Comparative experiments on polymer degradation technique of produced water of polymer flooding oilfield

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Abstract: The application of polymer flooding technology in oilfields can result in polymer content increased in produced water. This increasing made produced water quality become poor. The efficiency of produced water processing decreased significantly. Processed water quality seriously exceeded criterion's stipulation. The presence of the polymer in produced water is the main reason for more difficulties in processing of produced water, therefore the polymer degradation technology is a key coefficient in produced water processing for polymer flooding oilfields. We evaluated several physical and chemical polymer degradation methods with the solution of separated water from polymer flooding oilfields and hydrolyzed polyacrylamide. The experiment results can provide a basis for produced water processing technologies application in polymer flooding oilfields.

1. Introduction

China applied EOR technologies including polymer flooding massively in most oilfields in order to maintain stable oil production [1]. China has become the country with the largest application scale of polymer flooding technologies [2-5].But these also caused the content of polymer in produced water to increase year by year. For example, the polymer content was 480mg / L in separated water from wells liquids in an oilfield [1]. Polymer-containing water has these characteristics such as higher oil content, smaller average particle size of oil droplets, higher mass concentration of suspended materials, hydrolyzed polyacrylamide (HPAM) in produced water compared with non-polymer-flooding oilfields' produced water. These characteristics made the polymer-containing water became a complex oil-water system, in that polymer increase the viscosity of liquids, slow the speed of the oil-water separation, reduce the capacity of wastewater processing facilities, and all these changes can cause oil content and suspended materials content exceed criterion's stipulation seriously [6-11]. The presence of the polymer in produced water is the main reason of increasing difficulties in oilfield processing of produced water, therefore the polymer degradation technology is a key coefficient in produced water treatment for polymer flooding oilfields. At present researchers developed a variety of polymer degradation technologies with its own application scope [12-13]. We need to evaluate the various polymer degradation technologies in the laboratory first, so that technicians can select the appropriate and suitable polymer degradation techniques easily.

2. Experimental

2.1Materials and laboratory equipment

Test water: processed water from central process station (This kind of water is usually used for polymer solution preparation at polymer injection station);

Polymer: HPAM (hydrolyzed polyacrylamide), relative molecular weight is 20 million.

Other reagents: $NaCLO_3$, anhydrous HCL, Strong oxidants etc.

Experimental apparatus: WY5000-2-IC microwave source instrument, ultrasonic wave generator, the electrolytic cell, CF-G-3-10G ozone generator, electric-heated thermostatic water bath, electric mixer and so on.

2.2 Experimental Methods

Prepared solution containing polymer with HPAM and processed water, the polymer concentration was 250mg / L. Then taked the polymer solution with the same volume respectively, the efficiency of polymer degradation was tested and evaluated with three physical degradation methods and two chemical degradation methods in the laboratory. The method of preparation polymer solution referred and performed according to industry standard. The method of polymer concentration examination was the starch-cadmium iodine method.

3. Physical methods [14-17]

3.1 Microwave on polymer degradation

Microwaves can heat medium and applied in industry for many years. Compared with conventional heating methods, microwave heating has many advantages: higher efficiency, faster heating speed, clean and non-polluting, energy saving.

Mechanism of microwave degrading polymer:

1) Heating effect: because the microwave heating solution can cause a sharp temperature rise to form an instant high temperature in small area. These can degrade polymer. Degradation begins from the end of the molecular chain or a weak link of the molecular chain, connected monomer chain disconnected into monomers. Heating makes polymer molecular chain disconnect in an irregular way so that the big molecular polymer become relatively smaller molecular polymer. Heating makes the small side groups molecules of polymer molecular chain disconnect from the main chain of polymer molecules, and when the quantity of these small molecules polymer accumulate to a certain amount, main polymer chain scission occurs, polymer are degraded fully then.

2) Non-thermal effect: this non-thermal effect can disconnect C-C bond in long-chain polymer molecules, so that the polymer is degraded.

Took four prepared polymer solutions to microwave radiation to test rate of microwave degrading polymer. The frequency of microwave was 2450MHz, and the radiation power was 400W, 600W, 800W, 1000Wrespectively, Figure 1 showed changes of the polymer degradation rate with time at different radiation power.

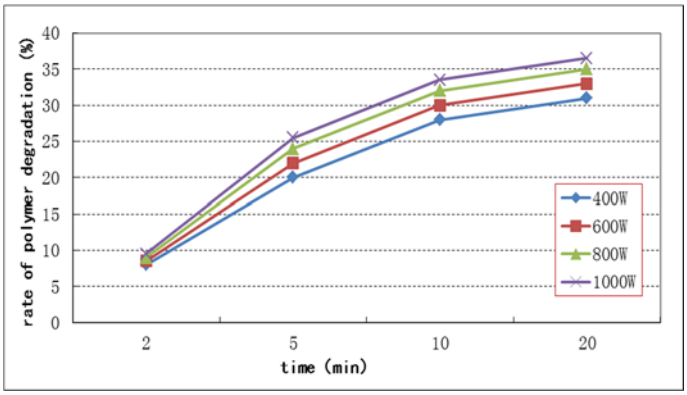

Figure 1 Microwave treatment to polymer degradation

Overall, the effect of polymer degradation with microwave was not ideal, even microwave radiate the four prepared polymer solutions 20 minutes, the degradation rate was also less than 40%.

