Study on Reinjection Technology of Sewage With $\text{SO}_4^{2-}$ in Oilfield

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Abstract
$\text{SO}_4^{2-}$ rich in reinjection sewage combined with $\text{Ca}^{2+}$, $\text{Mg}^{2+}$ in formation water to form precipitate which results clogging in the formation pore. Ion exchange method was chosen to remove $\text{SO}_4^{2-}$ in reinjection sewage and the anion exchange resin with $\text{OH}^{-}$ is selected as the exchange medium. It is necessary to evaluate alkali sensitivity of the formation rock due to the reinjection of sewage containing excess $\text{OH}^{-}$. The results indicate that ion exchange method can remove more than 90% of the $\text{SO}_4^{2-}$ and the rate of formation damage is negligible when the pH below the critical of 9.8.

Key words: $\text{SO}_4^{2-}$; Ion exchange method; Scaling; Alkali sensitivity

Reinjection technology can not only protect the environment, but also solve the problem of water injection to bring economic and social benefits[1]. But the sewage contains large amounts of sulfate ions which will be combined with magnesium and barium to form precipitation. It results in clogging in the formation pore. The best way to solve the scaling problem is the sub-mining dispensation, but pipeline design of most oilfields unable to meet this requirement[2]. In the oilfield existing conditions, the optimal scheme for removing sulfate ions is dealing sewage with the alkaline water to prevent fouling of low permeability reservoirs and enhanced oil recovery[3].

1. METHODOLOGY

Ion exchange is defined as excluding the inorganic ion dissolved in the water by ion exchange resin which is a kind of polymer material having an ion exchange function. According to the different nature of the exchange groups, the ion exchange resin can be divided into cation exchange resin and anion exchange resin. Anion exchange resin will give priority to be combined with $\text{SO}_4^{2-}$ and release $\text{OH}^{-}$. The sewage from Henan Oilfield in China is used for the experiment which removes $\text{SO}_4^{2-}$ by ion exchange resin.

2. RESULTS AND DISCUSSION

2.1 Ion Exchange Method to Remove $\text{SO}_4^{2-}$

The Adsorbing characteristics of anion exchange for anions are differences, the strength of adsorption as follows:

$$\text{SO}_4^{2-} > \text{NO}_3^{-} > \text{NO}_2^{-} > \text{Cl}^{-} > \text{HCO}_3^{-} > \text{OH}^{-} > \text{F}^{-}$$

Anion ion exchange resin will give priority to be combined with $\text{SO}_4^{2-}$ and release $\text{OH}^{-}$. The sewage from Henan Oilfield in China is used for the experiment which removes $\text{SO}_4^{2-}$ by ion exchange resin.
Sewage containing $\text{SO}_4^{2-}$ are implanted into the replacement tower filled with anion exchange resin. The content of the sulfate varies with time are shown in Table 1.

<table>
<thead>
<tr>
<th>Sewage samples</th>
<th>Time (min)</th>
<th>Concentration of $\text{SO}_4^{2-}$ (mg/L)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated sewage</td>
<td>0</td>
<td>2,243.39</td>
<td>6-7</td>
</tr>
<tr>
<td>Sample 1 in resin tower</td>
<td>15</td>
<td>1,503.65</td>
<td>7-8</td>
</tr>
<tr>
<td>Sample 2 in resin tower</td>
<td>30</td>
<td>1,195.38</td>
<td>8-9</td>
</tr>
<tr>
<td>Sample 3 in resin tower</td>
<td>45</td>
<td>902.29</td>
<td>8-9</td>
</tr>
<tr>
<td>Sample 4 in resin tower</td>
<td>60</td>
<td>743.97</td>
<td>8-9</td>
</tr>
<tr>
<td>Sample 5 in resin tower</td>
<td>75</td>
<td>605.67</td>
<td>8-9</td>
</tr>
<tr>
<td>Sample 6 in resin tower</td>
<td>90</td>
<td>506.57</td>
<td>8-9</td>
</tr>
<tr>
<td>Sample 7 in resin tower</td>
<td>105</td>
<td>398.21</td>
<td>8-9</td>
</tr>
<tr>
<td>Sample 8 in resin tower</td>
<td>120</td>
<td>280.33</td>
<td>8-9</td>
</tr>
<tr>
<td>Sample 9 in resin tower</td>
<td>150</td>
<td>195.73</td>
<td>8-9</td>
</tr>
</tbody>
</table>

As can be seen from Table 2, the concentration of $\text{SO}_4^{2-}$ in the wastewater was decreasing with the increase of the sampling time. Compared to the initial solution, the concentration decreased from 2,243.39 mg/L to 195.73 mg/L, the decrease range was 91.2%. Anion ion exchange resin will give priority to be combined with $\text{SO}_4^{2-}$ and release $\text{OH}^-$. The pH value of the solution is weakly alkaline by acid conversion. The experimental results show that the anion exchange resin can remove the $\text{SO}_4^{2-}$ effectively. But it is necessary to carry out the experiment of alkali damage to prove its feasibility.

2.2 Reservoir Alkali Sensitivity

2.2.1 Mechanism of Alkali Damage

In the reservoir, alkaline fluid is reacted with quartz to form a variety of silicate minerals which can be adsorbed on the solid to form a new precipitate and cause formation plugging.  

$$\text{SiO}_2 + \text{NaOH} \rightarrow \text{Na(H}_2\text{SiO}_3)$$

In clay component, the main mineral is affected by the alkaline fluid are kaolinite and montmorillonite. Kaolinite is in the strong base effect to generate sodium silicate which will affect the permeability of the formation.  

$$\text{Al}_4(\text{Si}_4\text{O}_{10})(\text{OH})_8 + \text{NaOH} + \text{H}_2\text{O} \rightarrow \text{Na(H}_2\text{SiO}_3) + \text{NaAl(OH)}_4$$

2.2.2 Experiment of Alkali Damage

The permeability of rock sample which is remembered as $K_1$, by injected KCl solution below the critical velocity of speed. According to the volume of 10-15 times of the core pore, injecting the test fluid with a certain pH value and then still more than 12 h to measure the rock sample permeability $K_2$ of the alkaline solution. Alkali sensitivity index ($S_b$) calculated by the following formula:

$$S_b = \frac{K_2 - K_1}{K_1}$$

When $S_b \geq 0.3$, the alkali sensitivity degree is defined as a medium above.

After removing the $\text{SO}_4^{2-}$ by anion exchange resin method, the pH of the sewage is 8-9 belongs to the weak alkaline. This needs to select reservoir a few natural core of reservoir for alkali sensitivity evaluation.

In condition of 75 °C, the impact of different alkalinity fluid on the permeability of the core was evaluated. Experimental results show that: When the pH value is higher than 10.0, with the increases of the pH the permeability decreased greatly. The critical pH value of alkali sensitivity is a 10.0-10.5.

![Figure 1](image-url)

**Figure 1**

$K$ and $S_b$ varies with pH

After removing the $\text{SO}_4^{2-}$ by anion exchange resin method, the pH of the sewage is 8-9 belongs to the weak alkaline. The value of pH is lower than the critical value, so it meets the demand of injection.

CONCLUSION

(a) $\text{SO}_4^{2-}$ can be effectively removed by using anion exchange resin.

(b) When the pH up to 10, the formation permeability decreased rapidly and the damage of the formation increased significantly, the critical pH is 9-10.

(c) Ion exchange method is feasible.

REFERENCES


