

Compatibility of Agents for Polymer-bearing Produced Water from Oilfield

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Abstract. The compatibility of polymer-bearing produced water and corrosion inhibitor, bactericide has been explored from the angle of suspended solids content (ssc) of produced water from water treatment process of a station in Shengli Oilfield. The results show that cationic corrosion inhibitor and bactericide can interact with negatively charged suspended solids and polymers in produced water, resulting in the increase of ssc of produced water. Therefore, the use of cationic agents should be avoided for polymer-bearing produced water, therefore non-ionic and zwitterionic agents should be alternatives. Experiments show that the zwitterionic bactericide not only effectively controls SRB, but also hardly effect on the ssc of produced water.

1. Introduction

It has been known that developed oilfields in central and eastern China generally have come to a production mode of water injection cycle. Produced water is not only the product of oil recovery, but also the driving source of oil production. Therefore, the treatment quality of produced water determines the production effect, and is also an important guarantee for oil production.

After treatment, the produced water must meet the corresponding injection standard [1-3]. Among them, the average corrosion rate and bacterial content are two very important indicators, which are related to the corrosion and scaling of pipelines and tank walls, as well as the formation blockage. Adding corrosion inhibitor and bactericide is a very important way to control the average corrosion rate and bacterial content in injection water. Therefore, the adaptability of corrosion inhibitors and bactericides has also been reported. In enhanced oil recovery or tertiary oil recovery technologies, polymer solutions are often prepared with treated produced water. It was found that [4] cationic bactericide can precipitate or flocculate polymer solution and reduce the viscosity of polymer solution. Corrosion inhibitors, bactericides and scale inhibitors, flocculants, demulsifiers must be compatible; otherwise it will decrease the performance of various agents [5].

In this paper the compatibility of polymer-bearing produced water and agents, hereinafter referred to corrosion inhibitor, bactericide has been explored from the angle of suspended solids content (ssc) of reinjection water from water treatment process of a station in Shengli Oilfield, and the direction of exploration in the near future on corrosion inhibitor and bactericide has also been mentioned.

2. Process and Effect of Produced Water Treatment

The produced water treatment in this station adopts two-stage sedimentation combined with filtration process, as shown in figure 1. The main equipment consists of 2 primary deoiling tanks of 2000 m³, 2 secondary coagulation tanks of 2000 m³, 2 buffer tanks of 1000 m³ and 8 walnut shell filters of Φ3.4



m. The daily treatment water volume is $2 \times 10^4 \text{ m}^3$. The total salinity of the produced water is 18457.8 mg/L and the water type is calcium chloride. The polymer content is 15 mg/L. The content of SRB bacteria is higher. The composition of produced water is shown in table 1.

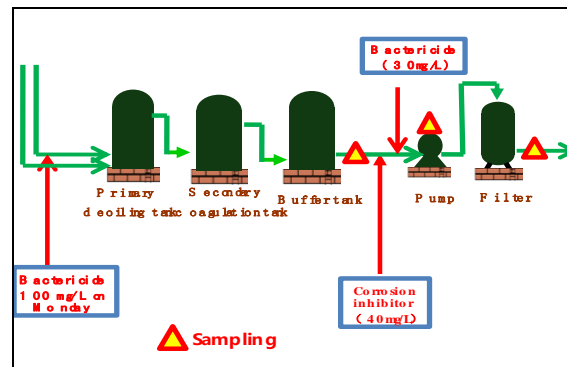


Figure 1. The Produced Water Treatment Process

Table 1. Components and Characterization for Produced Water

Items	Value	Items	Value
Na^+ , mg/L	6502.3	Temperature, $^{\circ}\text{C}$	50
Ca^{2+} , mg/L	615	pH	6.71
Mg^{2+} , mg/L	63.2	Dissolved oxygen, mg/L	0.03
Fe^{2+} , mg/L	4.8	Free carbon dioxide, mg/L	70.4
Cl^- , mg/L	10812.3	Sulfate, mg/L	0.214
HCO_3^- , mg/L	460.2	SRB, /mL	6.0×10^4
Salinity, mg/L	18457.8	FB, /mL	0
Polymer, mg/L	15	TGB, /mL	0.6

