Study on fracturing flowback fluid treatment technology for shale gas in Yangzhou

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Abstract. Shale gas fracturing flowback fluid has the characteristics of high viscosity, large displacement, complex components and difficult to deal with. Therefore, it is of great significance for environmental protection to treat and reuse it. In this paper, Yangzhou shale gas is taken as an object to study the treatment of shale gas fracturing flowback fluid. The results show that the viscosity of the fracturing flowback fluid before treatment was 16.75 mPa·s, and when the pH was adjusted to 3.5, with Cerium(III) sulfate and ferrous sulfate as catalyst and the dosage were 60 mg/L and 120 mg/L respectively, and hydrogen peroxide dosage was 0.5%, the viscosity of fracturing flowback fluid was reduced from 16.75 mPa·s to 1.97 mPa·s; After the oxidation treatment, adjusting pH to 7.5, and treating it with inorganic flocculant and organic flocculant, the water quality met the reinjection requirement of the average air permeability of less than or equal to 0.01 μm².

1. Introduction
With the continuous improvement of science and technology, shale gas has become one of the important sources of energy replacement [1]. During shale gas development and production process, hydraulic fracturing is a common measure [2]. According to the U.S. Environmental Protection Agency, the water consumption of one shale gas well is 7600 m³-19000 m³, and 15% to 80% of flowback fluid is discharged to the ground after fracturing operation [3]. The fracturing process will produce a large number of fracturing flowback liquid, which contains a large number of organic and inorganic pollutants such as: suspended solids, oil, soluble salts and other complex components [4]. If not treated and discharged directly, this will cause serious pollution to the surrounding environment, especially for crops and surface water systems, and cause serious waste of water resource [5-6]. Therefore, it is of great significance to develop an effective shale gas fracturing flowback wastewater treatment technology, which can protect the ecological environment and reduce production costs [7].

For the treatment of fracturing flowback fluid, chemical flocculation sedimentation method, biological and biochemical method, advanced oxidation method and Fe/C micro electrolysis method, etc [8] are common methods. These methods have different characteristics. The chemical flocculation sedimentation method has advantages of strong adaptability and fast processing speed. Also, it can remove emulsified oil and organic matter [9], control the reaction rate of hydroxyl radicals, and improve the oxidation and viscosity reduction efficiency. Therefore, the chemical flocculation
sedimentation method is an important measure to improve fracturing flowback wastewater treatment efficiency and effect. Taking shale gas in Yangzhou as an example, the “oxidation flocculation” process was applied to treat shale gas fracturing fluid in this paper, so as to provide the basis for reusing flowback fluid [10].

2. Water quality characteristics of the flowback fluid in Yangzhou
The flowback fluid is brown and high turbidity. No sediment is deposited after one day placement. Its pH value is 8, the density is 0.9968g/cm³, salinity is 9255.36mg/L, content of suspended solids is 325.00mg/L, oil content is 79.72mg/L, COD is 2016.0 mg/L, the viscosity is 16.75mPa • s, and colority is 1260 degree.

3. Experiment design
3.1. Experiment method
Suspended matter content and oil content determination were based on “clastic reservoir water injection recommended indicators and analysis method”(SY/T 5329-2012). Chroma determination was according to GB 11903-1989 standard requirements. Viscosity determination was based on GB/T 10247-2008. Flocculation test was according to GB/T 16881-2008.

3.2. Reagents and instruments
Main reagents: Sodium hypochlorite, hydrogen peroxide (mass fraction 30%), ferrous sulfate, cerium(III) sulfate, sulfuric acid and sodium hydroxide (both are chemical pure reagents), polymeric aluminum chloride (PAC), polyacrylamide (PAM, various models), polymeric ferric sulfate (PFS) (industrial product).
Main equipment: Ubbelohde viscometer and UV-2350 ultraviolet spectrophotometer.

