A New Application of Ethylenediamine to Improve CO2 Sweep Efficiency in Extremely-Low Permeability Reservoir

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HOU Ji-rui

Abstract: Gas breakthrough is a common problem in CO2 displacement. This paper provides a new method with ethylenediamine to improve the efficiency of CO2 injection, sealing off the breakthrough channel. Experiments in porous medium model show that the ethylenediamine system can be easily injected into extremely low permeability reservoir, it can react with CO2 and the generated carbonate will reduce the permeability of the flooding region, causing the breakthrough pressure reaches 22MPa, hence, the swept efficiency is improved. Oil displacement experiment with heterogeneous core shows that the recovery factor is improved by 19.8%. Additionally, the ethylenediamine system shows high temperature resistance and CO2 erosion resistance. It also has an advantage of selective plugging, it will not injure the reservoir where CO2 does not pass by as long as we chose the suitable injection speed, prepositive and postpositive slug. So we could control CO2 breakthrough by profile control.

Key words: ethylenediamine; plugging; CO2; heterogeneity; profile control

Low permeability reservoir takes up the majority of newly discovered reserve in China, but recovering oil in low permeability reservoir is difficult, natural productivity is low, and water injection is limited because of the geological conditions, the recovery factor is low. However, gas injection has special advantages in development of low permeability reservoirs because of high mobility, reducing oil viscosity, expanding oil volume and decreasing interfacial tension (CHEN, 2000; LI, ZHANG, & RAN, 2001; Tiffin, & Kremesec, 1988; YANG, YUE, & SHEN, 1991). CO2 miscible flooding is one of the most promising methods to enhance oil recovery (EOR). However, high microscopic sweep efficiency is not often achieved in reservoir operations, due principally to the non-uniformity of the flow patterns and unfavorable mobility ratio between injected CO2 and oil (Li et al 2006; GUO et al, 2003). A more supported by national project of 973 program: Geological storage of greenhouse gas and commercial unitization to enhance oil recovery (2006CB705800)
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*Received 11 February 2009; accepted 10 April 2009
common alternative to improve the problem of poor sweep efficiency of CO₂ in oil reservoirs is by blocking the high permeability streaks, and or fractures.

Ethylendiamine (H₂NCH₂CH₂NH₂) is a simple diammonium, belonging to small molecular organic amines. It is colorless, transparent, a viscous liquid with ammonia odor, melting point 8.5 °C, boiling point 116.5 °C and relative density 0.8995(20°C). It is a strong alkali, can react with acid forming amine salt. The salt forms hydrate when soluble in water.

In order to improve the sweep efficiency of CO₂ flooding, according to extremely-low permeability conditions, this paper presents a chemical reaction between injected carbon dioxide and injected ethylenediamine which improves reservoirs heterogeneity.

1. EXPERIMENT MATERIALS

Experimental materials are as follow, oil-free outcrop sands (60-100 meshes), CO₂ gas with 99.9% purity, two-dimension lengthways-heterogeneous physical core model (4.5 cm×4.5 cm×70 cm), oil mixed by white oil and jet fuel by 9:1. Ethylenediamine is provided by Beijing Chemical Works with 99.9% purity. All experiments are processed in 102°C.

Experiment equipments includes German HAKKE RS600 rheometre, constant speed and pressure pump(HXH-100B), sand pack model with pressure detecting points, corrosion resistant and high pressure resistant vessel, automatic pressure tester, gas flow meter, automatic constant temperature control equipment.

2. EXPERIMENT METHODS

Sand pack model (φ2.5 cm×100 cm) and two-dimension lengthways-heterogeneous physical model (4.5 cm×4.5 cm×70 cm) were prepared for displacement experiment, injecting performance and plugging performance of ethylenediamine were studied, as well as the selective plugging performance and recovery improving performance.

2.1 Experiment on plugging strength in single sand pack

Sand pack was prepared with water-test permeability of 2.45×10⁻³ μm² and porosity of 40.33%. The experiment was taken in the simulating conditions of Honggangbei Block in Jilin oil field (permeability less than 10×10⁻³ μm², 102°C). First, the sand pack was put in the automatic constant temperature control equipment, and evacuated for 12hs until pressure was -0.1MPa; After that, the sand pack was saturated with water and then was displaced with CO₂ with velocity of 5ml/min until no water came out in the exit end. Then, 0.1PV of prepositive N₂ protection slug, 0.2PV of ethylene diamine slug (0.1mL/min), and 0.1 PV of postpositive N₂ protection slug were injected one by one, and after that, CO₂ was injected continuously. Pressure along the pack and gas flow rate are recorded accordingly.

