Research and practice of seawater-based fracturing fluids

Jia Yunpeng
Petroleum Engineering Research Institute of PetroChina Dagang Oilfield, Tianjin 300280, China;
Tel.: +86-186-2228-8081
jiaypeng@petrochina.com.cn;

Abstract: The Dagang Oilfield, with 146 kilometers of coastline, is rich in seawater resources. In order to satisfy the demand of large-scale fracturing operation in low-permeability offshore reservoirs and to solve such technical difficulties as high-cost conventional fracturing fluid, incompatibility of seawater with conventional fracturing additives, and limitation of offshore operational space, which result in the inability to achieve industrial fracturing operation, fracturing thickening and cross-linking agents that can be formulated with seawater were studied and selected to form a seawater-based fracturing fluid system with temperature resistance of 80–180°C. The system does not need to shield or remove calcium and magnesium ions as seawater can be directly used after filtration. The thickening agent swells so quickly that it imparts viscosity to seawater to reach 92% of the maximum viscosity in 3 minutes, and can achieve continuous mixing. Additionally, it is possible to reuse the seawater-based fracturing fluid after processing such as removing sand and filtering suspended matter. Using it to prepare slippery water and new fracturing fluid, only a fewer additives are required, and the comprehensive cost is lower. In field test, the fracturing scale and process were adaptively optimized through integration of engineering and geology. For example, Well ZH50-16 produced 9.9 tons of oil per day through a 4 mm choke before fracturing operation, and after fracturing, the liquid produced increased to 77.5 m³/d, including 57.6 tons of oil, and 14800 m³ of gas through a 6 mm choke. Simple field preparation of seawater-based fracturing fluid and fracturing operation provided stable production performance.

1. Introduction
Block 3 of Chenghai in Dagang Oilfield is low-permeability reservoir, with average permeability of $13 \times 10^{-3}$ $\mu$m$^2$ and buried at 3000–4200 m. In order to enhance the development efficiency, a large amount of fresh water is required of fracturing fluids in large-scale industrial fracturing operations. The fracturing operation is generally carried out by fracturing vessels which have limited operation space for long-distance transportation of fresh water, resulting in the disadvantages of restricted fracturing scale and high cost. Therefore, research on seawater-based fracturing fluid to improve offshore fracturing technology is necessary.

2. Technical difficulties in seawater-based fracturing fluid
Thickeners used in conventional fracturing fluids mainly include natural polymers, synthetic polymers, and surfactants. Modified guar gel is alkaline cross-linked, where the cross-linker would react with seawater to generate precipitation$^{[1]}$. At present, modified guar gel seawater fracturing fluid is usually formulated by adding chelating agent and shielding agent. It has disadvantages such as high additive concentration$^{[2]}$, high cost, and high requirements for preparing conditions, and cannot meet the needs
of continuous mixing. The clean fracturing fluid system can maintain a viscosity of 40 mPa • s after 60 minutes of shearing under 170 S \(^{-1}\) at 120°C. Its temperature resistance needs to improve \(^{[3-5]}\).

Synthetic polymer thickeners are mainly polyacrylamide. The amide groups in polyacrylamide molecules are prone to hydrolysis reaction\(^{[6]}\), and are sensitive to high-valent metal ions with an inability to tolerate salt. In addition, they tend to suffer degradation at above 110°C or under mechanical actions, exhibiting a poor temperature and shear resistance.

3. Development and comprehensive evaluation of seawater-based fracturing fluid

3.1 Selection and development of new thickeners

Different types of thickeners were selected to conduct swelling test in seawater. The results show that conventional polyacrylamide and sulfonic polyacrylamide thickeners have such problems as low swelling rate, uncompleted swelling, and stratification after static suspension in seawater (thickeners 1# to 4#). In view of the difficulties in preparing fracturing fluids using seawater, a new thickener was developed. The optimized 5# thickener is a new type of thickener with multi-component copolymerized hyper-branched molecules. It is synthesized by 5 monomers through solution radical polymerization. The introduction of branching agent changes the linear structure of the molecule into a branched molecular structure, and results in abundant amino, hydroxyl, and carboxyl groups on the branch chain, and plentiful end groups on the molecular surface. They contribute a lot to better reactivity and improved the solubility rate of the thickener in seawater. Additionally, the introduction of hydro-phobic monomers of large molecular weights can improve the temperature and shear resistance of the thickener.

