

Research and Application of the Technology to Increase Viscosity and Viscosity Retention for Polymer Solution Prepared With Oilfield Wastewater

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Abstract

Large amounts of wastewater has been produced during the development of oilfield production, furthermore, plenty of freshwater has been consumed to prepare polymer solution. This paper take a type of Shengli oilfield produced water as the research object. The combined technology of biological oxidation and biological competition was developed and tested to treat produced water. Biological oxidation technology can remove COD and hydrogen sulfide effectively. The removal efficiency is above 65% and 100% respectively. Viscosity of polymer solution (the concentration was 1,700 mg/L) prepared with this water is above 30 mPa·s. Biological competition technology can weaken SRB activity considerably. The viscosity of the polymer solution can be maintained above 20 mPa·s for more than 14 days, which meet the production standard. Application of the technology, which can not only save fresh water, but also reducing pollution discharge, has significant social and economic benefits.

Key words: Oilfield wastewater; Biological contact oxidation; Bio-competitive exclusion process; Polymer solution; Viscosity

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INTRODUCTION

The majority of Chinese oilfields are in their middle or late years of development, and chemical flooding represented by polymer flooding is becoming an important technical guarantee for stabilizing oilfield output^[1]. In practical application, unfortunately, plenty of fresh water is used for preparing polymer solutions. This not only consumes valuable freshwater resources, but also results in surplus effluent that has to be discharged or ineffectively re-injected. On the other side, preparing polymer solutions with oilfield waste water can not only decrease the need for freshwater resources, but also reduce effluent discharge and protect the environment^[2]. However, the presence of ions, reductive matters, microbes and suspended substances in produced water decreases the viscosity of polymer solutions and limits its performance^[3]. Therefore, it will be of both economic and social interest if oilfield produced water is reused after treatment as an alternative for clear water in preparing polymer solutions to keep the viscosity and improve the viscosity retention.

This paper identifies some of the key contributors to the declined viscosity of polymer solutions prepared with produced water by examining the produced water from Chengdong Oilfield, and presents a way to maintain the viscosity of polymer solutions by removing the reductive matters in the effluent through bio-oxidation processes, and to maintain long-term stability of polymer solutions in the oil layers by inhibiting SRB activity through bio-competition. Polymer solutions prepared with the treated produced water show much greater viscosity and prove effective for field production. Wider application would not only decrease the need for freshwater resources, but also minimize the discharge of surplus effluent. This offers a new way to the reuse the oilfield waste water.

1. FACTORS CONTRIBUTING TO THE VISCOSITY LOSS OF POLYMER SOLUTIONS PREPARED WITH PRODUCED WATER

A pilot-scale application of foam combination flooding at Chengdong Oilfield started in 2004. However, in 2006, a decline was observed in the viscosity of the polymer

solution when injecting the main slug. The design viscosity for polymer solutions diluted with produced water at 1,800 mg/L is above 20 mP·s, whereas that of the polymer solution at the site was a merely 1-5 mPa·s. The declined viscosity of the polymer solution limited the development performance of foam flooding and became a bottleneck for further implementation of the process.

To investigate the cause of the decline, the produced water from this block was analyzed (Table 1).

Table 1
The Analysis of the Oilfield Produced Water

| Analyte | Suspended substance mg/L | Oil content mg/L | COD mg/L | H ₂ S mg/L | SRB pc/mL | TDS | Fe ²⁺ mg/L | pH |
|---------|-----------------------------|---------------------|----------|-----------------------|-----------|-------------|-----------------------|---------|
| Range | 8.0-40.2 | 20.0-60.7 | 260-420 | 4-8 | 110-600 | 5,998-6,500 | 0.1-0.3 | 6.6-6.9 |

Laboratory analysis showed presence of reductive matters like hydrogen sulfides and Fe²⁺, a large population of sulfate reducing bacteria, and high COD. Some of the key contributors to the declined polymer viscosity were subsequently identified after repeated laboratory and field test: (a) Free radical reaction between the dissolved oxygen present in the mother liquid of the polymer and the reductive matters and trace metal ions present in the produced water, under the action of the trace metal ions, which resulted in breakup of the polymer matrix and thereby significant loss in the polymer viscosity^[4]; (b) Elevated COD due to the foaming agent, corrosion inhibitor and demulsifier added

in the produced water treatment, which degraded the polymer and curled the molecular chain and thereby led to loss of viscosity; (c) Production of hydrogen and Fe²⁺ by the sulfate reducing bacteria present in the produced water when growing and reproducing using the polymer as its carbon source, which resulted in degradation of the polymer and thereby loss of viscosity.