2.2 Plugging stability

The sand pack used in the plugging experiment was put in constant temperature and constant pressure (102°C, 4MPa), gas flow rate at different times were recorded, and the corresponding permeability was obtained.
2.3 Experiments on selective plugging performance

2.3.1 Parallel sand packs
Two sand packs (18.3×10^{-3} \text{µm}^2, 1.2×10^{-3} \text{µm}^2) were paralleled in a constant temperature environment (102°C), pumped to vacuum, saturated with water, and experimented in the way of full injecting and separate recovery as the same steps as single sand pack experiment.

2.3.2 Two-dimension lengthways-heterogeneous physical model
This experiment was taken in a two-dimension lengthways-heterogeneous physical model with a relatively high permeability (26×10^{-3} \text{µm}^2) layer and a relatively low permeability (5×10^{-3} \text{µm}^2) layer. The core was put into a core holder with circling pressure, pumped to vacuum for 48 hours until -0.1MPa, saturated with water, and then displaced with CO_2 at a uniform speed of 5ml/min by the constant speed and pressure pump (HXH-100B) until no liquid came out from the output end. Then, 0.1PV of preposed N_2 slug, 0.2PV of ethylenediamine slug and 0.1PV of post N_2 slug were injected in turn, after that, CO_2 were injected continuously (5ml/min).

2.4 Oil displacement experiment in heterogeneous core
The core was put into a core holder with circling pressure, pumped to vacuum for 48 hours until -0.1MPa, saturated with oil, and then displaced with CO_2 at a uniform speed of 5ml/min by the constant speed and pressure pump (HXH-100B) until no liquid came out from the output end. Then, 0.1PV of preposed N_2 slug, 0.2PV of ethylenediamine slug and 0.1PV of post N_2 slug were injected in turn, after that, CO_2 were injected continuously (5ml/min).

3. DISCUSSIONS ON THE RESULTS

3.1 plugging strength
Pressure data and gas-test permeability (fig1, table1) in single sand pack experiment show that this plugging system has a breakthrough pressure of 22MPa, a big pressure drop can be observed within the 60cm distance from the injection point, while the largest pressure drop accrued in 20~40 cm distance, reached 13.5MPa. The permeability is reduced significantly within the 60cm distance from the injection point, which is in good conformity with the pressure result. Hence, it is suggested that this system has a good plugging strength and can meet the requirement of CO_2 breakthrough control.
Figure 1. Pressures of CO$_2$ flooding in different distances after injecting ethylenediamine

Table 1. Gas-test permeability in different distances before and after plugging

<table>
<thead>
<tr>
<th>distance/cm</th>
<th>10</th>
<th>30</th>
<th>50</th>
<th>70</th>
<th>90</th>
</tr>
</thead>
<tbody>
<tr>
<td>Permeability/10$^3$µm$^2$</td>
<td>Before plugging</td>
<td>38.8977</td>
<td>6.6000</td>
<td>0.3205</td>
<td>9.7800</td>
</tr>
<tr>
<td></td>
<td>After plugging</td>
<td>3.7680</td>
<td>0.1228</td>
<td>0.1178</td>
<td>12.5215</td>
</tr>
</tbody>
</table>

Injection pressure of ethylenediamine at the input end (Fig2) show that this system has a perfect mobility, the injection flow rate is 0.1 mL/min.
3.2 Stability of plugging

The sand pack of plugging strength experiment was provided with constant temperature and constant pressure (102°C, 4MPa), gas flow rate at different time was recorded, and the corresponding permeability was obtained (fig 2). The results show that this system has good resistance of high temperature and CO₂ corrosion. For 25 days, the average gas-test permeability was of little variation, with time passing by it became quite stable, this was because the ethylenediamine and CO₂ reacted gradually and generated carbonate without mobility.

Figure 2. Injection pressure of ethylenediamine at the input end
3.3 Selective plugging performance

3.3.1 Result of Parallel sand packs
Permeability values before plugging (table 2) are tested during the stable period of gas displacement with saturated water, and values after plugging are tested during the stable CO$_2$ injection after post slug (0.1PV) was injected. The values show that the permeability of high permeability pack was reduced distinctly, from $18.3723 \times 10^{-3}$ $\mu m^2$ to $0.1652 \times 10^{-3}$ $\mu m^2$; while the low permeability pack was not reduced, and even increased for water saturation decreased.

Different changes between two packs’ permeability provide a convenience for ethylenediamine flooding in the high permeability pack, in certain flow rate, ethylenediamine would flow along the CO$_2$ channel, selectively plugging the high permeability channel, while the area with low permeability would not be hurt.

