A Sulfur Plugging Experiment in the Presence of Ferric Ion


1School of Energy Resources, China University of Geosciences, Beijing, China
2CMOE Key Laboratory of Petroleum Engineering in China University of Petroleum, Beijing, China
3Southwest Oil & Gas Field Company, PetroChina, Chengdu, Sichuan, China

Abstract Acid fracturing is widely used as an effective reconstruction measure in sour gas reservoirs, but sulfur and ferrous sulfide plugging are still problems in reservoir secondary damage. In order to simulate reservoir damage in the presence of ferric ion in residual acid, an artificial core with ferric ion and supersaturated natural sour gas was adopted as a sample. A depletion-type damage experiment was carried out to observe sulfur precipitation and plugging in the core. The results show that core color became dark and weight was increased. Permeability decreased with increased time and the decreasing trend was steep at the beginning and then down to smooth rate slowly. Trace pyrite was discovered using X-diffraction. Severe damage was formed by sulfur deposition in the presence of ferric ion.

Keywords damage, deposition, elemental sulfur, ferric ion, percolation

1. Introduction

There are some differences between a sour gas reservoir and conventional gas development, the most important of which are reservoir features and H$_2$S physicochemical properties. More attention is currently focused on the gas phase in reservoirs (Zhu et al., 2006; Du, 2008), including consideration of elemental sulfur solubility (Bruce, 1997; Sun and Chen, 2003; Zhang et al., 2005), deposition damage models (Yang et al., 2004; Zeng et al., 2005; Du et al., 2006), and multicomponent numerical with sulfur deposition (Guo et al., 2006; Zhang et al., 2006; Zhao, 2007).

Hydraulic fracturing and acid treatment are the most important measures in low-permeability reservoir reconstruction. In sour gas reservoirs, these technologies face grave challenges, but less attention has been given to this issue, especially to acidizing fluid formula.

In order to effectively solve sulfur and iron problems during reservoir reformation, sour gas reservoir features and H$_2$S physicochemical properties should be investigated and reaction characteristics of Fe($\alpha$)-H$_2$S, Fe($\beta$)-H$_2$S, and acid–rock reaction mechanisms should be resolved under high-pressure and high-temperature conditions. Acidizing fluid systems and technology need to be researched (Chen, 2004). Iron control deposition and
scavengers are mainly researched in sour gas wells (Taylor et al., 2001; Nasr-El-Din et al., 2007). However, the damage to a reservoir due to ferric ion in residue acid has not been researched under high-temperature and high-pressure conditions. An artificial core with ferric ion and supersaturated natural sour gas was adopted to conduct this experiment. A depletion damage experiment was carried out to observe sulfur precipitation and plugging in an artificial core with ferric ion.

2. Damage from Ferric Ion in Acid Fluid

Industrial hydrochloric acid is used as an acid fracturing treatment fluid, which is the main source of Fe$^{3+}$ in acid fracturing treatment. It is inevitable that ferric ion (Fe$^{3+}$, Fe$^{2+}$) will exist in acid fracturing treatment. The deposition condition of Fe$^{3+}$ and Fe$^{2+}$ may change in the presence of H$_2$S and ferrous sulfide deposition is easily generated. Compared with a conventional gas reservoir, it is more complicated and difficult to control iron deposition. If extraneous fluid contains Fe$^{3+}$, a redox reaction may occur immediately with H$_2$S. Fe$^{3+}$ is restored into Fe$^{2+}$ and S$^{2-}$ is oxidized into S$^0$.

$$2Fe^{3+} + H_2S \rightarrow S \downarrow +2H^+ + 2Fe^{2+}$$

The reaction may be taken place under extreme low pH and hardly controlled by acidity. Elemental sulfur does not dissolve in acid, water, or oil. This deposition may cause permanent damage to the reservoir. In order to illustrate reservoir damage from sulfur deposition and the effect of ferric ion, a depletion-type damage experiment is described in this article.

3. Equipment and Methods

3.1. Equipment and Materials

1. Equipment included a core barrel catcher, back-pressure valve, booster pump, agitator, digital flow rate indicator, sample preparation tank, transfer equipment, and back-pressure pump.
2. Experimental materials included an artificial core (outcrop) and saturated sulfur gas.

3.2. Core Basic Data

The artificial core is dried. These basic data can be seen from Table 1.

3.3. Experimental Fluid Medium Preparations

Experimental fluid medium parameters are shown in Table 2.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample length, cm</td>
<td>7.12</td>
<td>Sample length, cm</td>
<td>2.533</td>
</tr>
<tr>
<td>Cross sectional area, cm$^2$</td>
<td>5.04</td>
<td>Experimental fluid</td>
<td>Saturated sulfur gas</td>
</tr>
</tbody>
</table>
Table 2
Sour gas ultimate compositions

<table>
<thead>
<tr>
<th>Components</th>
<th>Mol fraction, mol%</th>
<th>Components</th>
<th>Mol fraction, mol%</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂S</td>
<td>6.86</td>
<td>C₁</td>
<td>89.63</td>
</tr>
<tr>
<td>N₂</td>
<td>0.5</td>
<td>C₂</td>
<td>0.21</td>
</tr>
<tr>
<td>He</td>
<td>0.02</td>
<td>C₃</td>
<td>0.02</td>
</tr>
<tr>
<td>CO₂</td>
<td>2.76</td>
<td>C₄- C₇⁺</td>
<td>0</td>
</tr>
</tbody>
</table>

