Treatment of high viscosity fracturing flowback by electrolytic brine-catalyzed oxidation
Shaoxiong Si, Zhaobo Gong, Yongxia Yang, Shengli Liu, Yu Wang and Xinghua Wang

ABSTRACT
With the increasing application of hydraulic fracturing technology in exploration of tight oil and shale gas, the treatment of accompanying fracturing flowback fluids has become more urgent. Fe/Ni catalyst was successfully applied in the treatment of the flowback fluid for the first time in this paper. The effects of different oxidants and catalysts on the treatment of fracturing flowback were investigated. Electrolytic brine was an optimal oxidation gel breaker and molecular sieve loaded with Fe/Ni as catalyst for the treatment of fracturing flowback. Fe/Ni catalyst was characterized by SEM, EDS analysis, TEM and XRD, and the catalytic effect of the Fe/Ni proportion was explored. Fracturing flowback that dealt with catalytic oxidation was mixed with polyaluminum chloride (PAC) and polyacrylamide (PAM) for flocculation and sedimentation, through a filter, and was continuously treated for 20 days to simulate on-site operation. Finally, the suspended solids (SS) content of the fracturing flowback was steadily less than 15 mg/L, which meets the reinjection standard of fracturing flowback (SY/T 5329-2012 (China)). Hence, electrolytic brine-catalyzed oxidation treatment of high viscosity fracturing flowback possess broad application prospects.

Key words | electrolytic brine, Fe/Ni catalyst, fracturing flowback, reinjection water

HIGHLIGHTS
● Electrolytic brine was optimal for the treatment of fracturing flowback due to its low cost and high oxidation effect.
● The loaded Fe/Ni catalyst with 28 nm particle size could promote the oxidation of electrolyzed brine.
● Dynamic simulation tests for 20 days showed that the effluent could meet the standards of SY/T5329-2012 and SY/T 0097-2016 continuously.
● The catalytic oxidation of electrolyzed brine is an environmentally benign and cost-effective technique for fracturing flowback treatment with the existing filtration processes.
GRAPHICAL ABSTRACT

INTRODUCTION

At present, the tight oil accounts for 35% of the total newly proved crude oil in China (Dyni 2003; Jiao et al. 2012). According to the prediction of the U.S. Energy Information Administration, China ranks third in the world in terms of recoverable tight oil resources with up to $4.48 \times 10^8$ t (EIA 2013; Wang et al. 2014). Currently, tight oil has been exploited on a large scale by horizontal well stimulated reservoir volume (SRV) fracturing technology, and a large amount of fracturing flowback needs to be treated (Meyer & Bazan 2011; Wu et al. 2012). In addition, large scale SRV fracturing has also been used in shale gas to achieve effective production, such as at the Chang Qing oilfield, Yan Chang oilfield, Southwest oil and gas field, and North American (Schneising et al. 2014; Hu et al. 2019). Up to now, Chinese annual production of shale gas has exceeded 10 billion cubic meters. According to the document promulgated by the State Council ([2018] No.31, China), more than 1,400 oil wells will be drilled and plenty of fracturing flowback produced in the fracturing process also need to be treated (Meyer & Bazan 2011; Wu et al. 2012). In addition, large scale SRV fracturing has also been used in shale gas to achieve effective production, such as at the Chang Qing oilfield, Yan Chang oilfield, Southwest oil and gas field, and North American (Schneising et al. 2014; Hu et al. 2019). Up to now, Chinese annual production of shale gas has exceeded 10 billion cubic meters. According to the document promulgated by the State Council ([2018] No.31, China), more than 1,400 oil wells will be drilled and plenty of fracturing flowback produced in the fracturing process also need to be treated by 2020 (Hu et al. 2018). Therefore, it was necessary to carry out researches into the treatment of fracturing flowback and other industrial waste water (Yazdanbakhsh et al. 2016; Bhanot et al. 2020).