3.3.2 Water displacement with two-dimension heterogeneous model
For the CO$_2$ displacement of water, pressure at different distances before plugging show that pressure along the high permeability layer was high, while it was low along the low permeability and nearly zero after 15cm, which suggests that most of CO$_2$ flooded into high permeability layer, while the low permeability layer was not swept. After plugging, the pressure of injecting CO$_2$ was significantly increased, a big pressure drop was observed in the distance from 30cm to 60cm where plugging happened, while pressure along the low permeability pack after plugging had little change. Vertically splitting the core after experiment, flow crack of ethylenediamine was quit clear in the high permeability
layer, but not in low permeability layer.

Table 2. Gas-test permeability of high and low permeability sand packs before and after plugging

<table>
<thead>
<tr>
<th></th>
<th>Before plugging</th>
<th></th>
<th>After plugging</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pressure in input end (MPa)</td>
<td>Gas flow rate (mL min⁻¹)</td>
<td>Permeability (10⁻³ μm²)</td>
<td>Pressure in output end (MPa)</td>
</tr>
<tr>
<td>High Permeability pack</td>
<td>0.2640</td>
<td>18</td>
<td>17.6420</td>
<td>4.8</td>
</tr>
<tr>
<td></td>
<td>0.2600</td>
<td>18</td>
<td>18.0682</td>
<td>5.28</td>
</tr>
<tr>
<td></td>
<td>0.4480</td>
<td>44</td>
<td>18.2277</td>
<td>6.36</td>
</tr>
<tr>
<td></td>
<td>0.3120</td>
<td>26</td>
<td>19.5511</td>
<td>average</td>
</tr>
<tr>
<td></td>
<td>average</td>
<td></td>
<td>18.3723</td>
<td></td>
</tr>
<tr>
<td>Low Permeability pack</td>
<td>20.6</td>
<td>16</td>
<td>0.0045</td>
<td>19.4</td>
</tr>
<tr>
<td></td>
<td>21.3</td>
<td>16</td>
<td>0.0042</td>
<td>27.0</td>
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<tr>
<td></td>
<td>28.0</td>
<td>17</td>
<td>0.0026</td>
<td>average</td>
</tr>
<tr>
<td></td>
<td>average</td>
<td></td>
<td>0.0038</td>
<td></td>
</tr>
</tbody>
</table>

Table 3. Gas injection pressure of high and low permeability packs before and after plugging

<table>
<thead>
<tr>
<th>distances/cm</th>
<th>Gas injection pressure in High Permeability pack (KPa)</th>
<th>Gas injection pressure in low Permeability pack (KPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Before plugging</td>
<td>after plugging</td>
</tr>
<tr>
<td>0</td>
<td>164.0</td>
<td>2464.3</td>
</tr>
<tr>
<td>15</td>
<td>140.0</td>
<td>1940.2</td>
</tr>
<tr>
<td>30</td>
<td>164.0</td>
<td>2320.2</td>
</tr>
<tr>
<td>45</td>
<td>102.0</td>
<td>22.5</td>
</tr>
<tr>
<td>60</td>
<td>84.0</td>
<td>646.1</td>
</tr>
<tr>
<td>70</td>
<td>109.0</td>
<td>196.0</td>
</tr>
</tbody>
</table>

3.4 Oil displacement experiment in heterogeneous core
According to the results of oil displacement experiment in heterogeneous core, the recovery factor was increased by 19.8% after plugging, with 17.1% in high permeability layer and 2.7% in low permeability layer (figure 3).

Two effects increased the recovery factor of high permeability layer, one was that the reaction caused
reduction in the permeability of the flooded region in the high permeability layer, improving the conformance of the injected CO₂, the other was that higher pressure after plugging made CO₂ an ideal displacement fluid for multiple contact miscibility, high microscopic sweep efficiency was approached.

The increased recovery in the low permeability layer was mainly because the heterogeneity between two layers was reduced after plugging, thus the sweep volume was enlarged.

4. CONCLUSIONS

The following conclusions have been made based on the experiments conducted throughout this study:

1st. The ethylenediamine system has a good mobility, can be injected easily; this system have a good plugging strength and can reduce the permeability of a sandstone porous medium during CO₂ flooding.

2nd. This system has good resistance of high temperature and CO₂ corrosion.

3rd. Ethylenediamine can be injected in an absolutely environment-friendly manner, improve reservoir heterogeneities, such as fractures or high-permeability streaks that could intensify viscous fingering of CO₂ and cause early breakthrough of injected CO₂, which will reduce oil recovery efficiency.

REFERENCES


