Re-injection feasibility study of fracturing flow-back fluid in shale gas mining

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Abstract: Fracturing flow-back fluid in shale gas mining is usually treated by re-injecting into formation. After treatment, the fracturing flow-back fluid is injected back into the formation. In order to ensure that it will not cause too much damage to the bottom layer, feasibility evaluations of re-injection of two kinds of fracturing fluid with different salinity were researched. The experimental research of the compatibility of mixed water samples based on the static simulation method was conducted. Through the analysis of ion concentration, the amount of scale buildup and clay swelling rate, the feasibility of re-injection of different fracturing fluid were studied. The result shows that the swelling of the clay expansion rate of treated fracturing fluid is lower than the mixed water of treated fracturing fluid and the distilled water, indicating that in terms of clay expansion rate, the treated fracturing flow-back fluid is better than that of water injection after re-injection. In the compatibility test, the maximum amount of fouling in the Yangzhou oilfield is 12mg/L, and the maximum value of calcium loss rate is 1.47%, indicating that the compatibility is good. For the fracturing fluid with high salinity in the Yanchang oilfield, the maximum amount of scaling is 72mg/L, and the maximum calcium loss rate is 3.50%, indicating that the compatibility is better.

1. Introduction
In the process of fracturing in the shale gas mining will continue to produce a large number of fracturing flow-back fluid, with the composition of complex, high viscosity, high organic content, high solid content and low biodegradability and other characteristics [1-2]. If the disposal is improper, there is a risk of environmental pollution. And most of the shale gas mining areas for the lack of water, so most of the shale gas fracturing flow-back fluid are used to re-injection [3]. However, because of the suspended matter and the oil content will clog the stratum. The scaling ion in the fracturing flow-back fluid will deposit in the porous media of the reservoir and block the pore throat. Therefore, it has a strict standard for the treatment of fractured effluent after injection into the stratum [4-5]. At present, the water quality index of re-injection water is controlled according to the suspended matter, oil content and median value of particle size in SY/T 5329-2012 standard, the influence of injected flow-back fluid on the swelling of clay and scaling of water to the injection bottom is neglected, which results in the defect of feasibility evaluation of re-injection [6]. Based on the clay swelling method and compatibility experiment, two kinds of fracturing flow-back fluid with different degree of
mineralization were selected. Combined with the above SY/T 5329-2012 standards, the feasibility of re-injection after fracturing flow-back fluid treatment is evaluated [7].

2. Experimental

2.1. Apparatus and Reagents
Main equipment: TDL-80-2P low-speed desktop centrifuge; BT224S analytical balance; 211 pH meter; SHZ-D (Ⅲ) circulating water-type vacuum pump and supporting glass sand core filter device.

Main agents: standard montmorillonite; KCl (analytical grade): fracturing back from the Yangzhou oil field and Yanchang oil field; formation water from Yangzhou oil field and Yanchang oil field.

2.2. Experimental
(1) Water quality ion concentration analysis method:
According to the relevant methods of "water and waste water detection method" and "oil and gas field water analysis method" (SY/T 5523-2016), the water content of the treated fracturing fluid was measured and analyzed. Measurement and analysis of scaling ions may cause blockage in formations and pipelines in oil fields.
(2) Method of clay swelling rate:
According to the centrifugal method in the determination method of clay stabilizer for fracturing and acidizing (SY/T 5762-1995), the clay swelling rate was determined. Weigh the 0.50g bentonite powder, accurate to 0.01g, loaded 10mL centrifuge tube, add 10mL liquid to be measured, shake well, at room temperature for 2h, into the centrifuge, the speed of 1500r / min centrifugal separation 15 min, read out the volume of bentonite after expansion. The expansion rate was calculated based on the expansion volume of bentonite and 3% KCl solution.

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\text{Expansibility} = \frac{V_2}{V_1} \times 100\%
\]

V_1 is 3% of the KCl solution mixed with clay after the expansion of the volume, ml; V_2 to be measured water samples and clay after the expansion of the volume, ml.
(3) Determination of scaling:
Scale mass analysis method is the use of membrane filtration method. After the treatment was carried out for 72 hours at 40°C and then filtered through a 0.45 μm filter on a glass sand core filtration apparatus, the filter was subjected to filtration and the formation water (adjusted to different pH values and filtered through a 0.45 μm filter). And with distilled water or petroleum at least 3 times after cleaning, drying constant weight and weighing the quality of the filter before and after filtering the poor quality of the filter is the amount of water.