The laboratory result in Table 1 shows that the 5# thickener imparts 90% of the maximum viscosity to seawater in 3 minutes, and increases the swelling rate by 50% more than modified guar gum (the 6# thickener) as it requires 10 minutes to swell in seawater to reach 90% of the maximum viscosity. It has better fluidity and it is easier to form a uniform viscous liquid. The viscosity of the prepared basic fracturing fluid is 20–100 mPa•s, which meets the requirements of pipeline pumping at low pressure on site.

| Time                        | 1#     | 2#     | 3#     | 4#     | 5#     | 6#     |
|-----------------------------|--------|--------|--------|--------|--------|--------|
| Initial viscosity and state |        |        |        |        |        |        |
| after stirring for 3 minutes| 0 mPa.s| 0 mPa.s| 0 mPa.s| 0 mPa.s| 37 mPa.s| 25 mPa.s|
| Initial viscosity and state |        |        |        |        |        |        |
| after stirring for 10 minutes| 0 mPa.s| 0 mPa.s| 23 mPa.s| 3 mPa.s| 39 mPa.s| 56 mPa.s|
| Initial viscosity and state |        |        |        |        |        |        |
| after stirring for 30 min    | 0 mPa.s| 0 mPa.s| 65 mPa.s| 3 mPa.s| 40 mPa.s| 61 mPa.s|
| Viscosity and state         |        |        |        |        |        |        |
| after standing for 4h        | 200 mPa.s| 30 mPa.s| 100 mPa.s| Un-swelled polymer particles sank to the bottom of the beaker | 41 mPa.s| 62 mPa.s|
| Viscosity and state         |        |        |        |        |        |        |
| after standing for 24 hours  | Semi-solid| Good fluidity| 430 mPa.s| Polymer solution layered with semi-solid polymer at the bottom | 41 mPa.s| 62 mPa.s|

3.2 Selection and performance evaluation of cross-linking agents

Given the alkaline cross-linking environment of the organic boron cross-linking system where the hydroxide ions of the organic boron cross-linking agent react with calcium and magnesium ions in seawater to form precipitation, a cross-linking agent in an acidic cross-linking environment such as aluminum sulfate, inorganic zirconium, and titanium cross-linking agents should be considered as a crosslinking agent for seawater-based fracturing fluid. However, aluminum sulfate is poorly resistant
to temperature and shear, and inorganic zirconium and titanium cross-linking agents are highly corrosive. Existing inorganic acid ester cross-linking agents are poorly compatible with seawater, and the fracturing fluid using them has poor temperature resistance. A new cross-linking agent has been developed by changing reaction conditions, preferably selecting organic ligands, and strengthening cross-linking reaction with anionic polymers. The development principle of the cross-linking agent is weak acidic cross-linking with adjustable cross-linking time to meet the needs of reservoir stimulation at 150°C.

By varying the ratio of inorganic zirconium to organic ligand, five types of cross-linking agent samples were synthesized. The performance of the samples was evaluated under same conditions (Table 2). When the ratio of inorganic zirconium to organic ligand is 3 to 2, the 3# cross-linking agent has the best performance. A seawater-based fracturing fluid using the 3# zirconium cross-linker with concentration of 0.4% and 0.5% hyper-branched molecular thickener was thus prepared, which reached 110 mPa·s after sheering for 120 min under 170s⁻¹ at 150°C, and its performance is better than industrial standard indicator.

### Table 2. Performances of different cross-linking agents.

| Synthesized agent | Ratio of inorganic zirconium to organic ligands | Cross-linking environment (pH) | Cross-linking performance | Cross-linking time (s) | Temperature resistance |
|-------------------|-----------------------------------------------|-------------------------------|----------------------------|-----------------------|------------------------|
| 1#                | 1:01                                          | 3                             | Cross-linked               | 16                    | 90°C, 170s⁻¹, 90min, 63mPa·s |
| 2#                | 4:03                                          | 5                             | Good, cross-linked         | 161                   | 150°C, 170s⁻¹, 120min, 51mPa·s |
| 3#                | 3:02                                          | 5                             | Good, cross-linked         | 79                    | 150°C, 170s⁻¹, 120min, 110mPa·s |
| 4#                | 2:01                                          | 5                             | Quick linking, semi-solid  | 2                     | 150°C, 170s⁻¹, 120min, 381mPa·s |
| 5#                | 3:01                                          | 4                             | Dehydration                |                       |                        |

### 3.3 Comprehensive evaluation on seawater-based fracturing fluid

The performances of the synthesized seawater-based gelled fracturing fluid prepared using the developed multi-component copolymerized hyper-branched thickener, 3# zirconium cross-linking agent, and alkyl glycoside flow-aid agent at concentrations of 0.5%, 0.4%, and 0.1%, respectively, were evaluated through a series of laboratory experiments involving heat and shear resistance, gel breaking, static loss, anti-swelling, flow-back and compatibility.