According to the screening results in 2014, the imidazoline corrosion inhibitor and the double quaternary amine salt with 40 mg/L dosage respectively had the best performance for this produced water, then corrosion inhibitor and bactericide were designed to continuously pump into the produced water through two dosing points of 10 meter-distance along the pipeline before the buffer tank and the pump. Furthermore, the dosage of 100 mg/L bactericide was being pumped into the produced water for 8 hours on Monday through a dosing point on the pipeline before the primary deoiling tanks.

The ssc was analyzed for the produced water, which was sampled every hour at different nodes of the treatment process. According to standard [1], microporous nitrocellulose membrane (Merck Millipore in Ireland) with a pore size of 0.45 μm was applied. The results are shown in figure 2.

There is no treatment between pump and buffer tank except for the dosage of chemicals. Technically, the ssc should keep unchanged. However, on average, the ssc of water sample from pump outlet was averagely 20 mg/L higher than that of the outlet of buffer tank.

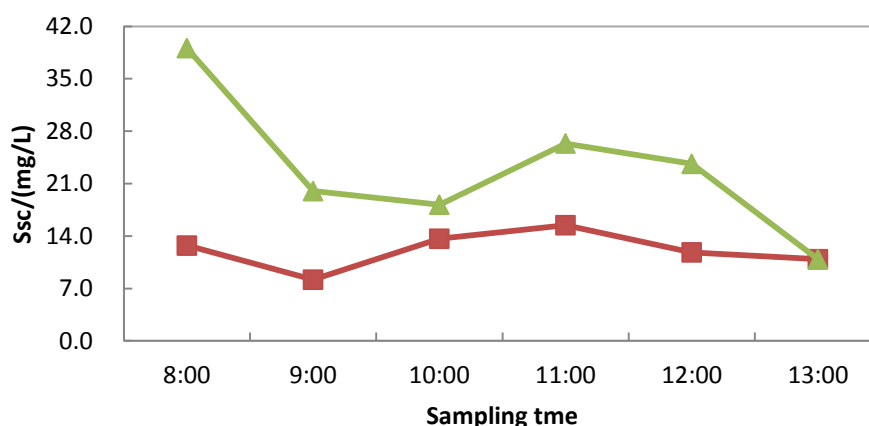


Figure 2. The ssc of Produced Water from Nodes along the Treatment Process

▲ Pump Outlet
■ Buffer Tank Outlet

3. Compatibility of Agents and Polymer-bearing Produced Water

The test above proves that the ssc of produced water along water treatment process is increased after the dosage of the agents. In order to evaluate the compatibility of produced water with agents applied, produced water samples without any agents were taken as blank for laboratory evaluation. The blank samples with addition of corrosion inhibitor and the bactericide respectively were taken as test samples. Afterwards the ssc was analyzed for all those samples, and the results are shown in figure 3. It can be seen that compared with the blank water sample, the ssc of water with the addition of 36.8 mg/L of corrosion inhibitor was increased by 18 mg/L averagely, and the ssc of water with the addition of bactericide 36.8 mg/L was increased by 22 mg /L averagely. Laboratory evaluation is consistent with the field test.