3.4. Experimental Methods and Procedures

1. Combined with sulfur and sulfur gas under high pressure and temperature in a sample preparation tank, oversaturated sulfur gas is formed.
2. Because the fluid medium is sulfur gas, in order to guarantee safety, the whole circuit must be tested for gas leakage under high pressure and temperature before the experiments are performed.
3. Saturated sulfur gas with an initial pressure is 40 MPa and temperature 70°C was used and core temperature was maintained at 70°C. In order to decrease the effects of effective stress, the value is 5 MPa. A back-pressure valve is used for safety and gauging stability, and the pressure of the core inlet and outlet are controlled in 1 MPa increments.
4. When the gas flow meter value is stable, data are recorded every half hour, and the pressures at the core inlet and outlet are also recorded; core permeability is calculated by Darcy’s law.
5. In order to prevent air pollution, tail gas is treated using a chemical method.
6. The experiment cycle hold is 5 days. The experiment is completed when core average pressure is 8 MPa.

3.5. Experimental Conditions and Setup

The equipment should be in a big draught cupboard. The actual flow table and structural drawing can be seen in Figure 1.

4. Experiment Conclusion Analyses

4.1. Artificial Core Properties Analyses

Core permeability and weight are measured under normal temperature and pressure. The conclusions can be seen in Table 3, and core color comparison is shown in Figure 2. The core is cut along end face, and the color inside the core is the same as core surface, the effects of rubber ring is removed. The results of X-diffraction are given in Table 4.

From Table 3 and Figure 3 it can be seen that permeability decreased sharply and weight increased, and from Table 4, pyrite is discovered after experiment.

In order to ensure safety, outlet gas was treated with chemicals, and the color of solid chemicals change from yellow to dark.
Figure 1. Experimental equipment table. 1, Duplex booster pump; 2, sample preparation tank; 3, filter; 4, 5, import and export pressure gauges; 6, confinement pressure pump; 7, back-pressure valve; 8, back-pressure pump; 9, gas flow meter; 10, tail gas treating units; 11, fume hood; 12, core barrel catcher.

Table 3
Core properties comparison

<table>
<thead>
<tr>
<th></th>
<th>Permeability, mD</th>
<th>Quality, g</th>
</tr>
</thead>
<tbody>
<tr>
<td>After experiment</td>
<td>0.0458</td>
<td>83.5475</td>
</tr>
<tr>
<td>Before experiment</td>
<td>0.317</td>
<td>79.6007</td>
</tr>
</tbody>
</table>

Figure 2. Core color comparison.

Table 4
X-diffraction results

<table>
<thead>
<tr>
<th>Clay concentration</th>
<th>Quartz</th>
<th>Calcite</th>
<th>Pyrite</th>
</tr>
</thead>
<tbody>
<tr>
<td>After experiment</td>
<td>6.8</td>
<td>—</td>
<td>3.4</td>
</tr>
<tr>
<td>Before experiment</td>
<td>4.8</td>
<td>95.2</td>
<td>—</td>
</tr>
</tbody>
</table>
4.2. Artificial Core Elemental Sulfur Deposition Analyses and Discussion

Permeability is an important parameter to evaluate reservoir damage. Gas flow velocity is guaranteed stable using a back-pressure valve. Darcy’s law is used to calculate core permeability when gas flow is steady.

Figure 3 is the relationship between core average pressure and permeability. Core permeability decreases when core average pressure decreases. Figure 3 shows the curve gradient, which is steep at first and slowly smooths down. The damage mechanism is composed of two parts. One is chemistry damage; the other is sulfur deposition damage with pressuring decreasing. The former decreasing mainly depends on chemical reaction and the latter is sulfur deposition. When the chemical reaction is not considered, core permeability may not decrease much (Abou-Kassem, 2000). Combined with increasing weight, X-ray, core color, and decreasing permeability, the chemical reaction is demonstrated and it is suggested that the chemical reaction may increase reservoir damage.

If a chemical reaction does not occur, a gas slippage effect should be seen in experiments. That is, core permeability increases as core average pressure decreases (X. F. Yang, 2008). But now the permeability is decreasing, because the artificial core has ferric ion, and a chemical reaction takes place when an acid condition is formed and the effect of the chemical reaction covers the gas slippage.

During the experiment, pressure gradually decreases over time. The main purpose is to simulate reservoir conditions as much as possible and core temperature is kept at 70°C. Gas flow velocity is controlled by a back-pressure valve, because gas flow is always unstable and the core outlet rubber tube may easily crack. The relatively stable velocity is 300–350 mL/min.

5. Conclusions

1. A depletion-type sulfur damage experiment was established and achieved with an artificial core containing ferric ion. Core permeability declined sharply due not only
to the sulfur deposition with the increase in pressure but to chemistry damage from ferric ion and H$_2$S.

2. During acid fracturing treatment and also in the flowback process, acid fluid containing ferric ion may lead to severe damage in sour gas reservoirs. It is significant to control and decrease ferric ion in acidizing fluid to improve reconstruction effects and decrease reservoir secondary damage.

References