3 .2 Ultrasonic on polymer degradation

Mechanism of Ultrasonic degrading polymer:

The main reason of Ultrasonic degrading polymer is part high temperature and part high pressure generated by ultrasonic cavitation. Ultrasonic cavitation can generate bubbles in solution and these bubbles collapse quickly. The entire process takes place during a very short time in ns, which result in abnormal high temperature (greater than 5000K) and high pressure (greater than 50MPa) in cavitation bubbles, at the same time also result in strong shock wave and jet flow with speed of 400km/h. These create an excellent physical and chemical environment for the degradation of organic matter, which is enough to disconnect chemical bonds with powerful chemical binds. So ultrasonic can be used to degrade water pollutants directly. In addition, hydroxyl radical with high oxidation potential generated at high temperatures and high pressures can oxidize many organic matters, so that it can degrade the intractable polymer under conventional conditions.

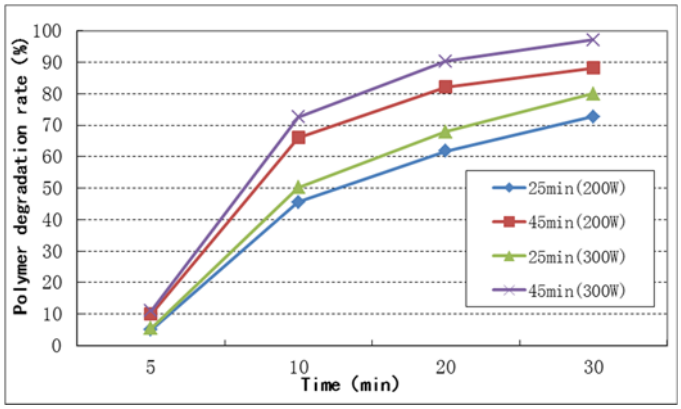

Figure 2 Ultrasonic on polymer degradation

Took four 500ml prepared polymer solutions to test at different test times, different frequencies and radiated power of ultrasonic. Figure 2 showed the degradation rate of four tests at Ultrasonic frequency of 2450MHz, the polymer solution temperature was 25℃, 45℃, the Ultrasonic radiation power was 200W and 300W respectively.

Figure 2 showed that ultrasonic has a good degradation effect on polymer, the degradation rate can reach to more than 90% after treating 20 minutes. Figure 2 also showed that temperature has obvious effect in polymer degradation.

3.3Electrolytic on polymer degradation

The mechanism of this method:

(1) HPAM in production fluids produced from polymer flooding oilfield is a kind of polyelectrolyte, the electrolyte can be separated by electrolysis.

(2) There are small amounts of $CaCl_2$ and NaCl in production fluids in polymer flooding oilfield, we will get hypochlorite when these two substances electrolyzed, while hypochlorite is a strong oxidizing agent, it can degrade HPAM.

The space between the electrode plates was 2mm, electrolysis voltage was 8V, electrolytic current was 220mA, electrolytic pool volume was 500ml. Titanium plate were used for Cathode and anode.

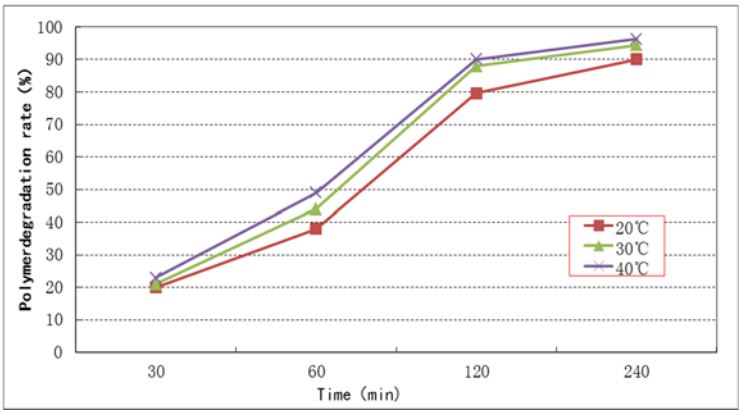

Figure 3 Electrolytic on polymer degradation

Figure 3 showed that the speed of polymer degradation was slow within the first 60 minutes, but the polymer degraded rapidly then. The polymer degradation rate can achieve to 90% after 120 minutes, but the whole processing took a longer time. The temperature had some influence on polymer degradation, the polymer degradation rate ascended quickly at higher temperatures.