3. Results and discussion

3.1. Analysis of water quality of backfill fracturing
According to the SY/T 5329-2012 standard, the fracturing fluid and the fracturing fluid after treatment are analyzed for water quality. The treatment of fracturing effluent is mainly carried out by flocculation sedimentation and oxidation-reduction method. After the fracturing solution is oxidized with Fenton reagent, the flocculant and coagulant are added to settle the suspended particles to realize solid-liquid separation [8-10]. (Table 1 and Table 2)
Table 1. Water quality of fracturing flow-back fluid after treatment in Yangzhou oil field.

| Parameters     | Flow-back fluid before treatment | Treated flow-back fluid |
|----------------|----------------------------------|-------------------------|
| Ca$^{2+}$(mg/L) | 28.7                             | 70.14                   |
| Mg$^{2+}$(mg/L) | 19.55                            | 23.09                   |
| ΣFe(mg/L)      | 4.96                             | 0.35                    |
| Cl(mg/L)       | 499.85                           | 623.4                   |
| CO$_3^{2-}$(mg/L) | 58.21                        | 0.00                    |
| HCO$_3$-(mg/L) | 790.21                           | 215.4                   |
| S(mg/L)        | 38.66                            | 39.65                   |
| SO$_4^{2-}$(mg/L) | 158.04                        | 761.1                   |
| K$^+$,Na$^+$(mg/L) | 742.14                      | 895.53                  |
| pH value       | 6.5                              | 7                       |
| Oil conten(mg/L) | 18.63                         | ≤1.0                    |
| Suspended matter conten(mg/L) | 1920                  | 1.2                     |
| Mineral content/(mg/L) | 2340.32               | 2628.66                 |

Table 2. Water quality of fracturing flow-back fluid after treatment in Yanchang oil field.

| Parameters     | Flow-back fluid before treatment | Treated flow-back fluid |
|----------------|----------------------------------|-------------------------|
| Ca$^{2+}$(mg/L) | 2599.19                          | 2553.10                 |
| Mg$^{2+}$(mg/L) | 130.06                           | 128.84                  |
| ΣFe(mg/L)      | 12.39                            | 0.49                    |
| Cl(mg/L)       | 8479.87                          | 10196.84                |
| CO$_3^{2-}$(mg/L) | 0.00                          | 0.00                    |
| HCO$_3$-(mg/L) | 363.37                           | 354.53                  |
| S(mg/L)        | 16.11                            | 8.06                    |
| SO$_4^{2-}$(mg/L) | 271.64                        | 255.17                  |
| K$^+$,Na$^+$(mg/L) | 2529.04                      | 3690.15                 |
| pH value       | 6.5                              | 7                       |
| Oil conten(mg/L) | 5.96                          | ≤1.0                    |
| Suspended matter conten(mg/L) | 246.50                      | 1.6                     |
| Mineral content/(mg/L) | 14403.71                | 17187.37                |

Through the analysis of water quality in Table 1 and Table 2, it can be seen that the salinity of fracturing flow-back fluid in Yangzhou oilfield is relatively low, which is 2628.66mg/L. After the treatment of Yanchang oilfield, the salinity of fracturing flow-back fluid is relatively high, which is 17187.3mg/L. Therefore, this paper studied the feasibility of re-injection for two kinds of fracturing flow-back fluid with different salinity.

3.2. Influence of water quality on clay swelling

According to the test method of determining clay swelling rate in 2.2.2, the influence of fracturing flow-back fluid after treatment with different salinity on clay stability was studied. (Table 3 and Table 4):
Table 3. Effect of fracturing flow-back fluid after treatment on the stability of clay in Yangzhou oilfield.

| Mixture ratio (distilled water / treated water) | volume/mL | Relative expansion rate/% |
|-----------------------------------------------|-----------|--------------------------|
| 0.5g + 10mL (distilled water)                 | 5.75      | 500.00                   |
| 0.5g + 8:2                                    | 5.02      | 436.52                   |
| 0.5g + 6:4                                    | 4.40      | 382.61                   |
| 0.5g + 5:5                                    | 4.15      | 360.86                   |
| 0.5g + 4:6                                    | 3.98      | 346.09                   |
| 0.5g + 2:8                                    | 3.76      | 326.96                   |
| 0.5g + 10mL (treated water)                   | 3.62      | 314.78                   |
| 0.5g + 10mL (3% KCl)                          | 1.15      | 100                      |

Table 4. Effect of fracturing flow-back fluid after treatment on the stability of clay in Yanchang oilfield.

