ISSN: 1813-4890

Performance Evaluation of an Enzyme for Secondary Biodegradation of Reservoir Damage Caused by Guar-Based Polymer

Qi'an Da, Chuanjin Yao, Xue Zhang, Chengcheng Chu, Guanglun Lei

School of Petroleum Engineering, China University of Petroleum (East China), Qingdao 266580, China

Abstract

Aiming at the problem of incomplete gel breaking of guar gum fracturing fluid at low temperature, an enzyme breaker suitable for low temperature was prepared by using guar gum degrading bacteria, and the feasibility of secondary biodegradation of enzyme breaker on fracturing fluid damage in low temperature reservoir was explored. The results showed that the enzyme preparation had good effect on reducing viscosity, and produced less residue compared with the traditional oxidizing breaker. Core displacement experiments showed that the enzyme preparation could effectively reduce fracturing fluid damage. Besides, the enzyme breaker also has a permeability recovery effect on the core which was treated by oxidation breaker. This study provides a possible solution to relieve the damage of guar-based polymers in low temperature reservoirs.

Keywords

Enzyme; Fracturing Fluid; Displacement Experiment; Reservoir Damage; Gel Breaker.

1. Introduction

Energy is the driving force for the normal progress and development of human social production activities and an important material basis for national economic and social stability. The total amount of energy consumption of China ranks at the front of the world for many years continuously. In the past ten years, the proportion of oil consumption in primary energy consumption in China has remained at 18% to 19%.

At present, more than 65% of China's petroleum consumption is still dependent on imports, and as of around 2016, the proportion of low-grade reserves such as low-permeability reserves and ultra-low-permeability reserves is as high as about 70%[1,2]. In 2017, according to the annual total oil and gas production report,, oil production from low-permeability reservoirs accounted for about 30%, and gas production from low-permeability reservoirs accounted for about 50%. As the main body of development, low permeability oil and gas resources have always been the focus of development.[3,4]. Among them, middle and shallow low-permeability hydrocarbon reservoir is playing a very important role in oil and gas resources of our country[5-8].

The permeability of low permeability reservoirs is less than 50×10-3μm2, and the heterogeneity is serious. In addition, the porosity and permeability are relatively low, which requires great water injection pressure, which increases the difficulty of water injection development. At present, hydraulic fracturing is the main method for low permeability oil and gas fields. The application of hydraulic fracturing in the development of coal-bed methane, shale gas, condensate gas and other special oil and gas reservoirs is becoming more and more extensive[9].

At present, hydraulic fracturing is the most important stimulation technology of shallow low permeability reservoirs in common use in China. The performance of fracturing fluid directly

ISSN: 1813-4890

affects the effect of fracturing. At present, guar-based fracturing fluid system is more commonly used, in which the effect of the gel breaker will affect the fracturing effect[10,11]. Traditional gel breakers are usually peroxides, such as potassium persulfate, ammonium persulfate (APS) and so on. However, this kind of oxidant has some shortcomings, such as the reaction is not specific, cannot completely degrade guar gum; It is easy to consume and will react with pipelines and formation substrates that come into contact, which will also increase the time of gel breaking. Incomplete gel breaking of fracturing fluid will result in formation damage. In addition, when the reservoir temperature is lower than 50℃, the free radical activity of the oxidized breaker becomes low. In this case, if the conventional oxidizing agent is still used, it will cause problems such as poor gel breaking effect and great damage to the formation, and it is difficult to meet the requirements of field construction. The low temperature enzyme breaker provides the possibility for fracturing fluid to break quickly in shallow low permeability reservoirs. Enzyme technology is a relatively new method, which has been successfully applied to many fields such as industry and medicine, and will be one of the key points to be solved in fracturing fluid breaking technology in the future. Compared with oxidizing gel breakers, low-temperature enzymes have many advantages, such as being environmentally friendly, reacting only with specific polymers, rapidly reducing viscosity, producing less residue, and causing no additional damage to pipelines and formation. Therefore, the study of low temperature enzymes is of great help to reduce the damage of fracturing fluid and solve the problem of oil and gas fracturing.

This study aims to solve the problem that guar-based fracturing fluid is not completely broken by oxidants at low temperature (<= 50℃). Based on guar gum degradation bacteria, the low-temperature enzyme breaking agent is prepared by fermentation, and the feasibility of the secondary biodegradation of the damage by the low-temperature enzyme breaker is studied.

2. Materials and Methods

2.1. Materials

The microbial strain used to prepare the enzyme breaker was derived from the laboratory strain bank, and the strain was identified as Bacillus licheniformis. Nutrients and inorganic salts: Beef extract, NaCl, agar, guar gum, K_2HPO_4, KNO_3, $(NH_4)_2S_2O_8$, $CaCl_2$, $MgCl_2$, etc. The source of reagents is shown in Table 1.