Fracturing flowback contains various components such as guar gum, stabilizer, fungicide and various solid particles, resulting in high values of suspended solids (SS), viscosity and chemical oxygen demand (COD), which increased the cost and difficulty of treatment (Stringfellow et al. 2014). And the multiple oxidation and flocculation of composite processes are mostly used for treatment of fracturing fluids (Estrada & Bhamidimarri 2016; Huang et al. 2016). The five-step process, coagulation + oxidation + Fe/C microelectronics + $\text{H}_2\text{O}_2$/Fe$^{2+}$ catalytic oxidation + activated carbon adsorption, was employed in Nanyang Oilfield, Henan Province; PAC and PFS (polyferric sulfate) were used as the inorganic coagulants, while the electrolytic brine was used as the oxidant. Although the fracturing flowback treated by the five-step process can meet the national secondary emission standards (China), the cost of treatment was high. The microelectrolysis + Fenton oxidation process, which was applied in Changqing oilfield, the removal rate of COD was 58.9% and the viscosity decreased from 2.97 mPa·s to 1.6 mPa·s after adding $\text{H}_2\text{O}_2$ and Fe$^{2+}$. Therefore, the oxidation process is essential to break the stability of the guar gum colloid and reduce the viscosity of the fracturing flowback, and to facilitate subsequent treatment further. Common oxidation includes ammonium persulfate, electrolytic brine, hydrogen peroxide and other oxidants. However, the expense of fracturing flowback treatment was extremely high since the oxidation requires plenty of oxidant (Gregory et al. 2011). Iron-nickel bimetallic catalyst has drawn great attention in waste water treatment due to its large reactive surface area (Weng et al. 2017; Wu et al. 2017; Xian et al. 2019), although there are some limitations associated with practical applications, such as aggregation and being difficult to recycle because of its particle characteristics. Hence, technologies that use mechanical supports have been developed to broaden the application of various particles (Theofanidis et al. 2015).

In this paper, Fe/Ni catalyst was successfully applied in the treatment of the flowback fluid for the first time. The catalyst can improve the oxidation efficiency of electrolytic brine and reduce the viscosity of fracturing flowback...
during the treatment process. The effect of the Fe/Ni proportion on the catalytic performance was studied. The oxidation efficiency of electrolytic brine and the viscosity reduction are distinct due to the addition of Fe/Ni catalyst, which can greatly cut down the treatment cost of fracturing flowback in enterprise practice. Furthermore, the SS content of the filtered fracturing flowback were evaluated. Complete fracturing flowback treatment process is displayed in Figure 1. The catalytic oxidation fracturing flowback was mixed with polyaluminum chloride (PAC) and polyacrylamide (PAM) for flocculation and sedimentation, and through filtration. In order to demonstrate the feasibility, the fracturing flowback was continuously treated in the dynamic simulation process (Figure 1) for 20 days. The treated effluent was changed from brown and sticky liquid to clear and bright water, and the sulfate reducing bacteria, saprophytic bacteria and iron bacteria in effluent had not picked out after adding electrolytic brine. Compared with other similar work, the catalytic efficiency of nickel based catalyst is similar, while the removal rate of ClO⁻ was greatly increased after the addition of iron oxide in our study (Kim et al. 2012).

**MATERIALS AND METHODS**

Regents and materials

Fracturing flowback sample A with a higher viscosity was taken from the Jinlong area of Xinjiang oilfield. The parameters were as follows: pH 6.8, viscosity 43.7 mPa·s, SS 3,447 mg/L, Fe²⁺ 4 mg/L, COD 5,657 mg/L, oil content and S²⁻ were not detected. Fracturing flowback sample B, with a slightly lower viscosity, was taken from the Mahu area of Xinjiang oilfield. The parameters were as follows: pH 7.2, viscosity 7.3 mPa·s, SS 1,359 mg/L, Fe²⁺ 10 mg/L, COD 3,904 mg/L, oil content and S²⁻ were not detected.

Fe(NO₃)₃·3H₂O and Ni(NO₃)₂·6H₂O were purchased from Shanghai Aladdin Biochemical Technology Co., LTD (China), analytical grade. Molecular sieves were supplied by Dalian Haixin Chemical Co., LTD (China), industrial grade (chemical composition: Na₂O·Al₂O₃·2.45SiO₂·6.0H₂O, particle diameter: 1.5–1.9 mm, pore radius: 10 Å). H₂O₂ (30%) solution and bleaching powder were obtained from Sinopharmacology Group Chemical Reagent Co., LTD (China). Ammonium persulfate was acquired from Kelon Chemical Co., LTD (China); PAC and PAM were provided by a process station of Xinjiang Oilfield 2# Oil Production Plant, industrial grade. The electrolytic brine (available chlorine content is 6%) was taken from the electrolytic unit in 2# Oil Production Plant. The properties of samples were analyzed based on SY/T 5329-2012, SY/T 5523-2016 and HJ/T 70-2001.

