Research the effect of metal ions on polymer flooding

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Abstract: In the physical model experiment, the polymer is usually manufactured by means of distilled water and sewage. In this paper, it was found by scanning electron microscopy that Ca²⁺ and Mg²⁺ contained in the formulated water reacted with -COO in the polymer. A sharp drop in the viscosity capacity of the solution, And the effect of Mg²⁺ on the viscosity of the solution is about 1.2 to 1.5 times than Ca²⁺. Metal ions have a negative impact on the extraction of polymers., The polymer's adaptability to three ply of oil layers is reduced. Under the condition of high extent of mineralization, the displacement characteristics of the high-efficiency, Viscosity and Salt-resisting polymer is better than middle-divided HPAM, and the enhanced oil recovery value is 3.13% higher than middle-point HPAM.

1. Introduction
At present, the tertiary oil recovery technology based on polymer technology has been applied in industrial applications in major oil fields. Taking Daqing Oilfield as an example, the polymer solution injected in the actual mine is usually manufactured by means of distilled water and sewage. Indoor physical simulation experiments are usually based on this method, and the metal ions contained in the water (mainly Ca²⁺ and Mg²⁺) have little research on the influence of polymer structure and displacement characteristics.

In this paper, the basic structure of high-viscosity salt-tolerant polymer (TS) and HPAM was tested by scanning electron microscopy. The characteristics of TS molecular structure were obtained by comparative analysis, And further study on the morphological changes of several polymers under metal ion conditions. Finally, three kinds of oil layer indoor flooding experiments were carried out on the two polymers to study the oil displacement effect of TS under metal ion conditions and the adaptability to three types of oil layers.

2. Study on the effect of metal ions on the structural morphology of polymers
In this part, the basic forms of high-efficiency viscosity salt-resistant polymer and medium-part HPAM were tested by scanning electron microscopy.

2.1 Experimental conditions
Experimental temperature: 45 °C;
Experimental drug: TS with a concentration of 1000 ppm, 12 million molecular weight HPAM, prepared with distilled water and a solution of 10000 ppm CaCl₂ and MgCl₂.
2.2 Experimental results and analysis

![Image](a) Medium polymer base form (400X)  
(b) Highly viscosity salt-resistant polymer base form (400X)

Figure 1 Two polymer concentration test results prepared in distilled water

According to the test results of the basic structure of the molecular structure (Figure. 1), The distribution of the network structure of the mid-point HPAM is relatively flat and unevenly distributed, Molecular chains are mostly in the form of single chains or unidirectional windings. Space mesh structure has not yet been formed; At the same concentration, the molecules of TS are more likely to form a distinct spatial network structure. It is generally elliptical in shape with a hollow shape in the middle and surrounded by chain links. The structure is different in size.

![Image](Figure 2: Morphology of HPAM added to Ca^{2+})  
![Image](Figure 3: Morphology of HPAM added to Ca^{2+})

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Figure 3: Morphology of HPAM added to Ca^{2+}

![Image](Figure 4 TS molecular form of Ca^{2+} added)  
![Image](Figure 5 Form of TS molecule added with Mg^{2+})

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![Image](Figure 6 Change of viscosity of polymer solution under different concentrations of metal ions)
As shown in Figure 5, a part of the metal ions present in the solution is adsorbed in the vicinity of the -COO⁻ on the molecular chain. An electric double layer is formed on the surface of -COO⁻ an adsorption layer and a diffusion layer. As shown in Figure 6, since Ca and Mg are alkaline earth metals, the extranuclear phase is 8 electrons apart, and the ionic radii of Ca²⁺ and Mg²⁺ are 0.099 nm and 0.08 nm, respectively. The stern layer of Ca²⁺ is relatively thick. The potential drop is slower, the polarity of Mg²⁺ is greater than Ca²⁺, and the ability to compress the electric double layer is strong; And the ability of Ca²⁺ to bind to -COO⁻ is greater than that of Mg²⁺.

3. Study on the effect of metal ions on polymer flooding
In order to obtain the displacement effect of two kinds of high-efficiency viscosity polymers in three types of reservoirs, this part will use heterogeneous artificial cores to carry out oil displacement experiments of different types of polymers under oil layer conditions. In comparison with HPAM, the oil displacement effect of the Viscosity salt-resistant polymer under metal ion conditions was investigated.