2. LABORATORY STUDIES

2.1 Laboratory Apparatuses and Principles

The laboratory process is as indicated below.

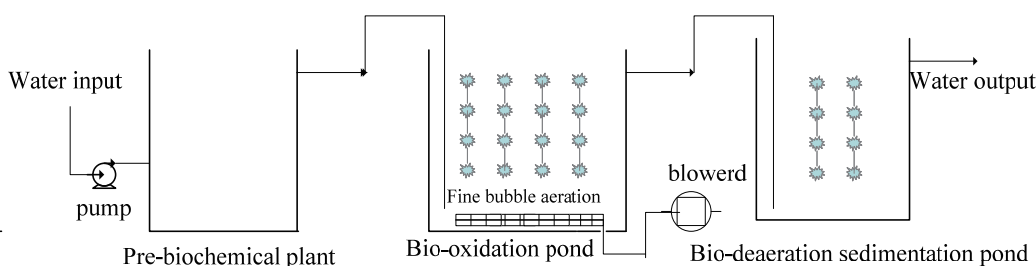


Figure1
Laboratory Process of Physical Simulation of Treatment

In the laboratory experiment, produced water was pumped into the pre-biochemical plant to remove the majority of suspended oil and other contaminants and reduce the subsequent biochemical treatment load^[5]. The recovered crude oil was reusable. The output water was directed into the bio-oxidation pond, where biological filler and an aeration system are installed and sulfur oxidizing bacteria (SOB) and hydrocarbon degrading bacteria are inoculated. Under the action of SOB, the reducing substances in the produced water were transformed into high-valence compounds, and the hydrogen sulfides were thereby removed. Hydrocarbon degrading bacteria, on the other side, could remove most of the nutrition substrate on which oil, COD and other bacteria rely for reproduction. Water from the bio-

oxidation pond was then directed into the deaeration and sedimentation pond, where oxygen was consumed by the growing aerobic bacteria down to below 0.1 mg/L. Nitrate reducing bacteria (DNB) was also inoculated to the pond, where the growth of sulfate reducing bacteria was inhibited through bio-competition.

2.2 Laboratory Results and Discussions

2.2.1 Removal of Sulfides

S²⁻ in the produced water is one of the key contributors to the declined polymer viscosity^[6]. S²⁻ hydrolysis produces harmful sulfides. Free radicals produced by the oxygen-sulfur system play an important role in the degradation of polymers. The sulfur oxidizing bacteria (SOB) inoculated during the biochemical treatment is able to

transform the reducing substances in the produced water into high-valence compounds and thereby remove the hydrogen sulfides in the produced water and maintain the polymer viscosity. The performance of biochemical treatment in removing sulfides from the produced water is indicated in Figure 2.

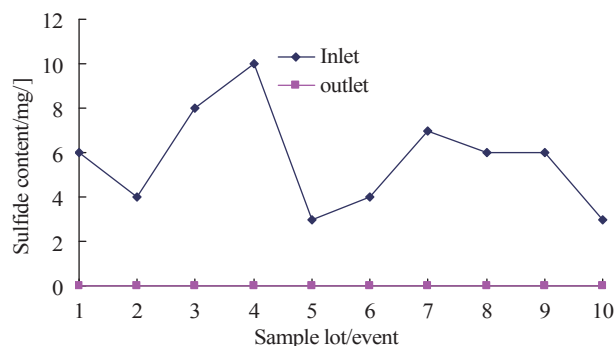


Figure 2
The Removal Effect of Hydrogen Sulfide

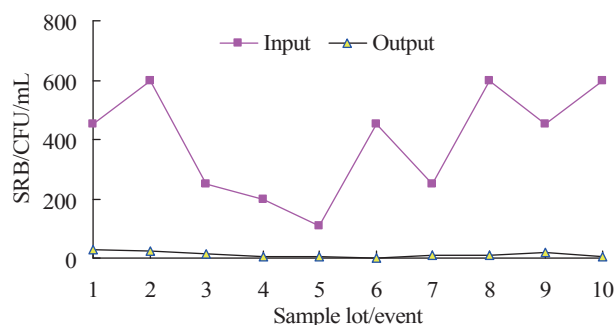


Figure 3
The Removal Effect of SRB

2.2.2 Removal of SRB

Figure 3 shows the performance of the system in removing SRB. The figure above shows that the SRB was 110-600 CFU/mL in the inlet, and was nearly 0 CFU/mL in outlet after biochemical treatment. This was primarily due to the aerobic aeration, and the competition mechanism of dominant microbes on the bio-film that inhibited and killed the SRB. The DNB inoculated inhibited the