**Oxidant optimization experiment**

In order to determine the optimal oxidation breaker, the treatment capacity of the four frequently-used oxidants (include electrolytic brine, bleaching powder, ammonium persulfate and hydrogen peroxide) were investigated. The treatment capacity was evaluated by viscosity reduction value. Oxidants with different concentration were added into fracturing flowback sample A and sample B, the viscosity change were detected in proper time points.
Preparation of catalyst

Different proportion of Fe(NO₃)₃·3H₂O and Ni(NO₃)₂·6H₂O were dissolved in distilled water. And molecular sieve was added into solution and ultrasound for 1 h. Then a desired amount of NaOH were fed until pH ≈ 12, keep static overnight. As prepared product was washed and centrifuged for several times, then calcinated in muffle furnace at 200°C for 2 hours and 450°C for 4 hours.

Catalytic oxidation experiment

The catalytic oxidation device was a plastic tube (the length and diameter were 1 m and 5 cm, respectively) that filled with Fe/Ni catalyst (the length and diameter were about 1 cm and 0.3 cm, respectively). A desired amount of electrolytic brine was added to the device, and the effective residence time of fracturing flowback in the device was 8 h. Then the fracturing flowback was added with 150 mg/L PAC and 10 mg/L PAM in the settling device for flocculation, sedimentation, and passes through the filter, the effluent was detected at last.

Characterization

Field-emission scanning electron microscopy (FE-SEM) were observed on Zeiss Supra55 electron microscope. Energy Dispersive Spectrometer (EDS) was recorded on Energy Dispersive Spectrometer (Oxford IE350). Transmission electron microscope (TEM) was characterized by Talos F20 electron microscope. X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Advance (λ Kα = 1.5418Å, 2θ = 20–90°). The SS contents of the water were analyzed according to the procedure of standard methods (SY/T 5523-2016). The median particle size was detected by Mastersizer 2000 particle analyzer.

RESULTS AND DISCUSSION

Treatment effects of four oxidants on fracturing flowback

To study the treatment effects of oxidants on fracturing flowback, four oxidants with three different concentrations were tested, respectively. Tables 1 and 2 illustrate the viscosity reduction effect of the four oxidants on sample A are accord with sample B. The optimal oxidant was ammonium persulfate and electrolytic brine at the concentration of 1×10³ mg/L. And the preferred oxidant was electrolytic brine both at the concentration of 5×10³ mg/L and 1×10⁴ mg/L. Remarkably, the bleaching powder could enhance the viscosity of fracturing flowback at a lower concentration, which may account for the complexing reaction of Ca(ClO)₂ (main component of bleaching powder) and guar gum from fracturing flowback. Overall, electrolytic brine has the best breaking effect among the four oxidants. Furthermore, the brine can be produced in real-time by the electrolytic unit in oil production plant, which was cheap and convenient for industrial use. Therefore, the electrolytic brine was chosen as a gel breaker for fracturing flowback.

Characterization of Fe/Ni catalyst

Figure 2(a) and 2(b) show the appearance of the molecular sieve has changed from white to brown after loading with

| Viscosity reducing effect of oxidants on fracturing flowback (sample A) |
|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|
|                            | 0          | 3             | 15            | 40            | 80            | 120           |
| Electrolytic brine 1×10³(mg/L) | 43.7       | 39.2          | 38.3          | 38.3          | 30.5          | 27.6          |
| 5×10³(mg/L)               | 43.7       | 33.3          | 13.7          | 14.6          | 12.8          | 11.9          |
| 1×10⁴(mg/L)               | 43.7       | 13.2          | 8.3           | 8.2           | 3.8           | 2.7           |
| Ammonium persulfate 1×10³(mg/L) | 43.7       | 43.4          | 41.7          | 39.2          | 35.6          | 26.9          |
| 5×10³(mg/L)               | 43.7       | 26.9          | 26.9          | 21.4          | 21.4          | 21.0          |
| 1×10⁴(mg/L)               | 43.7       | 22.8          | 19.6          | 17.3          | 16.4          | 15.1          |
| Bleaching powder 1×10³(mg/L) | 43.7       | 47            | 48.7          | 49.3          | 49.9          | 52.5          |
| 5×10³(mg/L)               | 43.7       | 43            | 40.6          | 21.4          | 17.4          | 15.1          |
| 1×10⁴(mg/L)               | 43.7       | 30.6          | 14.1          | 9.5           | 8.9           | 7.7           |
| Hydrogen peroxide 1×10³(mg/L) | 43.7       | 37.0          | 39.2          | 40.6          | 38.9          | 36.5          |
| 5×10³(mg/L)               | 43.7       | 31.5          | 30.1          | 33.8          | 34.1          | 34.7          |
| 1×10⁴(mg/L)               | 43.7       | 43.1          | 41.1          | 38.2          | 30.5          | 24.2          |
| Distilled water –          | 43.7       | 43.2          | 43.6          | 43.1          | 42.8          | 42.5          |
### Table 2 | Viscosity reducing effect of oxidants on fracturing flowback (Sample B)