4. Results and discussions
4.1. Oxidation treatment
Using viscosity and chroma as indexes of evaluation, this study investigated treatment effects of commonly used oxidant, like hydrogen peroxide, sodium hypochlorite and fenton. The experiment results were shown in Figure 1. and Figure 2.

![Figure 1. Effect of sodium hypochlorite and hydrogen peroxide on viscosity reduction.](image1)

![Figure 2. Effect of ferrous iron on the viscosity reduction rate of flowback liquid in Fenton reagent.](image2)

When the amount of hydrogen peroxide and sodium hypochlorite were 0.5% and 0.4% respectively, pH value was 3 and the oxidation time was 1 h, the viscosity of flowback fluid was reduced from 16.75 mPa•s to 8.74 mPa•s, 10.93 mPa•s. When the amount of hydrogen peroxide was 0.5% and the
dosage of ferrous sulfate was 120 mg/L, the viscosity reduction rate reached 88%, and the viscosity reduction effect was the best among the three kinds of oxidants.

This is because the essence of Fenton reagent is the role of chain reaction between Fe$^{2+}$ and H$_2$O$_2$. The reaction can catalyze the formation of ·OH radicals. Jospeh thinks the reaction process of Fenton reagent is as follows [11]:

$$\text{H}_2\text{O}_2 + \text{Fe}^{2+} \rightarrow \text{OH} + \text{Fe}^{3+} + \text{OH}^- \quad (1)$$

$$\text{Fe}^{2+} + \text{OH}^- \rightarrow \text{Fe}^{3+} + \text{OH} \quad (2)$$

During the process, ·OH is produced as a step-up step, and ·OH is gradually consumed by reacting equation (2) or reacting with organic matter. By separating the H in the organic matter, and filling unsaturated C-C bond, ·OH reacts indiscriminately with most organic molecules and produce harmless products, such as CO$_2$, H$_2$O [12]. In Fenton reaction, H$_2$O$_2$ can not be too much, otherwise ·OH will be captured by excessive H$_2$O$_2$ which weakens the oxidation effect [13]. Fe$^{2+}$ is a necessary condition for catalyzing H$_2$O$_2$ to generate free radicals [14].

pH had a great influence on oxidation effect of Fenton reagent as shown in Figure 3. Because when the pH value was too low (<3), Fe$^{2+}$ catalyzed the decomposition of H$_2$O$_2$ to accelerate the formation of O$_2$. It was not conducive to formation of ·OH. While when pH value was too high (>4), Fe$^{2+}$ generated precipitation. So the optimal pH value of Fenton reagent was 3 to 4. However, when pH value rose, Fe$^{2+}$ was easily oxidized to Fe$^{3+}$, which caused chroma to increase. So, the study selected pH value as 3.

![Figure 3. Effect of pH on Oxidation.](image1)

![Figure 4. Effect of catalyst on oxidation time.](image2)

Oxidation effect of Fenton reagent was good, but the oxidation time was too long. After 45min treatment, viscosity of flowback fluid was only reduced to below 2mPa·s. This limited treatment efficiency. Because adding catalysts shortened oxidation time and improved the processing efficiency, the study investigated synergistic effects between Fenton reagent and Cu$^+$, Mn$^{2+}$ and Ce$^{3+}$ respectively. As shown in Figure 4, oxidation effect was the best with addition of Fenton reagent, Cu$^+$ and Ce$^{3+}$. However, because Cu$^+$ was easily oxidized to Cu$^{2+}$, the study selected cerium(III) sulfate as the catalyst.

The experiment results revealed that when cerium(III) sulfate dosage was 100mg/L, Fenton reagent dosage reached the optimal (0.5% hydrogen peroxide dosage and 120 mg/L ferrous sulfate dosage). The experiment results were shown in Figure 4.

