Improving the Viscosity of Polymer Solutions Prepared with Sewage through Bio-competitive Exclusion in Shengli Oilfield

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Abstract. This paper summarized and analyzed the research and application of biocompetitive exclusion technique to remove sulfides produced in wastewater and inhibit SRB from producing new sulfides to mitigate the loss of viscosity of polymer solutions prepared with sewage water in the Shengli Oilfield. The results indicated that by adding a regulator can activate NR-SOB and RB in sewage water, which inhibit SRB activity and prevent them for producing new sulfides by competing for nutrient substrates and living space. The inhibition of SRB leads to improved polymer solution viscosity and high viscosity stability.

1. Introduction
During the advanced water injection stages in most oil fields, chemical flooding has become an important method for increasing and stabilizing oil production. According to an evaluation of the petroleum resource potential in China, the enhanced oil recovery (EOR) method could add 1.18billion tons of recoverable crude oil reserve, with oil obtained using chemical flooding methods, including polymer flooding, alkali-polymer combination flooding and alkali-surfactant-polymer flooding, accounting for 76% of the reserve. The polymer flooding method improves oil recovery by increasing the viscosity and residence time of the flooding solution, reducing the permeability of the oil layer to adjust the water absorption profile, and improving the oil-water flow ratio and the actual sweep coefficient. Thus, polymer solution viscosity is an important factor affecting the effectiveness of chemical flooding development.

The polymer preparation method of “preparing a mother solution with water and then diluting it with sewage” has been generally adopted in China, where the sewage used is water from united stations. The closed environment of an oilfield sewage system and the presence of nutrient substrates such as carbon, nitrogen and phosphorus in the sewage system cause the widespread growth of sulfate-reducing bacteria (SRB) during sewage transportation, with the sulfides produced during SRB metabolism leading to a loss in polymer solution viscosity.

Currently, various measures are taken to mitigate the effect of sulfides on the viscosity of polymer solutions, such as the application of SRB-killing bactericides and aerobic desulfurization [1, 2]. However, the application of antibiotics consumes large amounts of bactericidal agents in SRB-containing sewage, and development of antibiotic resistance by the SRB decreases the effectiveness of this method. The aerobic desulfurization method still has a number of issues, such as a lower than expected viscosity of the polymer solution at the wellhead position and difficulty in evaluating the
oxygen exposure levels. Moreover, the above two methods poorly inhibit the adherence of bacteria to the walls of the injection pipeline and the biofilms that are generated on the inner wall of the wellbore. These bacteria cause a loss in polymer solution viscosity due to the sulfides produced by SRB metabolism during the transportation of the solution from the polymer preparation station to the injection station and during the injection process.

The biological suppression of SRB, an emerging technology that has been developed in recent years, abandons the traditional thinking of completely eliminating SRB and mobilizes denitrifying bacteria (DNB) by injecting a functional activation agent or endogenous DNB that compete with SRB for living space and nutrient substrates after they are introduced into the environment or after the native beneficial bacteria are activated. The increased competition for nutrient substrates by DNB leads to insufficient nutrient supply for SRB, suppressing and even decreasing the activity that ultimately inhibits sulfide production [3-5].

In this study, we report the application of the bio-competitive exclusion technique in the Shengli Oilfield to remove sulfides produced in wastewater and inhibit SRB from producing new sulfides to mitigate the loss of viscosity of polymer solutions prepared with sewage water.

2. Chengdong West Block

2.1. Lock Overview
The west block of the Chengdong Oilfield is located in the mid-west region of the Ng331 unit of the Chengdong Oilfield. This region has a reservoir depth of 1, 110-1, 135 m and loose cementation that yields shallow heavy oil with a high relative density, viscosity and sand content. The oil layer of this block exhibited good physical properties, with an average effective porosity of 37%, an air permeability of $2304 \times 10^{-3}$ μm$^2$ and an original oil saturation of 62%. In 2004, a five-year base/HPAM binary combination flooding pilot test was initiated that included 24 injection wells and 45 beneficiary wells that was expected to increase the recovery factor by 11.8%, with an increase of $68 \times 10^4$ tons of crude oil production. The polymer preparation method was: 5000 mg/L polymer mother liquor was prepared with tap water and then was diluted to about 2500 mg/L by produced water treated in Chengdong united station. The scheme required that the viscosity of diluted polymer solution of 2500 mg/L sewage was over 35 mPa·s. At the late stage of the test, the viscosity of the injection solution at the wellhead was generally decreased to 1-5 mPa·s, seriously impacting the efficiency and effectiveness of the polymer solution. Subsequently, it was determined that the sulfides produced by SRB were the primary cause of the loss in polymer viscosity.