| Mixture ratio (distilled water / treated water) | volume/mL | Relative expansion rate/% |
|-----------------------------------------------|-----------|--------------------------|
| 0.5g + 10mL (distilled water)                 | 5.52      | 501.82                   |
| 0.5g + 8:2                                    | 1.72      | 156.36                   |
| 0.5g + 6:4                                    | 1.34      | 121.82                   |
| 0.5g + 5:5                                    | 1.28      | 116.36                   |
| 0.5g + 4:6                                    | 1.24      | 112.73                   |
| 0.5g + 2:8                                    | 1.15      | 104.55                   |
| 0.5g + 10mL (treated water)                   | 0.96      | 87.27                    |
| 0.5g + 10mL (3% KCl)                          | 1.10      | 100                      |

From tables 3 and 4 can be seen, the fracturing flow-back fluid of the oil in the Yangzhou oil field with a salinity of 2628.66 mg/L, compared with the aqueous solution of 3% KCl, makes the expansion degree of clay larger, the expansion rate increased from 314.78% to 436.52%. While the salinity of 17187.3mg/L after the treatment of Yanchang oilfield fracturing flow-back the clay hydration degree is smaller, the expansion rate only increased from 87.27% to 156.36%. The lower the ion content in the two fracturing effluents, the larger the expansion volume. This is because the bentonite belongs to the expansive material, after the treatment of fracturing flow-back fluid in minerals, especially Ca$^{2+}$, Mg$^{2+}$ and other high-priced ions will spread to the clay layer, inhibit the further hydration between the clay expansion[11]. Through the above results can also be obtained, because the salinity of the treated fracturing flow-back fluid is higher than that of the clear water, the re-injection will not make the reservoir clay the expansion, suitable as a re-injection of the formation of water.

3.3. Effect of pH on Clay Stability

According to the method of 2.2.2, the effect of the pH value of the fracturing solution after treatment on the stability of the clay was determined. (Table 5):
Table 5. Effect of pH value of post fracturing flow-back fluid on clay stability.

| pH | Expansion volume/mL sample | Fracturing flow-back fluid after treatment in Yangzhou | Fracturing flow-back fluid after treatment in Yanchang | 3%KCl+distilled water |
|----|---------------------------|--------------------------------------------------------|-------------------------------------------------------|----------------------|
| 6.5| 3.50                      | 0.98                                                   | 1.04                                                  |
| 7.0| 3.68                      | 1.02                                                   | 1.10                                                  |
| 7.3| 3.80                      | 1.06                                                   | 1.16                                                  |
| 7.5| 3.72                      | 1.12                                                   | 1.21                                                  |
| 8.0| 3.98                      | 1.20                                                   | 1.36                                                  |

From table 5, the Yangzhou oilfield fracturing flow-back fluid with low degree of mineral content, clay swelling volume increases with the increase of pH, the growth rate of the larger; the Yanchang oilfield fracturing flow-back fluid with high degree of mineral content, the clay swelling volume increases with the increase of pH, the growth rate is smaller. This is due to the bentonite belongs to the expansion of the material, the pH value in the fracturing flow-back fluid increases and the corresponding OH⁻ concentration increases and the clay swelling property increases[11-12]. And the low fracturing flow-back fluid with relatively low salinity has relatively large expansion rate, so the growth rate is relatively large. The relative expansion rate of the fracturing flow-back fluid with high salinity is small, so the growth rate is relatively small. When the pH value is between 7.0~7.3, the relative expansion volume increases little. Therefore, in order to protect the reservoir, the pH value of the fracturing flow-back fluid to be re-injected should be controlled between 7.0~7.3. The experimental results show, compared with the treated fracturing fluid, the swelling rate of clay swelling is lower than the mixed water of fracturing flow-back fluid and distilled water. Therefore, the treatment of fracturing flow-back fluid re-injection and pH value control between 7.0~7.3 is more conducive to reservoir protection, and it also shows that the fracturing flow-back fluid is better than clean water re-injection in terms of clay expansion.

3.4. Effect of mixed treatment of fracturing flow-back fluid and formation water on scaling

According to the method of 2.2.3, the influence of the amount of scaling when the fracturing flow-back fluid is mixed with formation water is determined. (Table 6 and table 7).

Table 6. Determination of scaling after fracturing flow-back fluid and formation water treatment in Yangzhou Oilfield.

| V treated water : V formation water | Transmittance% | Scale amount/(mg·L⁻¹) | Calcium loss rate% |
|-------------------------------------|----------------|-----------------------|-------------------|
| 10:0                                | 99             | 1                     | 0.35%             |
| 9:1                                 | 99             | 1                     | 0.32%             |
| 8:2                                 | 98             | 2                     | 0.45%             |
| 7:3                                 | 98             | 4                     | 0.68%             |
| 6:4                                 | 98             | 4                     | 0.99%             |
| 5:5                                 | 97             | 5                     | 1.08%             |
| 4:6                                 | 97             | 7                     | 1.20%             |
| 3:7                                 | 97             | 7                     | 1.47%             |
| 2:8                                 | 97             | 8                     | 1.26%             |
| 1:9                                 | 96             | 9                     | 1.01%             |
| 0:10                                | 96             | 12                    | 0.88%             |
Table 7. Determination of scaling after fracturing flow-back fluid and formation water treatment in Yanchang Oilfield.