3.1 Experimental conditions
(1) Experimental temperature: 45 °C;
(2) Physical model for experiment: three-layer positive rhythm heterogeneous core, core parameters are shown in Table 1:

| Core layer         | Core length (cm) | Effective sectional area (cm²) | Air permeability (10⁻³μm²) | Average porosity (%) | Original oil saturation (%) |
|--------------------|------------------|--------------------------------|---------------------------|----------------------|--------------------------|
| Low permeability   | 30               | 20.25                          | 100                       | 22.1                 | 61.82                    |
| Medium permeability|                  |                                 | 200                       |                      |                          |
| Hypertonic layer   |                  |                                 | 300                       |                      |                          |

(3) Experimental water: Prepare Daqing simulated formation water with a salinity of 6778mg/L, and clear water and sewage from Daqing Oilfield No. 1 Oil Production Plant;
(4) Experimental oil: a simulated oil having a viscosity of 9.8 mPa was measured at 45 °
(5) Experimental reagent: TS of equal viscosity, medium part of HPAM (specific corresponding concentration is shown in Table 2), metal ion solution: total concentration of CaCl₂, MgCl₂ 10000ppm;
(6) Polymer preparation method: clear and dirty;
(7) Injection speed: 0.3 mL/min.

Table 2 Concentration of polymer target liquid of equal viscosity

| order number | Polymer type | Whether to add metal ions | Viscosity (mPa/s) | Concentration (mg/L) |
|--------------|--------------|----------------------------|-------------------|----------------------|
| 1            | Middle score HPVM | no                        | 30                | 1000                 |
| 2            | yes          |                             | 24                |                       |
| 3            | TS           | no                          | 30                | 600                  |
| 4            | YES          |                             | 27                |                       |

3.2 Experimental plan

Table 3 Oil flooding experimental scheme

| Serial number | Specific plan                          |
|---------------|---------------------------------------|
| plan 1        | IPV divide from the middle HPVM       |
| plan 2        | IPV divide from the middle HAVM+ metallic ion |
| Plan 3        | 1PV TS                                |
| plan 4        | 1PV TS+ metallic ion                  |
3.3 experimental results and analysis
The experiment obtained the degree of recovery in the polymer flooding stage before and after the addition of metal salt ions. See Table 4 for details:

Table 4 Comparison of the degree of recovery in the polymer flooding stage before and after metal ion addition

| Order number | Polymer type                          | Whether to add metal ions | Enhanced recovery ratio during the polymer flooding phase (%) | Change in recovery ratio before and after metal ion variation (%) |
|--------------|--------------------------------------|---------------------------|---------------------------------------------------------------|------------------------------------------------------------------|
| Project 1    | IPV divide from the middle of HPAM    | NO                        | 12.81                                                         | -1.34                                                            |
| Project 2    | YES                                  |                           | 11.47                                                         |                                                                  |
| Project 3    | 1PVTS                                | NO                        | 15.77                                                         | -1.17                                                            |
| Project 4    | YES                                  |                           | 14.60                                                         |                                                                  |

![Figure 7 Curves of various parameters in the efficient boost-viscosity and salt-resisting before and after metal ion addition](image-url)
After metal ion addition, the ultimate recovery ratio and the divide from the middle of HPAM has a degree of reduction, and the injection pressure drops significantly. This is because of the greater extent of mineralization condition, Negatively charged polymer groups are combined with cations in solution to reduce their own electro negativity, The potential of the surface of the polymer group can even reach 0. At this time, the polymer molecules gradually recover from the stretched state, the viscosity of the system is lowered, and the oil displacement effect is deteriorated. Therefore, the adaptability of the polymer to the three types of oil layers after the metal ions were reduced.

According to Figure 4, on the condition of high extent of mineralization, The flooding effect of TS is still better than ordinary divide from the middle of polymer, The final recovery grade is 3.13%. It can be seen that TS has strong adaptability under high extent of mineralization.

4. conclusion
(1) Ca\(^{2+}\) and Mg\(^{2+}\) not only combine with the –COO\(^{-}\) hydrolyzed by the polymer to reduce the viscosity of the solution. (2) The effect of Ca\(^{2+}\) and Mg\(^{2+}\) on the viscosity of the solution includes three aspects. Compressed diffusion double layer, Binding ability and ionization ability with –COO\(^{-}\). Integrate these three points, The effect of Mg\(^{2+}\) on the viscosity of solution is greater than Ca\(^{2+}\), About 1.2 to 1.5 times that of Ca\(^{2+}\).

(3) After adding metal ions, the final recovery of TS and mid-point HPAM is reduced to some extent, The flooding effect is obviously worse, The polymer's adaptability to three types of oil layers is reduced.

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