis considers that 1.5mg/L matches the amount of stabilizer added. The complexation between each other; while 0.5mg/L is complexed by the stabilizer, the excess stabilizer replaces Fe\textsuperscript{3+} to damage the polymer solution, so 1.5mg/L shows a good viscosity recovery phenomenon.

Based on the macroscopic experimental results of the effect of stabilizer on the performance of polymer solution, in order to further analyze the control of Fe\textsuperscript{2+}/Fe\textsuperscript{3+} in the polymer solution by stabilizer, the microscopic morphology analysis by environmental scanning electron microscopy is shown in Figure 9 and Figure 10:

It can be seen from Figure 9 that the destruction of the polymer solution by Fe\textsuperscript{2+} with a
concentration of 0.5 mg/L is irreversible, and the addition of the stabilizer cannot repair the broken polymer molecular chain, but merely complexes the remaining Fe$^{2+}$ and Fe$^{3+}$ to form a stable. The structural complex is present in the polymer solution.

It can be seen from Figure 10 that for the Fe$^{3+}$ polymer solution with a concentration of 0.5 mg/L, before the addition of the stabilizer (left) (middle), the flocculation of the polymer due to the presence of Fe$^{3+}$ is alleviated, and Fe$^{3+}$ is stabilized. The complexation of the agent is stable, forming the water-soluble complex microparticles shown in the middle figure, and further magnifying the microscopic ratio of the solution (as shown in the right of Figure 10), it can be seen that many tiny granular particle complexes are formed in the solution, It shows that an appropriate amount of stabilizer can effectively complexing Fe$^{3+}$ to form a complex to achieve the purpose of protecting the polymer solution.

Therefore, the effective control of Fe$^{2+}$ and Fe$^{3+}$ caused by process corrosion and scaling needs to meet the following two points: 1) The added stabilizer should be mainly complex metal cations, and does not have oxidation, otherwise it will further damage polymer solution in the oxidation of Fe$^{2+}$; 2) Stabilizer should be added in a high-pressure process line that is prone to corrosion. It is added to the diluted aqueous solution and mixed with the polymer mother liquor to dilute the injection layer. Premature addition will affect the polymer mother liquor.

4. Conclusion
(1) The higher the content of Fe$^{2+}$/Fe$^{3+}$ in the polymer solution, the longer the contact time with the polymer, the greater the viscosity loss to the polymer (Fe$^{2+}$>Fe$^{3+}$); the oxidative degradation of Fe$^{2+}$ is irreversible However, the damage to the polymer by Fe$^{3+}$ is reversible.

(2) Excessive stabilizer will increase the sodium salt content of the solution, and causing the electrostatic shielding to reduce the viscosity of the polymer solution. The higher the content, the greater the damage caused; the proper amount of stabilizer can effectively control the corresponding amount of Fe$^{3+}$ to form water-soluble complex.

(3) For the prevention and treatment of Fe$^{2+}$/Fe$^{3+}$ generated by corrosion scale in the process, an appropriate amount of complex stabilizer should be added to the dilution water pipe before the high-pressure process pipeline poly/water mixing.

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