<table>
<thead>
<tr>
<th>Viscosity (mPa-s)</th>
<th>Time(min)</th>
<th>0</th>
<th>3</th>
<th>15</th>
<th>40</th>
<th>80</th>
<th>120</th>
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<td>7.32</td>
<td>6.52</td>
<td>5.89</td>
<td>4.38</td>
<td>3.87</td>
<td>2.43</td>
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<td>$5 \times 10^3$ (mg/L)</td>
<td>7.32</td>
<td>5.63</td>
<td>3.94</td>
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<td>2.04</td>
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<td>$1 \times 10^4$ (mg/L)</td>
<td>7.32</td>
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<td>2.64</td>
<td>1.02</td>
<td>1.02</td>
<td>1.02</td>
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<tr>
<td>Ammonium persulfate</td>
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<td>6.17</td>
<td>5.62</td>
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<td>$5 \times 10^3$ (mg/L)</td>
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<td>$1 \times 10^4$ (mg/L)</td>
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<td>3.63</td>
<td>2.64</td>
<td>1.02</td>
<td>1.02</td>
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<tr>
<td>Bleaching powder</td>
<td>$1 \times 10^3$ (mg/L)</td>
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<td>7.32</td>
<td>7.32</td>
<td>7.38</td>
<td>8.17</td>
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<td>7.32</td>
<td>7.32</td>
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<td>7.38</td>
<td>8.17</td>
<td>8.51</td>
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<td></td>
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<td>7.32</td>
<td>7.32</td>
<td>7.32</td>
<td>7.38</td>
<td>8.17</td>
<td>8.51</td>
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<tr>
<td>Hydrogen peroxide</td>
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<td>7.32</td>
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<td>5.1</td>
<td>4.96</td>
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<td>$1 \times 10^4$ (mg/L)</td>
<td>7.32</td>
<td>7.32</td>
<td>6.4</td>
<td>5.2</td>
<td>2.66</td>
<td>1.87</td>
</tr>
<tr>
<td>Distilled water</td>
<td>–</td>
<td>7.32</td>
<td>7.32</td>
<td>7.29</td>
<td>7.25</td>
<td>7.25</td>
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**Figure 2** | Pictures, SEM images and EDS analysis of Fe/Ni catalyst (a), (c) and (e) blank molecular sieve, (b), (d) and (f) molecular sieve loaded with Fe/Ni catalyst.
Fe/Ni catalyst. Meanwhile, SEM images (Figure 2(c) and 2(d)) exhibited the blank molecular sieve composed of homogeneous particles. After having been loaded with Fe/Ni, the surface of the molecular sieve formed a catalyst-loaded object that combined irregular aggregate with partial plate-like structures. Figure 2(e) shows that the main component of the molecular sieve was aluminosilicate. Figure 2(f) reveals that the Al and Si components from the molecular sieve were covered by the character elements of Ni and Fe from the catalyst. The TEM image (Figure 3(a)) showed that the two nanoparticles of Fe/Ni catalyst were agglomerated, and the particle size of the catalyst was calculated by Image J software (Zhang et al. 2020); the average particle size is 27.84 nm (Figure 3(b)). The XRD pattern of the catalyst is exhibited in Figure 4. A distinct diffraction peak at $2\theta = 54.1^\circ$ was observed, which is assigned to the Fe$_2$O$_3$ phase (Chang & Hsieh 2012). The other peaks (37.8°, 43.4° and 63.1°) were attributed to the NiO structure (Theofanidis et al. 2015). All the results suggested that Fe/Ni catalyst had successfully loaded on the molecular sieve and the coating effect was excellent.