#### 3.3.1 Viscosity and temperature

Figure 1 shows the results of the viscosity and temperature of the seawater-based fracturing fluid. When sheared at 150°C for 120 min, the viscosity reached 110 mPa·s, which completely meets the requirements of fracturing operation.

![Figure 1. Viscosity and temperature.](image)
3.3.2 Gel breaking performance
The fracturing fluid whose viscosity and temperature performances meet the industry standards was tested for its gel breaking performance. The results (Table 3) show that the gel breaking time is 6 hours, the viscosity is 1.87 mPa·s and the residual content is 61.3 mg/L. The residual content is only one tenth of the industry standard, exhibiting a high degree of cleanliness.

| Temperature (°C) | Breaking time (min) | Viscosity (mPa·s) | Residual content (mg·L⁻¹) |
|------------------|--------------------|-------------------|--------------------------|
| Experimental result | 150 | 480 | 1.87 | 61.3 |
| Industry standard | ≤720 min | ≤5 | ≤600 |

3.3.3 Static fluid loss
The static fluid loss of the fracturing fluid was determined by the laboratory measurement of the leak-off coefficient C₃ controlled by a mud cake. Experimental data shows that the leak-off coefficient of the seawater-based fracturing fluid is higher than that of a guar gel fracturing fluid (Table 4) because the water-insoluble matter of the thickener in the seawater-based fracturing fluid is less than that of the guar gel fracturing fluid, the resulting mud cakes are different in permeability.

| Temperature / °C | Leak-off coefficient of seawater fracturing fluid / (mm·min⁻¹/²) | Leak-off coefficient of super guar gel fracturing fluid / (mm·min⁻¹/²) | Industry standard |
|------------------|---------------------------------------------------------------|---------------------------------------------------------------|-------------------|
| 90               | 0.63                                                          | 0.39                                                          | ≤1×10⁻³ m/min¹/²  |
| 120              | 0.45                                                          | 0.37                                                          |                   |
| 150              | 0.49                                                          | 0.41                                                          |                   |

3.3.4 Evaluation of anti-swelling performance
Clay minerals in formations usually exist in lamellar crystals that naturally accumulate or randomly arrange in pores, and are surrounded by initial formation water which contains sodium and calcium salts. When water at a low salinity enters the formation, it dilutes the initial formation water and causes the clay to swell. As seawater has such a high content of salts that it effectively avoids and reduces the dilution of the initial formation water, the seawater-based fracturing fluid exhibit excellent anti-swelling properties. As shown in Table 5, the anti-swelling experiment on the seawater-based fracturing fluid carried out using rock cuttings gathered from the second section of the Shahejie Formation in the Erhai oilfield shows that the fracturing fluid has a good anti-swelling performance which is equivalent to that of the solution with 1% compound anti-swelling agent.

| Anti-swelling agent | Anti-swelling rate/% |
|---------------------|----------------------|
| Gel breaker         | 86.54                |
| 1% compound anti-swelling agent | 87.05                |
| 0.5% compound anti-swelling agent | 78.84                |
| 2% KCl             | 82.1                 |

3.3.5 Flowing performance
According to the gel breaking data of the fracturing fluid (Table 6), the new flow-aid agent can dramatically reduce the surface tension of the fracturing fluid and the interfacial tension between the fracturing fluid and kerosene to 9.6% of the industry standard, indicating an excellent performance.
Table 6. Experimental result of surface and interfacial tensions of the seawater based fracturing fluid.

|                          | Temperature (℃) | Breaking time (min) | Surface tension (mN·m⁻¹) | Interfacial tension between the fracturing fluid and kerosene (mN·m⁻¹) |
|--------------------------|-----------------|---------------------|---------------------------|---------------------------------------------------------------------|
| Seawater based fracturing fluid | 150             | 480                 | 23.3                      | 0.21                                                                |
| Industry standard        | ≤720            | ≤28                 |                           | ≤2.0                                                                |

4. Field Application

4.1 Basic data and design optimization of the field test well

In order to verify the practical performance of the seawater-based fracturing fluid in field, pilot tests were carried out in Well ZH50-16 in the Dagang Oilfield. The fracturing section of Well ZH50-16 is from 4887.1 m to 4895 m, the perforated oil layers are 17.8 m thick, the average porosity is 12.8%, and the measured temperature in the middle of oil layers is 196.2℃.