2.2. Culture Medium

Enzyme production medium: Guar gum, 5g/L; Beef extract, 1.5g/L; K_2HPO_4, 2g/L; $(NH_4)_2S_2O_8$, 2g/L; KNO_3, 2g/L; $CaCl_2$, 0.15g/L; $MgCl_2$, 0.15g/L; NaCl, 5.0 g/L; Agar, 10 g/L.

Table 1. List of reagents

Reagent name	Reagent source
Guar gum	Yibang Chemical Co., Ltd.
Beef extract	Bo Aoxin Biotechnology Co., Ltd
Agar	Chinese Medicine Group Chemical Reagent Co., Ltd
NaCl	
K_2HPO_4	
KNO_3	
$(NH_4)_2S_2O_8$	
$CaCl_2$	
$MgCl_2$	

ISSN: 1813-4890

2.3. Culture Medium

The experimental methods and procedures are as follows:

(1) Enzyme-producing medium was prepared, pH was adjusted to 7.0, and sterilized at 121 ° C for 20 min.

(2) The strain was inoculated in enzyme producing medium at 2% (V/V) at 30℃, 100 rpm for 18 h in an ultra-clean platform.

(3) The fermentation liquid was centrifuged at 4000 rpm for 20 min, then the supernatant was taken, and the pore size of 0.8, 0.65, 0.45, 0.22 μm microporous filter membranes were successively used for negative-pressure filtration, which could remove bacteria and other impurities, and the filtrate was used as enzyme solution for subsequent experiments.

2.4. Gel Breaking Performance of Enzyme

The experimental methods and procedures are as follows:

(1) The container with enzyme was placed in a constant temperature water bath, and the temperature was set to 20, 25, 30, 35, 40, 45, 50 ℃.

(2) 0.5% guar gum solution was prepared, and after fully hydration, 8% enzyme was added while stirring, and the same amount of distilled water was added to the control group.

(3) The viscosity of guanidine was measured at 25℃ at regular intervals.

(4) 5 g/L guar gum solution was prepared and hydrated for more than 4 h.

(5) 100 mL guar gum solution and 1 mL enzyme solution were stirred evenly and placed in 40℃ oven for 4 h. When the viscosity of guar gum solution was lower than 5 mPa·s, the reaction solution was centrifuged at 5000 rpm for 10 min, and the mass of residue obtained at the bottom of the centrifuge tube was weighed.

(6) The similar experiment in (5) was carried out with $(NH_4)_2S_2O_8$. Finally, the mass of the residue obtained from the bottom of the centrifuge tube was weighed.

(7) Calculate the residue content according to Equation 1.

$$m = \frac{m_0}{V_0} \times 100\% \tag{1}$$

Where, m is the residue content, mg/L; m_0 is the mass of residue, mg; V_0 is the volume of guar gum solution, L.

2.5. Gel Breaking Performance of Enzyme

The device is shown in Figure 1, and the experimental methods and procedures are as follows:

(1) The intermediate container was used to inject 5 mL of 5% guar gum solution and 1mL of 0.1% $(NH_4)_2S_2O_8$ solution into the core, and the core permeability was tested with deionized water after the reaction at 40℃ for 4h;

(2) Inject 5 mL of 8% enzyme solution into the core, and react at 40℃ for 4 h.

(3) After the enzyme reaction, deionized water was injected into the core to measure the permeability of the core after enzyme biodegradation. Core permeability is calculated by Darcy's formula, as shown in Equation 2;

(4) The permeability recovery rate R shown in Equation 3 was used to evaluate the secondary biodegradation effect of enzyme.

$$k = \frac{Q\mu L}{A\Delta P} \tag{2}$$

ISSN: 1813-4890

Where, k is the permeability of core, 10^{-3} μm²; Q is volume rate, cm³/s; μ is the viscosity of water, mPa·s; L is the length of core, cm; A is the cross-sectional area of the core, cm²; ΔP is the pressure difference between the two ends of the core, 0.1 MPa.

$$R = \frac{k_2}{k_0} \times 100\% \tag{3}$$

Where, R is the permeability recovery rate, %; k_0 is the permeability after gel breaking by $(NH_4)_2S_2O_8$, 10^{-3} μm²; k_2 is permeability after the biodegradation by enzyme, 10^{-3} μm².