SRB typically through both substrate competition and intermediate products from denitrification^[7]. That is, both the denitrifying bacteria inhibit the SRB growth by consuming their substrate, and the nitrite ions and other ions from denitrification also serve as a good inhibitor to the SRB.

2.2.3 Polymer Solutions Prepared With Treated Produced Water

The polymer solution prepared was sampled for viscosity measurement during the experiment, and the results are presented in the Figure 4. The viscosity of the polymer solution prepared with the produced water after treatment by the proposed process remained at 24-30 mPa·s and demonstrated stable treatment performance, compared to the polymer solution prepared with the untreated produced water, which was around 3 mPa·s. Sulfides, COD and SRB were effectively removed from the produced water and the polymer viscosity was hence increased.

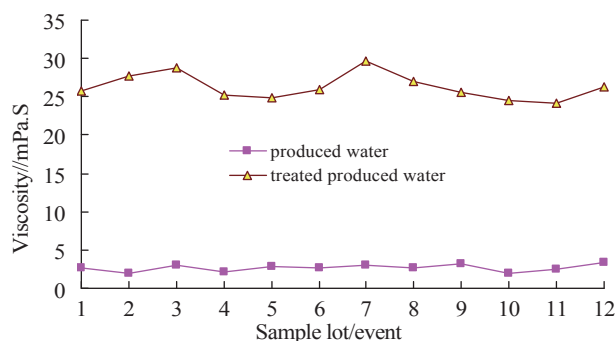


Figure 4
The Viscosity of the Polymer Solution Prepared With the Treated Produced Water

3. INDUSTRIAL APPLICATION

3.1 Process Flow and Structures

After laboratory studies, a 3,600 m³/d demonstration application was built in Chengdong Oilfield. The process used in the laboratory experiment is indicated in Figure 5.

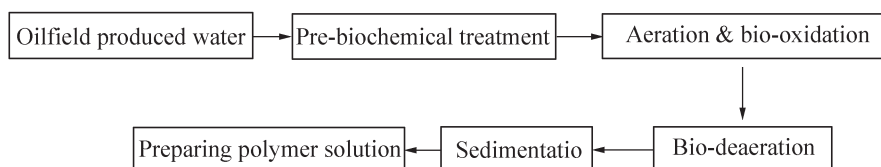


Figure 5
Process Flow for Industrial Application

Three treatment units are typically included: bio-oxidation, bio-deaeration and sedimentation.

(a) Bio-oxidation pond

Bio-oxidation takes advantage of the sulfate oxidizing bacteria and hydrocarbon bacteria on the bio-film to remove reductive matters in and produced water and degrade some of the organic matters. The bio-oxidation pond is a skid-mounted system consisting of 4 ponds

installed in parallel, each sized 14.4 m×2.4 m×3.1 m (in 4 stages). The filler is a frame-type combined elastic fiber material that features fast culturing, high biological attachment, compactness and resistance against detachment and clogging. Roots blowers, each rated 8.54 m³/min, supplied oxygen at 39.4 kPa. To allow for uniform water distribution and aeration, water distributors were installed at the bottom for each cell of the pond.

(b) Bio-deaeration pond

Oxygen consumption by aerobic bacteria could reduce the oxygen content to below 0.1 mg/L. Nitrate reducing bacteria inoculate to the pond inhibited the growth of sulfate reducing bacteria by consuming their substrate on the one hand, and by taking advantage of the sound inhibitory effect of nitrite ions and other ions produced from denitrification on SRB on the other hand.

(c) Sedimentation pond

This removes suspended substances in the produced

water through gravity sedimentation and ensures the output performance.

3.2 Water Quality Analysis

After conditioning for a period of time, each of the treatment units remained stably functional. The proposed process allows for 100% removal of hydrogen sulfides and other reactive matters in the produced water, and proves effective in inhibiting the SRB activity and significantly reducing the COD and oil content in the produced water. The performance of the treatment is indicated in Table 2.