2.2. Test and Effectiveness
In November 2013, we initiated a field trial to improve the polymer solution viscosity through bio-competitive exclusion at a treatment capacity of 2400 m$^3$/d. In this trial, the TS-1 functional bacterial solution and the WS-40 activator were added through an inlet line to the 700 m$^3$ buffer tank located upstream of the water pipeline of the polymer preparation station of the Chengdong Oilfield (figure 1).

![Figure 1. Flow chart of field test process in Chengdong block.](image-url)
The changes in the SRB, DNB and sulfide contents before and after implementation are shown in table 1, while those of the viscosity of the polymer solution at the wellhead of the injection well are shown in figure 2. The results show that before the bio-competitive suppression technique was implemented, along the wastewater transport way both the amount of SRB and the content of sulfides gradually increased and exhibited a positive correlation, while the amount of DNB was reduced. After adding the regulator, both the amount of SRB and the content of sulfides decreased, while the amount of DNB increased.

Table 1. Changes of concentration of bacterial and sulfur ions before and after implementation of biocompetitive suppression.

|                      | SRB (cells/mL) | NRB (cells/mL) | The content of sulfides (mg/L) |
|----------------------|----------------|----------------|-------------------------------|
|                      | Before         | After          | Before                       | After |
|                      | implementation| implementation| implementation                |       |
| Effluent of Chengdong| 250            | 60             | 110                          | 0.3   |
| United station       |                |                |                               | 0.2   |
| Sample at polymer    | 2500           | 25             | 25                           | 2500  |
| preparing station    |                |                |                               | 3.5   |
| Sample at injecting  | 6000           | 6              | 25                           | 6000  |
| wellhead             |                |                |                               | 5.4   |
|                      |                |                |                               |       |

After implementing the biocompetitive exclusion method, the mobilized DNB inhibited SRB activity and the production of sulfides. The average viscosity at the wellhead increased from 22 to 39.4 mPa·s, while the polymer concentration at the wellhead decreased from 2750 to 2450 mg/L, increasing the viscosity of the polymer solution while decreasing the amount of polymer used.

Figure 2. The viscosity improvement by biocompetitive suppression at Chengdong block.

3. Gudao East Block

3.1. Lock Overview
In the east block of the Gudao Oilfield, a two-component flooding protocol was implemented from 2010 to 2012, and the wastewater used to prepare the polymer solution was primarily obtained from
outside of the Gudao Oilfield. With the gradual expansion of polymer injection flooding and heavy oil thermal recovery in the Gudao Oilfield, the application of various chemical stimulation measures led to complex physical properties of the resulting fluid as well as an increased difficulty in oil-water separation and sewage treatment. The water quality deterioration of the off loading sewage resulted in serious outgrowth of SRB and significantly increased sulfide production, as the sewage sulfide concentration at the polymer solution preparation station reached 3-5 mg/L, while the viscosity of the polymer solution at the injection wellhead was only 17mPa.s, seriously affecting the viscosity and effectiveness of the polymer solution flooding.

3.2. Test and Effectiveness
On June 13, 2016, biological desulfurization and viscosity-sustaining field trials at 9500 m³/d were conducted at the Gu 4 injection station of the Gudao Oilfield, where the functional bacterial solution and the regulating agent were used in the pipeline prior to the buffer tank of the Gu 4 injection station and behind Gu 3 united station. Effluents from the buffer tank were used to dilute the polymer mother fluid, and then the polymer solutions were transported to the injecting well and were injected in the well.

The bacterial community structure of each node before and after implementation is shown in figure 3. Before implementing the biocompetitive exclusion method, the abundances of nitrate-reducing Thauera and Marinobacter were significantly reduced from the Gu 3 united station to the Gu 4 injection station and then from the diluted polymer solution to the wellhead of the polymer-injected well. Thauera is a common denitrifying bacterium species in sewage and was observed to be capable of simultaneously oxidizing sulfides and acetates using nitrates as electron acceptors. Marinobacter is a facultative anaerobic and halophilic genus that exhibits highly efficient denitrification under anaerobic and aerobic conditions. We did not detect a significant increase in the abundance of SRB in this block, likely due to the small proportion of SRB present in the entire community structure of the block.

After adding regulators, a slight increase was observed in the abundance of Arcobacter, a genus of bacteria that obtain energy needed for growth and reproduction by oxidizing S2- using nitrates or molecular oxygen as an electron acceptor. In contrast, the abundances of Thauera and Marinobacter were significantly increased, indicating that the addition of a regulator activated the denitrifying bacteria in sewage, which subsequently competed with SRB for nutrient substrates and living space and inhibit SRB activity, ultimately suppressing sulfide production.