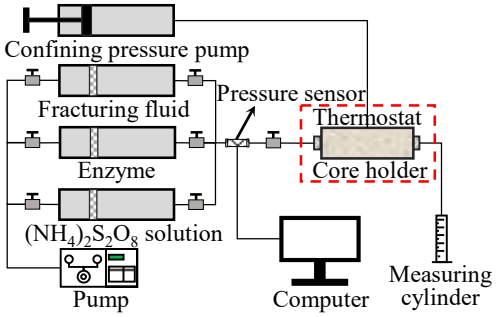

Fig 1. The device of core permeability recovery experiment

3. Results and Discussion

3.1. Viscosity Reduction Ability of Enzyme at Different Temperatures

The solution viscosity changes with time after the reaction of enzyme and guar gum fracturing fluid at different temperatures are shown in Figure 2. The results showed that at the temperature range of 25-50 ℃, the enzyme could completely break the guar gum fracturing fluid within 3 h. In addition, the reaction time of the enzyme with guar gum fracturing fluid was different at different temperatures. As shown in Figure 3, the appropriate temperature for the interaction between enzyme breaker and guanidine gum is in the range of 25-50℃, and the time of breaking glue is shorter in this temperature range.

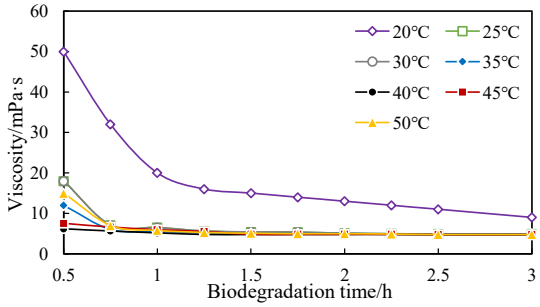

Fig 2. The viscosity changes with time during enzyme reaction

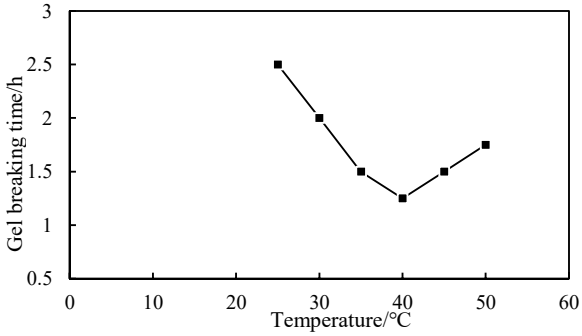

Fig 3. The gel breaking time of the enzyme with guar gum fracturing fluid

ISSN: 1813-4890

3.2. Comparison of Residue Content

According to the calculation results, the contents of guar gum, $(NH_4)_2S_2O_8$ and the residue after enzymatic breaking are 596 mg/L and 185 mg/L, respectively, which meet the requirements of the national standard of 600 mg/L. In addition, the residue content produced by $(NH_4)_2S_2O_8$ was 3.22 times that of the enzyme. However, the residue content under the action of $(NH_4)_2S_2O_8$ is close to 600 mg/L, so it can be speculated that when the reservoir temperature is lower than 40℃, the residue generated by $(NH_4)_2S_2O_8$ breakage will be more, and the damage to the reservoir and fracture will be greater.

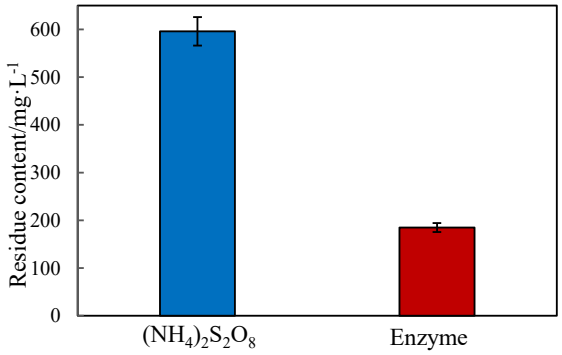

Fig 4. Contrast of residue content

3.3. Comparison of Residue Content

After the displacement pressure is stable, the initial core permeability, core permeability after gel breaking, and core permeability damage rate are calculated according to Equation 1. The calculation results are shown in Table 2. It can be seen that at the same temperature, the damage rate of $(NH_4)_2S_2O_8$ to the core is greater, because $(NH_4)_2S_2O_8$ cannot completely break the guar gum in the core, resulting in guar gum and its residue to cause serious pollution to the formation, especially in the low-permeability reservoir, the core permeability reduction rate can reach up to 90.33%. By using $(NH_4)_2S_2O_8$ with enzyme reaction, $(NH_4)_2S_2O_8$ and guar gum will make the guar gum degradation for small molecule guar gum and residue, and enzyme will react with this part of the small molecule guar gum and residue, but relatively speaking, residue more is not easy to degrade in the low permeability core.