It could be seen from Figure 4 that oxidation time was shortened after adding a certain amount of catalyst. The viscosity of flowback fluid was reduced to less than 2mPa·s after 25 minutes, which was shorter than before. However, some studies have shown that the catalytic effect of Ce$^{3+}$ alone on hydrogen peroxide is not significant [15]. This is mainly because Ce$^{3+}$ improves the cycling performance of Fe$^{3+}$ and Fe$^{2+}$ by accelerating reduction of Fe$^{3+}$, and promotes the generation of ·OH within the system, thus improving the oxidation efficiency to a certain extent [16-17].
4.2. Study on flocculation treatment of flowback fluid after oxidation
Optimization of inorganic flocculants
Flowback fluid was oxidized under conditions of 2.1. Adjusting its pH to 7.5, this study used PAC and PFS respectively to perform flocculation experiments, and observed their flocculation effects. The experiment results were shown in Table 1. When flocculant dosage was 1000 mg/L, after treatment with PAC and PFS, transmittance of supernatant was 98.9% and 56.3% respectively, and colority was 87 degree and 1180 degree respectively. So the effect of PAC was obviously better than that of PFS. Therefore, this experiment selected PAC as the flocculant.

Table 1. Optimization of inorganic flocculants.

| Parameters      | PFS  | PAC  |
|-----------------|------|------|
| Transmittance/% | 56.3 | 98.9 |
| Colority /degree| 1180 | 87   |
| Suspension floc volume | more | less |

During the flocculation process, as pH value changed, flocculation effect also changed a lot. As was shown in Figure 5, when the amount of flocculant was 1000mg/L, as pH value gradually increased, the transmittance increased first and then decreased, and the chroma decreased first and then increased. When pH was 7, the light transmittance reached 99.0%, colority was 80 degree. The treatment effect was the best. So the study selected flocculation pH as 7.

![Figure 5. Effect of pH on Flocculation Effect.](image)

As was exhibited in Figure 6, as PAC dosage increased from 200mg/L to 800mg/L, light transmittance of supernatant gradually increased from 45.7% to 98.8%, and the chroma decreased from 1571 degree to 87 degree. When PAC dosage exceeded 800mg/L, the concentration of supernatant increased, light transmittance and chroma tended to be stable. Because when PAC dosage is not enough, flocculant can’t fully touch impurities in water, portions of impurities are not flocculated. When PAC dosage increases gradually, flocculant can touch impurities more completely, so the treatment effect becomes better and better. While when PAC dosage is too large, ionic surface activity points that are required for flocs bridging are insufficient. So adsorption bridging effect gets worse. However, flocculation effect is stable because of large dosage. Therefore, in the follow-up experiment, PAC dosage was selected as 800mg/L.

![Figure 6. PAC dosage on the flocculation effect.](image)

4.3. The compound of organic flocculant and inorganic flocculant
After treated with inorganic flocculant, the system will produce a large number of tiny flocs, and the precipitation time was fairly long. The addition of organic flocculants could promote the formation of
large flocs and speed up the floc precipitation rate. Because cationic PAM has surface electrical neutralization and “bridging” mechanism, after cationic PAM is added to fracturing fluid, large flocs can quickly form through “bridging” effect, and the settlement and separation velocity are accelerated. When the dosage was 20mg/L, coagulation aid effects of different organic flocculant PAM were displayed in Table 2. The results revealed that when combining PAC with cationic PAM whose molecular weight was 8 million and ion degree was 60%, the effect of compound treatment was the best.

| Parameters                  | Cationic |
|-----------------------------|----------|
| Molecular weight/ten thousand | 800 800 1200 800 800 |
| Ionic degree/%              | 20 30 40 50 60 12 |
| Transmittance/%             | 95.4 95.1 96.3 93.1 98.2 92.3 |
| Colority /degree            | 176 171 148 224 97 267 |

When PAM dosage is small, if the concentration increases, the “bridging” effect is enhanced. While PAM dosage is too large, the surface of the colloidal particles will be covered by the adsorbed organic macromolecules, which reduces the possibility of combining with other particles. So this will steady protect particles [18], and weaken its efficiency of accelerating floc formation. What’s more, with the amount of pharmaceuticals increased, the cost of handling backlash will increase, too. So the optimal PAM dosage should be selected. The selected results were showed in Figure 7. When the PAM dosage reached 20mg/L, light transmittance and chroma tended to be stable. So the optimal PAM dosage was 20mg/L.