The results also showed that the abundance of Hydrogenophilus during the transport process in the polymer solution dilution to the wellhead of the injection well was increased before the regulator was added but significantly decreased afterwards. Hydrogenophilus is a hydrogen-oxidizing bacterium that obligately lives on inorganic nutrients, obtaining energy using H2or by oxidizing sulfur. The addition of the regulator removed sulfides from the system, causing the decrease in Hydrogenophilus abundance due to the loss of an energy source.

The abundance of Tepidiphilus decreased before the regulator was added and was further reduced after the regulator was added. Tepidiphilus is a petroleum-degrading bacterium, and the decrease in its abundance may result from the weaker competition of this bacterium for nutrient substrates.

At the same time, we observed that each sample contained unclassified bacteria that accounted for 13-20% of the total bacteria, indicating that the strain distribution in the oilfield sewage-polymer preparation system is complicated and likely contains novel and non-cultivable bacteria.

To verify the viscosity stability of the polymer after the biocompetitive exclusion treatment, the wellhead viscosities of ten wells with different injection well pipeline lengths were monitored and the results are shown in table 2. The single-well pipeline length and the concentration of the solution injected had little effect on the viscosity retention rate after denitrification suppression of SNB. Under the test condition, the wellhead viscosity of the selected ten injection wells was stable, where the viscosity retention rate was increased to over 88%, with an average of 92.2%.
3.3. Oilfield Development Status
After the implementation of the denitrification suppression of SNB, the development status of the oilfield in the test area is shown in figure 4. The results showed that due to the significant increase in the viscosity of the polymer solution, the comprehensive water content of the test block was slightly decreased, and the daily oil yield was increased.

Figure 3. Microbial community structure changes before and after implementation.

Table 2. Stability and effectiveness of the single-well during denitrification inhibition test.

| Injecting well | Length of pipe line (m) | Viscosity before implementation (mPa·s) | Viscosity after implementation (mPa·s) | Viscosity retention before implementation (%) | Viscosity retention after implementation (%) |
|----------------|-------------------------|-----------------------------------------|----------------------------------------|-----------------------------------------------|-----------------------------------------------|
| GDD5N18        | 138                     | 21.5                                    | 49.1                                   | 52                                            | 91                                            |
| GDD1N13        | 334                     | 37.5                                    | 67.5                                   | 63                                            | 95                                            |
| GDD5N33        | 460                     | 35.6                                    | 64.4                                   | 53                                            | 90                                            |
| GDD1-14        | 462                     | 35.6                                    | 49.7                                   | 61                                            | 88                                            |
| GDD5-24        | 483                     | 15.4                                    | 31.8                                   | 67                                            | 92                                            |
| GDD5N29        | 616                     | 18.3                                    | 42.4                                   | 76                                            | 95                                            |
| GDD1-31        | 700                     | 33.7                                    | 67.9                                   | 66                                            | 94                                            |
| GD2-37N9       | 749                     | 30.1                                    | 43.3                                   | 55                                            | 91                                            |
| GDD5N23        | 931                     | 16.5                                    | 41.8                                   | 65                                            | 94                                            |
| GDD5N14        | 1483                    | 31.1                                    | 48.0                                   | 57                                            | 92                                            |

Figure 4. Development situation of test block during denitrification inhibition process.
4. Gudong Oilfield Dong 4 Injection Station
Since the third oil recovery in the Gudong Oil Production Plant, a bacteriostatic measure of continuously adding formaldehyde has been adopted to ensure the stability of the polymer solution viscosity. However, although formaldehyde is self-aggregating, it is extremely irritating and may cause cancer in humans with long-term exposure. Furthermore, the added formaldehyde exhibited a highly propensity to cause the clogging of the formaldehyde tank, liquid level gauges and pipelines, which seriously affected its normal use. Therefore, a new process that can replace formaldehyde to ensure the viscosity stability of the polymer solution diluted with sewage water.

4.1. Lock Overview
The field test was conducted at the No. 12 polymer preparation station (figure 5). In this test, sewage water was utilized in the biological bacterial inhibition and viscosity-stabilizing treatment at a capacity of 3,500 cubic tons/day by adding a bacterial solution and the regulator at the original formaldehyde dosing position without changing the existing process.