**Catalytic oxidation effect of Fe/Ni catalyst**

Fe/Ni catalyst can improve the oxidation efficiency of electrolytic brine and reduce the viscosity of fracturing flowback. As shown in Figure 5, the residual chlorine (ClO$^-$) in water remained stable after 16 hours without catalyst. The concentration of residual chlorine in water decreased after nickel-based catalyst (without Fe) was added, in light of the formation of active free radical (NiO$_2^-$) generated from reaction of the catalyst and residual chlorine (King & Hancock 1996; Kim et al. 2012). More chlorine was consumed, indicating a higher concentration of the free radicals and higher activity of the catalyst. Furthermore, the addition of iron oxide could improve the activity of the single Ni catalyst, because the iron and nickel could generate an Fe-O-Ni transition zone (Zhang et al. 2006). The transition zone was beneficial to the formation of free radicals. These free radicals could improve the oxidation effect of sodium hypochlorite, and the pollutants was decomposed by the oxidation reaction of sodium hypochlorite. However, the increasing iron proportion couldn’t significantly improve the catalyst activity when the molar ratio of iron to nickel exceeded 10%, due to excess iron impeding the contact reaction between the nickel and residual chlorine despite being beneficial to the formation of free radicals. In addition, the residual chlorine content of all samples remained stable after 12 hours.
The viscosity of fracturing flowback was relatively high due to the guar gum. Therefore, the fracturing flowback was different from conventional oilfield wastewater, which couldn't be treated by flocculation and sedimentation directly. Hence, degrading the molecular chain of guar gum was essential for the subsequent treatment process. The free radicals promoted the decomposition of guar gum in the fracturing flowback, as the Fe/Ni catalyst reaction with residual chlorine could produce free radicals. Figure 6 shows the viscosity reduction effect of the residual chlorine ($1 \times 10^3$ mg/L) and Fe/Ni catalyst on fracturing flowback. After adding catalyst, the viscosity reduction rate was increased from 34.10% to 63.16% for sample A (from 66.16% to 85.91% for sample B), which means the catalyst could improve the oxidation reaction of electrolytic brine significantly. However, the blank test with the presence of a molecular sieve (without Ni and Fe) showed that the oxidative gel breaking effect of electrolytic brine on fracturing flowback fluid was decreased with the addition of the molecular sieve, which was due to the introduction of potassium hydroxide in the molecular sieve preparation process and resulted in an alkaline surface of the molecular sieve. Guar gum tends to be polymerized and cross-linked under alkaline conditions and this leads to the decrease of the gel breaking effect.

**Treated fracturing flowback after continuous treatment**

The dynamic simulation experiments (continuous operation in Figure 1 process) were carried out in order to demonstrate the feasibility of treating fracturing flowback with brine-catalyzed oxidation. Compared with static laboratory experiments, dynamic simulation experiments have higher authenticity for simulating on-site operation. Firstly, the fracturing flowback was pumped into the catalytic oxidation device and oxidation reaction for 8 h. Then the fracturing flowback was introduced into the flocculation, sedimentation device and filtration device in series. The brine-catalyzed oxidation experiment was continuously performed for 20 days. Then, the SS content of the effluents was analyzed.

As shown in Figure 7, the concentrations of SS in sample A and sample B were all less than 15 mg/L, while the filter device was not blocked during the process. The treated effluent was changed from a brown and sticky liquid to clear and bright water (Figure 8(a)). In addition, the sulfate reducing bacteria, saprophytic bacteria and iron bacteria in the effluent were not picked out after adding electrolytic brine. And the median particle size of the fracturing flowback (Sample A) was decreased from 19.2 μm (original) to 1.2 μm (final treated) (Figure 8(b) and 8(c)). All the...
indexes meet the reinjection requirements of standard SY/T 5329, which suggests that brine-catalyzed oxidation is applicable to fracturing flowback treatment.

CONCLUSION

The paper combined practice of enterprise, and explored the effects of different oxidants and catalysts on the treatment of fracturing flowback. Electrolytic brine was selected as an optimal oxidation from four oxidants and Fe/Ni was loaded on the molecular sieve as a catalyst. The oxidation efficiency of electrolytic brine and the viscosity reduction are distinct due to the addition of Fe/Ni catalyst. The SS content and median particle size (bacteria content) of the fracturing flowback also decreased obviously after being treated. In addition, the fracturing flowback was continuously treated in the dynamic simulation process to simulate the on-site operation. The electrolytic brine-catalyzed oxidation treatment of high viscosity fracturing flowback.

Figure 6 | Viscosity reduction effects of the fracturing flowback ((a) Sample A, (b) Sample B) after Fe/Ni catalyst was added into the electrolytic brine.
Figure 7 | Effect of operation time to SS removal (a) Sample A, (b) Sample B.

Figure 8 | Picture of fracturing flowback (a) 1# original, 2# after catalytic oxidation treatment, 3# after flocculation and sedimentation treatment, 4# after filtration treatment, size distribution of fracturing flowback (b) original and (c) final treated.
flowback can reduce the cost of treatment and is easy to control in practice, possessing broad application prospects.

CONFLICTS OF INTEREST

There are no conflicts to declare.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

REFERENCES


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