When organic flocculant and inorganic flocculant were combined to disposed flowback fluid, the dosing interval of them had a great effect on the treatment effect. So this study tried to find the optimal dosing interval. The experiment results were exhibited in Figure 8.

As was shown in Figure 8, when the dosing interval was between 10s and 40s, as the time interval increased, the flocs became larger, the light transmittance of supernatant gradually increased after compound treatment; when the dosing interval exceeded 40s, the treatment effect became worse. Therefore, when the dosing interval was controlled at 40s, the light transmittance of supernatant was the highest, and the treatment effect was the best. This is because when the dosing interval is short, the addition of PAC has not yet broken the colloidal system completely, and small floc has not yet fully generated. So PAM can not transform small flocs into large flocs through “bridging” effect. While
when the dosing interval is too long, flocs formed from PAC may be broken after adding PAM and stirring. This will result in an increase in the number of small flocs in the system, so treatment effect becomes worse [19]. Hence, in the follow-up experiment, the dosing interval of PAC and PAM were selected for 40s.

5. Comparative analysis of water quality before and after treating shale gas fracturing flowback fluid

The water quality analysis was performed on supernatant after shale gas fracturing flowback fluid treatment using the method introduced in part 1, and then the analysis result was compared with Water Quality Recommended Standard and Practice for Analysis of Oilfield Injecting Waters in Clastic Reservoirs (SY/T 5329-2012). The comparison results were showed in Table 3.

Table 3. Shale gas fracturing flowback fluid before and after treatment of water quality analysis table.

| Parameters                  | Flowback water before treatment | Treated flowback liquid | SY/T 5329-2012 |
|-----------------------------|---------------------------------|-------------------------|-----------------|
| pH value                    | 7.5                             | 6.5                     | /               |
| Viscosity(20 °C)/(mPa·s)    | 16.75                           | 1.97                    | /               |
| Colority /degree            | 1260                            | 81                      | /               |
| Total iron content/(mg/L)   | 3.60                            | 0.34                    | /               |
| Suspended matter content/(mg/L) | 325.00                        | 0.7                     | ≤1.0            |
| Oil content/(mg/L)          | 79.72                           | 0.75                    | ≤5.0            |
| Average corrosion rate/(mm·a⁻¹) | 0.2835                      | 0.054                   | ≤0.076          |
| Bacterial content / Per milliliter |                     |                         |                 |
| SRB                        | 2×10⁹                           | 2.5                     | ≤10             |
| FB                         | 2×10⁹                           | 2.5                     | nx10²           |
| TGB                        | 2.5×10³                         | 5.0                     | nx10²           |

As was exhibited in Table 3, after treated by Oxidation-flocculation method, water quality indexes of shale gas fracturing flowback fluid met requirements of low permeability formation [20].

6. Conclusions

(1) Shale gas fracturing flowback fluid in the pH value to 3, with 100mg/L of cerium(III) sulfate as a catalyst, hydrogen peroxide, ferrous sulfate dosage of 0.5%, 120mg/L, viscosity can be reduced to 1.97mPa·s. The addition of Ce³⁺ in the oxidation can reduce the oxidation time from 50min to 25min, improve the efficiency of treatment.

(2) With organic flocculant and inorganic flocculant compound treatment has been oxidized flowback fluid. The pH adjusted to 7, plus PAC800mg/L flocculation treatment, after 40 seconds, add PAM20mg/L coagulation, precipitation back to the drainage Suspended matter content and oil content dropped to 0.7mg/L and 0.75mg/L respectively, which met the reinjection standard.

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