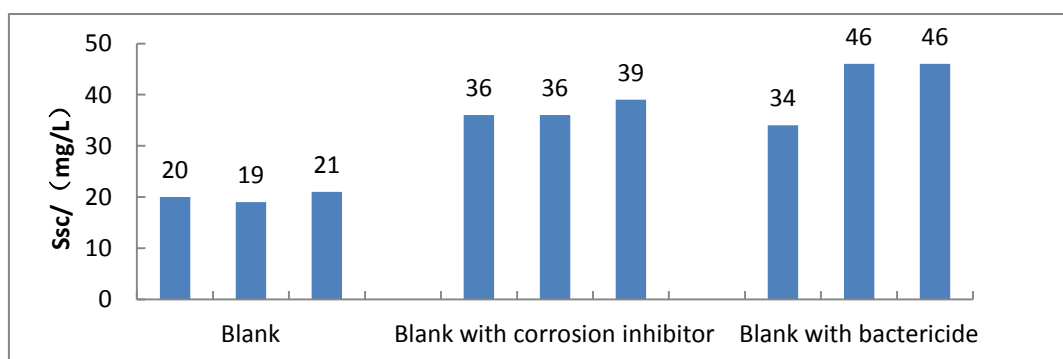


Figure 3. The ssc of Produced Water, of that with the Addition of 36.8 mg/L of Corrosion Inhibitor, and of that with the Addition of Bactericide 36.8 mg/L Respectively

4. Reasons for Incompatibility between agents and Polymer-bearing Produced Water

Corrosion inhibitors are classified into three types: oxidation film, precipitation film and adsorption film. Adsorption film is the most widely used type, and imidazoline compounds are the main ones, see figure 4. Among many bactericides, because bacterial cell walls are usually negatively charged, cationic surfactants are the earliest and most widely used bactericide, such as double quaternary amine salt, as shown in figure 5.

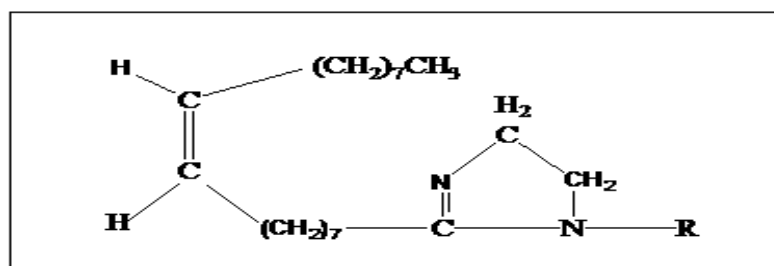


Figure 4. Imidazoline Corrosion Inhibitor

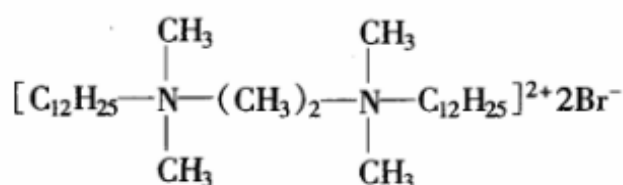


Figure 5. Double Quaternary Amine Salt Bactericide

Double quaternary amine salt is cationic and can ionize into cationic quaternary ammonium group in water. In preparation of imidazoline corrosion inhibitor, tertiary amine cation is formed by adding hydrochloric acid to increase the water solubility of the product. Negatively charged suspended solids and polymer for oil displacement exist in produced water. Polymers for oil displacement are generally anionic partially hydrolyzed polyacrylamide.

Generally, polymer will further degrade and its molecular weight will decrease while migrating and working in the reservoir. According to long-term follow-up analysis, the molecular weight of residual polymer in produced water is generally about 500,000. At the same time, hydrolysis and curl of polymer molecules will occur [6]. Therefore, the polymer in the produced water is negatively charged soft particles.

Polymer soft particles are negative, and the suspended solid particles in produced water are negative, too. They all aggregate with cationic agents because of electrical attraction, that is, cationic agents act as flocculants. There are three reasons for the increase of ssc in the suspended solids test process based on filter membrane filtration. Firstly, cationic agents' aggregate small particles which could pass through 0.45 μm filter membrane into larger particles which could not pass through 0.45 μm filter membrane and those large particles remain on the filter membrane. Secondly, agents and polymers also remain on the filter membrane. Thirdly, the retention of larger particles, polymers and agents in the filter membrane results in dense plugging of the filter membrane, and pore size of the filter membrane getting smaller and smaller, through which the smaller particles in produced water can't pass. Any one of the above reasons will lead to the increase of ssc.