In general, the core permeability decrease rate was 36.67%-70.83% when the low-temperature enzyme was used as the gel breaker, while that by $(NH_4)_2S_2O_8$ is 48.29%-90.33%. When enzyme and $(NH_4)_2S_2O_8$ were used as the gel breaker, the permeability of core decreased by 34.84%-75.24%. At the same time, the closer the temperature is to the optimum temperature of enzyme, the better the breaking effect of enzyme. The experiment showed that the enzyme had better gel breaking effect than $(NH_4)_2S_2O_8$ in low temperature formation.

Table 2. Permeability measurement under different breaker system at 40℃

Core No.	Gel breaker	Porosity%	Initial permeability /(10^{-3} μm²)	Damage permeability /(10^{-3} μm²)	Reduction rate/%
50-1	Enzyme	11.86	38.63	11.27	70.83
50-2	$(NH_4)_2S_2O_8$	12.36	47.83	4.63	90.33
50-3	Enzyme+$(NH_4)_2S_2O_8$	10.59	36.82	9.12	75.24

3.4. Effect of Enzyme Secondary Biodegradation on Permeability Recovery

The core contaminated by guar gum fracturing fluid that used $(NH_4)_2S_2O_8$ as breaking agent in 3.3 was selected, and the experiments of enzyme secondary biodegradation of fracturing fluid

ISSN: 1813-4890

damage in core were carried out at 40 ℃ to study the recovery effect of enzyme biodegradation on fracturing fluid damage. The experimental results are shown in Table 3.

Table 3. Result of damaged cores secondary biodegradation by enzyme

Core No.	Temperature/℃	Porosity%	Damage permeability /(10^{-3} μm^2)	Recovery permeability /(10^{-3} μm^2)	R/%
50-2	40	12.36	4.63	34.69	72.52

4. Conclusion

The enzyme preparation had good effect on reducing viscosity, and produced less residue compared with the traditional oxidizing breaker. Core displacement experiments showed that the enzyme preparation could effectively reduce fracturing fluid damage. Besides, the enzyme breaker also has a permeability recovery effect on the core which was treated by oxidation breaker.

Acknowledgments

This research was supported by the National Natural Science Foundation of China (No. 51874330, 51974341), the Fundamental Research Funds for the Central Universities (No. 20CX06070A), the Opening Fund of Shandong Key Laboratory of Oilfield Chemistry and the Fundamental Research Funds for the Central Universities (No. 19CX05006A).

References

[1] W.R. Hu, Y. Wei, and J.W. Bao: Development of the theory and technology for low permeability reservoirs in China. Petroleum Exploration and Development, Vol. 45 (2018) No.4, p.685-697.

[2] X. Wang: China Energy Statistical Yearbook. Department of Energy Statistics, (China Statistics Press, China 2013).

[3] C.Z. Jia, X.Q. Pang and F.J. Jiang: Research status and development directions of hydrocarbon resources in China. Petroleum Science Bulletin, Vol. 1 (2016) No.1, p.2-23.

[4] J.Z. Zhao, S.B. Wu and F.L. Wu: The classification and evaluation criterion of low permeability reservoir: An example from Ordos Basin. Lithologic Reservoirs, Vol. 19 (2007) No.3, p.28-31.

[5] Z.Q. Zhang and J.W. Zheng: Advances in exploration and exploitation technologies of low-permeability oil and gas. Advances in earth science, Vol. 24 (2009) No.8, p.854-864.

[6] Y.L. Kang and P.Y. Luo: Current status and prospect of key techniques for exploration and production of tight sandstone gas reservoirs in China. Petroleum Exploration and Development, vol. 34 (2007) No. 2, p.239.

[7] W.R. Hu and G.M. Zhai. Practice and sustainable development of oil and nature gas exploration and development in Ordos Basin. Engineering and Science, Vol. 12 (2010) No.5, p.64-72.

[8] H.J. Zhou, Y.J. Fan and Q.C. Meng, Study on optimum temporary plugging fracturing process for Chang-6 reservoir at Wuliwan and its application. Drilling & Production Technology, Vol. 39 (2016) No. 6, p.58-61.

[9] Y.J. Li, Y.Y. Feng, H. Liu, L.H. Zhang and S.X. Zhao. Geological characteristics and resource potential of lacustrine shale gas in the Sichuan Basin, SW China. Petroleum Exploration and Development, Vol. 40 (2013) No.4, p.454-460.

[10] P. Liu, L. Zhang, X. Yan and X. Lan. Characteristics of formation damage by Guar-gum fracturing fluids. Oilfield Chem, Vol. 31 (2014) No.3, p.334-338.

[11] J. L. Doublier and B. Launay. Rheology of galactomannan solutions: comparative study of guar gum and locust bean gum. Journal of texture studies, Vol. 12 (1981) No.2, p.151-172.