4. Chemical oxidation method [18-23]

The mechanism of this method:

Oxidants can change chemical composition and structure of polymer, which decreases the polymerization degree of polymer molecule, so the main chain of polymer are disconnected, then the polymer is degraded. Polymers oxidation can form peroxide. The peroxide is easily to be decomposed and produce free radicals for they are unstable. Free radicals can reduce chemical energy of decomposition reaction during the process of chemical degradation, which can promote the degradation of polymers.

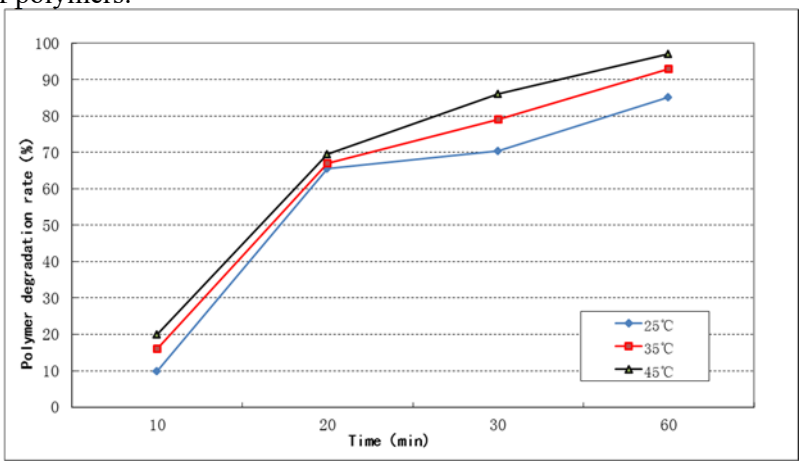

Figure 4 Ozone on polymer degradation

4.1 Ozone on polymer degradation

The experiment adopted a 15w ozone generator which used oxygen as oxygen source. The ozone generator produced ozonized gas. The mixture gas of ozone and air flowed into the test solution then. Figure 4 was the test results of three test conditions with different temperatures and the same amount of ozone gas. The result showed that ozone had good effects on the polymer degradation. The degradation rate can reach to more than 90% after a 30min treatment. Figure 4 also showed that the effect of temperature on ozone degrading polymers are obvious. Compared with other strong oxidants the cost of ozone is higher, but residual quantity is less in the treated water. And ozone will not affect the subsequent processing.

4.2 ClO_2 on polymers degradation

ClO_2 can remove downhole blockage in the polymer flooding oilfields because ClO_2 can degrade plugged HPAM formed in formation conditions. Based on this, this experiment tested the degrading ability of ClO_2 under the condition of the ground, in order to explore a new ways for the oilfield polymer-containing wastewater treatment on the ground.

This experiment applied ClO_2 mixture gas ,the mixture gas contained ClO_2 60%, Cl_2 40%.

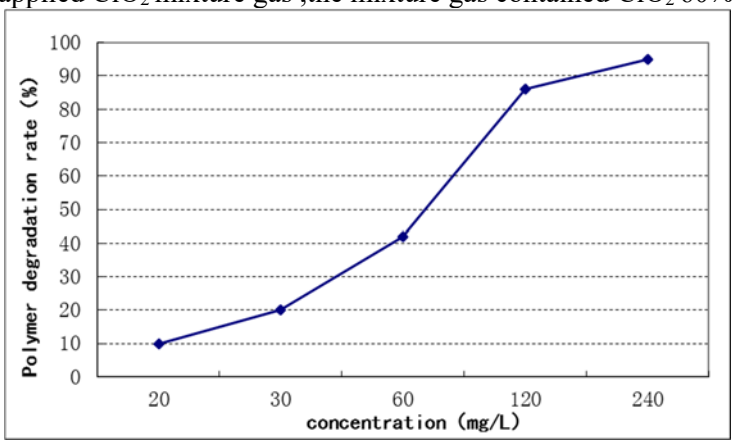

Figure 5 ClO_2 on polymers degradation

Figure 5 showed that the rate of polymer degradation can reach to 90% when ClO_2 concentration was more than 120mg/l in solution. So ClO_2 can be used in practical polymer degradation in the oilfield.

5. Analysis and Conclusion

1) From the above experimental results, the physical degradation of the polymer method requires some processing time, but even in adequate processing time, microwave is still difficult to achieve the desired effect of degradation. Ultrasonic method and electrolysis degradation effect is good, but electrolysis degradation need solve the problem of electrode plate corrosion. On the other hand, physical methods have its own advantages: smaller size of facilities, less space occupation, simple and flexible operation. It is easy to use in oilfields.

2) Compared with the physical methods, chemical methods of oxidation polymer degradation have advantages: higher polymer degradation rate, shorter processing time, but its need a certain concentration of oxidants.

3) Polymer-containing wastewater treatment in oilfields should not only used one single method, processing design should also consider the synergistic effect of physical and chemical oxidation methods to improve the polymer degradation efficiency, reduce the cost of polymer containing water treatment.

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