![Diagram of field test](image)

**Figure 5.** Schematic diagram of field test.

4.2. Field Test Results
During the test, samples were collected from three locations (i.e., the wellhead, 20-m underground and 1000-m underground) of two injection wells, and the stability of the polymer viscosity was examined (table 3). At Well 28-141, after being delivered to a depth of 1000 m, the polymer solution maintained a viscosity that was 78.4% of the wellhead viscosity, which was significantly higher than that observed before the implementation of the protocol (26.4%). At Well 28-10, after being delivered to a depth of 1000 m, the polymer solution maintained a viscosity that was 82.8% of the wellhead viscosity, which was significantly higher than that observed before the implementation of the protocol. These results indicate that after implementing the biological competitive inhibition method, the polymer solution maintained a high stability when during transport and when injected into the well.

| Well Number | Sampling spot           | Before implementation | After implementation |
|-------------|-------------------------|-----------------------|----------------------|
|             | Concentration (mg/L)    | Viscosity (mPa·s)     | Concentration (mg/L) | Viscosity (mPa·s) |
| 28-141      | Polymer preparing station| 2190                  | 23.5                 | 2241              | 24.7              |
|             | Well head               | 2178                  | 22.7                 | 2203              | 24.1              |
|             | 20-m underground        | 1585                  | 14.1                 | 2049              | 22.0              |
|             | 1000-m underground      | 1717                  | 6.8                  | 1964              | 18.9              |
| 28-10       | Polymer preparing station| 2755                  | 28.9                 | 2776              | 54.7              |
|             | Well head               | 2672                  | 27.4                 | 2769              | 54.1              |
|             | 20-m underground        | 2053                  | 28.7                 | 2457              | 47.3              |
|             | 1000-m underground      | 1984                  | 4.1                  | 2446              | 44.8              |
The microbial community structure changes before and after the implementation of the protocol are shown in figure 6. After adding the regulator, the bacterial community structure of the sewage system in the polymer solution preparation station changed significantly, but it was significantly different from trial at Gudao east block. The amount of the aerobic denitrifying *Thauera*, which was dominant bacterial community of Gudao east block, was not rich and decreased after implementation of the protocol. The *Arcobacter*, which was reported can simultaneously desulfurize and denitrify by oxidizing sulfide ions into elemental sulfur or $SO_4^{2-}$ using nitrate as electron acceptor while reducing NO$_3$ to N$_2$, increased. It was also found that after implementation of the protocol, the abundance of *Desulfovibrio*, which has both sulfate reduction and denitrification functions, increased significantly indicating that its denitrification function was activated.

**Figure 6.** Microbial community structure changes before and after implementation.

### 5. Inhibition Mechanism

The growth and metabolism of SRB results in the production of sulfides that destroy the polymer structure by breaking the polymer chain, yielding small molecular substances that in turn serve as nutrient substrates for bacteria reproduction and thus the accelerated polymer degradation.

On the one hand, the addition of a regulator can activate NR-SOB in sewage water, e.g., *Arcobacter*, which use nitrates or nitrites as electron acceptor, oxidizing S$_2$-derived from SRB metabolism into SO$_4^{2-}$, mitigating the polymer degradation caused by sulfides. On the other hand, the activated NRB can use various carbon sources such as low-grade fatty acids as electron donor and oxidize them to CO$_2$, while reducing NO$_3$ or NO$_2$- to various nitrogen oxide intermediates (NO$_2$, NO, N$_2$, etc.). These bacteria inhibit SRB activity and prevent them from producing new sulfides by competing for nutrient substrates and living space [6, 7]. The sulfur removal and suppression activities of the two types of bacteria contribute to stabilizing the polymer solution viscosity.

### 6. Conclusion

In this study, we demonstrated that it is feasible to improve polymer solution viscosity by adding a regulator to mobilize NR-SOB and NRB in sewage water to address the issue of the sulfide-mediated loss in polymer solution viscosity through the removal of sulfur removing and the inhibition of SRB. We observed that in different test blocks, after adding a regulator, the mobilized denitrifying bacterial species differed but their abundances increased, leading to improved polymer solution viscosity and high viscosity stability. However, the competition inhibition process among different microflora and the carbon-nitrogen-sulfur conversion pathway needs to be further investigated to provide parameter optimization references for improving polymer solution viscosity through biocompetitive exclusion.
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References
[1] Johnson R J, Folwell B D, Wirekoh A, Frenzel M and Skovhus T L 2017 J. Biotechnol. 256 57.
[2] Ganshyam P, Sandeep R, Shikha J and Akhil A 2018 Int. Biodeter. Biodegr. 132 30.
[3] Kamarisima, Miyanaga K and Tanji Y 2019 Biochem. Eng. J 143 75.
[4] Fan F, Zhang B, Liu J, Cai Q and Chen B 2019 Chemosphere 238 124655.
[5] Obot I B, Solomon Moses M, Umoren Saviour A, Suleiman R, Elanany M, Alanazi Nayef M and Sorour Ahmad A 2019 J. Ind. Eng. Chem. 79 1.
[6] Wu Y, Cheng Y, Hubbard C G, Hubbard S and Ajo-Franklin J B 2018 Chem. Geol. 476 180.
[7] Dopffel N, Kögle Felix, Hartmann H, Costea P I, Mahler E and Herold A 2018 Int. Biodeter. Biodegr. 135 71.