5. Attempts to Use Zwitterionic Bactericide

Regarding the influence of cationic corrosion inhibitor on suspended solids in produced water, the investigation on preparation, performance and contribution to suspended solids for a non-ionic Imidazoline corrosion inhibitor has been explored in previous work [7]. Since bactericide should contain cationic groups to adsorb to negatively charged bacteria, bactericides won't contribute to suspended solids only when the bactericide molecules are electrically uncharged. Therefore, this study tried to find a type of zwitterionic bactericide, and checked its performance [2] and the effect on the suspended solids in the produced water.

From table 2, it can be seen that the growth index of SRB is 221, the number of sulfate reducing bacteria (SRB) corresponding to the table [1] was 70 /mL, the dilution factor is 10^4 , that is, the number

of bacteria in the blank sample was 7×10^4 per milliliter, while table 3 and table 4 indicate that the inhibitory concentration for zwitterionic bactericide was 30-50 mg/L, which satisfies the current standard: when SRB numble is 10^4 - 10^5 /mL, the inhibitory concentration is less than 70 mg/L [2].

Table 2. Numbering of SRB in Blank Water Samples

Order	0	1	2	3	4	5	6	7	8	9
Bottle 1	+	+	+	+	+	-	-	-	-	-
Bottle 2	+	+	+	+	+	+	-	-	-	-

Table 3. Numbering of SRB in Blank Water Samples with Zwitterionic Bactericide

Order	Agent concentration mg/L									
	30 mg/L		50 mg/L		70 mg/L		100 mg/L		120 mg/L	
0	+	-	-	-	-	-	-	-	-	-
1	-	-	-	-	-	-	-	-	-	-
2	-	-	-	-	-	-	-	-	-	-
3	-	-	-	-	-	-	-	-	-	-
4	-	-	-	-	-	-	-	-	-	-
5	-	-	-	-	-	-	-	-	-	-

Table 4. Numbering of SRB in Blank Water Samples with Zwitterionic Bactericide

Order	Agent concentration mg/L									
	30 mg/L		50 mg/L		70 mg/L		100 mg/L		120 mg/L	
0	-	-	-	-	-	-	-	-	-	-
1	-	-	-	-	-	-	-	-	-	-
2	-	-	-	-	-	-	-	-	-	-
3	-	-	-	-	-	-	-	-	-	-
4	-	-	-	-	-	-	-	-	-	-
5	-	-	-	-	-	-	-	-	-	-

The contribution of the zwitterionic bactericide to ssc of produced water was also tested. The results are shown in the table 5. The ssc of blank water sample was 3.0 mg/L, with the addition of 40 mg/L of double quaternary amine salt bactericide was 19.4 mg/L averagely, and the ssc of water with the addition of zwitterionic bactericide was 4.8 mg/L averagely. Zwitterionic bactericide has little contribution to polymer-bearing produced water.

Table 5. The Contribution of the Zwitterionic Bactericide to ssc in Produced Water

Sample	Agent added	Agent concentration mg/L	Ssc mg/L	Average ssc mg/L
1	None	-	2.5	3.0
2	None	-	3.6	
3	Double quaternary amine salt bactericide	40	17.4	19.4
4	Double quaternary amine salt bactericide	40	21.5	
5	Zwitterionic bactericide	40	2.8	4.8
6	Zwitterionic bactericide	40	6.9	

6. Conclusions and Suggestions

The results show that cationic corrosion inhibitor and bactericide can interact with negatively charged suspended solids and polymers in produced water, resulting in the increase of ssc of produced water. Therefore, the use of cationic agents should be avoided for polymer-bearing produced water, and non-

ionic and zwitterionic agents should be used instead. Experiments show that the zwitterionic ion bactericide not only has good bactericidal effect, but also has little effect on the ssc of produced water.

7. Acknowledgments

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8. References

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