| $V_{treated \ water}:V_{formation \ water}$ | Transmittance% | Scale amount/(mg·L$^{-1}$) $^1$ | Calcium loss rate% |
|-------------------------------------------|----------------|---------------------------------|-------------------|
| 10:0                                      | 98             | 11                              | 1.35%             |
| 9:1                                       | 96             | 21                              | 2.04%             |
| 8:2                                       | 95             | 33                              | 2.53%             |
| 7:3                                       | 93             | 47                              | 3.02%             |
| 6:4                                       | 92             | 49                              | 3.21%             |
| 5:5                                       | 92             | 56                              | 3.32%             |
| 4:6                                       | 90             | 62                              | 3.33%             |
| 3:7                                       | 88             | 72                              | 3.50%             |
| 2:8                                       | 87             | 60                              | 3.23%             |
| 1:9                                       | 83             | 42                              | 2.91%             |
| 0:10                                      | 84             | 36                              | 2.63%             |

Table 6 shows the Yangzhou oilfield after fracturing fluid with low degree of mineralization, and the formation of water compatibility test, the maximum amount of fouling in the Yangzhou oil field is 12mg·L$^{-1}$, the maximum value of calcium loss is 1.47%. The compatibility is good.

Table 7 shows the Yanchang oilfield after fracturing fluid with high degree of mineralization, and the formation of water compatibility test, the maximum amount of fouling is 72mg·L$^{-1}$, the maximum calcium loss rate is 3.50%, and the compatibility is better.

4. Conclusions

After treatment, the fracturing flow-back fluid will make the clay expand, and the volume of expansion is closely related to the pH value. As the degree of mineralization increases, the rate of expansion of clay will be smaller. And the salinity of fracturing flow-back fluid after treatment is higher than that of the clean water, so the relative expansion rate is lower and the feasibility of the re-injection is better.

In the compatibility test, the maximum amount of fouling in the Yangzhou oilfield is 12mg·L$^{-1}$, the maximum value of calcium loss rate is 1.47%. The compatibility is better; The maximum amount of fouling in the Yanchang oilfield is 72mg·L$^{-1}$, the maximum value of calcium loss rate is 3.50%, and the compatibility is well.

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Reference

[1] ZHUANG Zhao-Feng and ZHANG Shi-Cheng 2006 Feasibility of Reusing Boron/Hydroxypropyl Guar Gelled Fracturing Fluid Oilfield Chemistry 02 120-123
[2] Ma Yun and HE Shun’an 2009 Hazard and progress in treatment of fracturing waste-waters Petrochemical Industry Application 8 1-3
[3] QU Cheng-tun. 2009 Introduction to Oil and Gas Field Protection (Beijing:Petroleum Industry Press) p 134-135
[4] HU Xue-bin and XU Yong-gao 2002 Experiment Evaluation of Formation Damage Induced by Water Injection Journal of Jianghan Petroleum Institute 24 53-55
[5] Rimassa S. M. and Howard P. R. 2009 Optimizing fracturing fluids from flow-back water, Soc.
Pet. Eng 6 24

[6] Oliver Olsson and Dirk Weichgrebe 2013 Hydraulic fracturing waste water in Germany: composition, treatment, concerns. Environmental earth sciences 8 8-9

[7] SHU Yong and JIA Yao Qin 2003 Laboratory experimental investigation on reservoir formation damage by recycled produced water at Zhangxi oilfield. Oilfield Chemistry 20 129-132

[8] FAN Wei 2016 Treatment Technology of Fracturing Fluid Flow-back Technology & Development of Chemical Industry 3 55-56

[9] Yan Zhihu and Dai Caili 2015 Research and Application Progress on Treatment Technology of Fracturing Flow-back Fluid Oilfield Chemistry 3 444-448

[10] Lu Zheng guang 2016 Discussion on Treatment Technology of Fracturing Flow-back Water in Oil and Gas Field Environmental Science and Management 5 104-107.

[11] Olphen H Van. 1979 Geologists and Soil Scientists. (Beijing:China Agriculture Press) p 114-115

[12] Alba Carrero-Parreño and Viviani C. 2017 Optimal Pretreatment System of Flow-back Water from Shale Gas Production Ind. Eng. Chem. Res 56 4386–4398