Table 2
The Analysis of the Water From Each Treatment Processes

| | Hydrogen sulfide mg/L | Dissolved oxygen mg/L | SRB CFU/mL | Oil content mg/L | Suspended substance mg/L | COD mg/L |
|------------------------------------|--------------------------|--------------------------|------------|------------------|-----------------------------|----------|
| Produced water | 5.0 | 0.01 | 600 | 40.0 | 22 | 396.2 |
| Bio-oxidation pond | 0 | 4.00 | 25 | 15.0 | 18 | 105.8 |
| Bio-deaeration pond | 0 | 0.50 | 10 | 15.0 | 16 | 99.6 |
| Deaeration & sedimentation pond | 0 | 0.05 | 2.5 | 14.7 | 10 | 90.4 |

3.3 Viscosity of the Polymer Solution

The viscosity of polymer solution prepared with the produced water before and after treatment was sampled and tested during the system application, and the results are presented in the Figure 6. The viscosity of the polymer solution prepared with the produced water after treatment by the proposed process remained at 25-35 mPa·s, compared to the polymer solution prepared with the untreated produced water which was around 3 mPa·s, and demonstrated stable treatment performance. Sulfides, COD and SRB were effectively removed from the produced water and the polymer viscosity was hence increased.

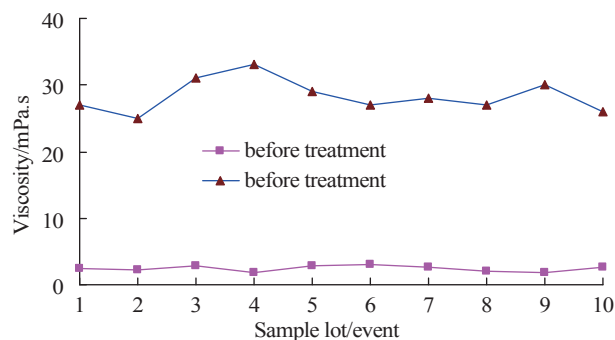


Figure 6
Viscosity of Polymer Solution Prepared With Produced Water Before and After Treatment by the System

3.4 Long-Term Stability of the Polymer Solution

Oil displacement is a long-term process. The polymer solution injected will not substantially increase the petroleum recovery unless its viscosity remains constantly stable in the reservoir. The long-term stability of polymer solutions prepared with the treated produced water under 70°C was examined (as presented in Figure 7). The polymer solution remained highly

stable, with its viscosity constantly above 20 mPa·s after 14 days, well suitable for field application.

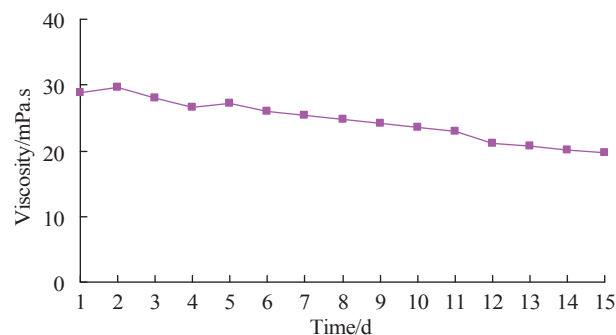


Figure 7
Long-Term Stability of the Polymer Solution Under Simulated Reservoir Conditions

3.5 Economic Benefit

Polymer solutions prepared with produced water after treatment prove economically and environmentally beneficial as they not only maintain the viscosity of the solutions, guarantee the development performance of foam combination flooding and polymer flooding processes and increase the oil production, but also decrease the need for freshwater resources and disposal of surplus effluent. The project can save 131.4×10^4 m³ freshwater per year, the direct economic benefit is above 637,200 yuan.

CONCLUSION

(a) Integrated bio-oxidation and bio-competition process is effective in removing sulfate reducing bacteria, hydrogen sulfides and other reductive matters in oilfield produced water, significantly reduces the oil and COD content in the water and provides stable water quality.

(c) Polymers prepared with treated produced water have much greater viscosity that accommodates field application. Wider application of the process would not only decrease the need for freshwater resources, but also reduce effluent discharge and offers a new way for reusing oilfield effluent as a source of production water.

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