According to the reservoir properties, the "large-scale volume fracturing" technology and the fracturing software Fracpro were adopted to optimize the fracturing process. The static pressure in an adjacent well Z1504 in the same oil layer with Well ZH50-16 was 38.23 MPa and the mid-reservoir was 4446.91 m measured on April 4, 2018, so the pressure coefficient of the layer to be perforated in Well ZH50-16 is estimated to be 1.1. Considering the reservoir physical properties, the fracturing fracture of Well ZH50-16 is predicted as shown in Figure 2. With more sand added, the production after fracturing would increase, but the rate may be gradually decreasing. The optimized scale of sand addition is approximately 6.0 m³/m, which is able to meet the needs of reservoir stimulation.

4.2 Fracturing effect and evaluation

The fracturing operation of Well ZH50-16 was successfully completed as designed (Figure 3). The total fluid volume injected is 1981.4 m³, of which 1135 m³ is slippery water; the total sand volume is 126.1 m³; the average pumping rate is 7 m³/min; the fracture pressure gradient is 0.0185 MPa/m. When injecting seawater-based slippery water, the average pressure is 68 MPa, the friction reduction rate is 75.2%. When injecting seawater-based fracturing fluid, the average pressure is 55 MPa, the friction reduction rate is 82.6%. The well produced 9.9 tons of oil per day through a 4 mm choke before fracturing, but produced liquid of 77.5 m³/d after fracturing, including 57.6 tons of oil, and 14800 m³ of gas through a 6 mm choke.

5. Conclusions

(1) The multi-component copolymerized hyper-branched polyacrylamide thickener, organic zirconium cross-linking agent, and alkyl glycoside flow-aid agent all have good compatibility with seawater, and
can be cross-linked under weak acid-neutral conditions. They can reduce precipitation caused by the reaction of alkaline plant gel fracturing fluid with $\text{Ca}^{2+}$ and $\text{Mg}^{2+}$ ions. The seawater-based fracturing fluid works well at 150°C. It meets the industry standard in any aspect.

(2) The suspended solid matter in the seawater filtrated in field is less than 14.3 mg/L and the turbidity is less than 8 NTU, indicating seawater can be directly used for preparing fracturing fluid in field.

(3) The seawater-based fracturing fluid has good cross-linking and sand-carrying performances. The pilot well produced 9.9 tons of oil per day through a 4 mm choke before fracturing, but its liquid production significantly increased to 77.5 m³/d through a 6mm choke after fracturing, including 57.6 tons of oil and 14800 m³ of gas.

Acknowledgement
As I finished this paper, I am really willing to give my sincere gratitude to those who have kept giving me so much help. First, I would like to thank Zhang Shengchuan with all my heart. Without his constant encouragement and guidance, I would not finish this paper. Professor Zhang is such an intellectual and serious scholar who always gives me a lot of help and revises my paper again and again. Second, my good wishes to all the colleagues in Petroleum Engineering Research Institute of Petrochina Dagang Oilfield. They have given me not only professional knowledge but also their care about our daily life. Third, thanks to the editors for their careful review. Last but not least, thank my family for supporting and providing me a comfortable atmosphere to finish this paper.

References
[1] Song A.L., An Q., Liu Q.G. et al. (2014) Study on the selection and performance of seawater based thickening agent. Journal of Oil and Gas Technology, 1 (36): 119-120.
[2] Lu Y.J., Chen Y.D., She C.H. (1997) Boron Cross-linked hydroxypropyl guar gel fracturing fluid properties. Drilling Fluid and Completition Fluid, 14 (6): 18-20.
[3] Zhao M.Y., Jia Z.L., Zhao Q. et al. (2004) Middle-high temperature VES fracturing fluid surfactant NTX-100. Oilfield Chemistry, 21 (3): 224-226.
[4] Luo M.L., Zhao Z.Y., Liu J.L. et al. (2010) Research progress of viscoelastic surfactant solutions applied to hydraulic fracturing and matrix acidizing. Applied Chemical Industry, 39 (6): 913-915.
[5] Tang S.F., Zhao C.Y., Tian L. et al. (2016) Temperature-resistance clean fracturing fluid with carboxylate Gemini surfactant: A case study of tight sandstone gas reservoirs in the Tarim Basin. Natural Gas Industry, 36 (6): 45-50.
[6] Lin M.Q., Li M.Y., Han F.X. et al. (2003) The influence of salt concentration on the properties of the linked polymer solution. Acta Petroleisinica (Petroleum Progressing Section), 19 (3): 44-46.