Sulfur deposition experiment in the presence of non-movable water

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A R T I C L E   I N F O

Article history:
Received 30 September 2009
Accepted 18 November 2012
Available online 5 December 2012

Keywords:
sour gas reservoir
sulfur deposition
non-movable water
experiment
damage

A B S T R A C T

With the decreasing of pressure and temperature near wellbore, elemental sulfur may precipitate and block sour gas reservoir pores. In order to analyze the effect of non-movable water on core permeability, depletion types of experiments were carried out to observe sulfur precipitation and plugging in carbonate rocks. During the experiment, reservoir carbonate cores and supersaturated sour gas were adopted. Under a certain differential pressure, normal saline was used to establish non-movable water. The experimental pressure and temperature were set and maintained to simulate actual reservoir. The experimental results show that non-movable water can contribute to improve core permeability. The more non-movable water is, the more improvement would be. The reason is investigated that the acid environment which has been built when H2S dissolves in the water, reacted with reservoir carbonatite cores. As a result, core flow capacity is improved. Compared with the sulfur damage on dry reservoir core, the improvement arisen from this reaction lays more effect in this experiment, thus the core permeability is ultimately increased.

1. Introduction

With the rapid development of sour gas reservoir, fundamental research on sulfur deposition such as gas reservoir phase (Zhang et al., 2005; Du, 2008), elemental sulfur solubility (Bruce, 1997; Chrastil, 1982; Sun and Chen, 2003), deposition damage models (Yang et al., 2004; Zeng et al., 2005; Mei and Zhang, 2006), and multi-component numerical models (Du and Guo, 2006; Guo and Du, 2006; Zhang and Du, 2006) have caught more and more attention in public. However, all these theoretical models are based on the assumption that precipitated sulfur may in-situ deposit in spite of that the precipitated sulfur may be carried over by gas and sulfur deposition is actually a process of dynamic equilibrium sediment.

Sulfur deposition damage researches are mainly concentrated on oil reservoir. Abou-Kassem executed a transport experiment on deasphalted oil in long carbonate core and established sulfur deposition model based on surface adsorption theory (Al-Awadhy and Abou-Kassem, 1998). Shedid and Zekri (2002) have also used the crude oil from which asphalt and paraffin have been removed to do some researches on the effects of flow velocity, initial sulfur concentration and core permeability on elemental sulfur deposition. The reservoir damage of sulfur and asphalt was researched by Shedid (2006). Sulfur deposition during carbon dioxide miscible flooding in carbonate reservoir was researched by Shedid (2009).

With the increase of concentration of hydrogen sulfide, the solubility of elemental sulfur in sour gas increases rapidly. And this increase is connected greatly with the pressure effects. The solubility of elemental sulfur is decreasing rapidly while the pressure is decreasing. In other words, a part of the dissolved elemental sulfur will precipitate during the process (Bruce, 1997; Sun and Chen, 2003). Due to the danger factors may be arisen during sulfur deposition experiment, there were fewer papers published. Sublimed sulfur is carried into the core by nitrogen gas, the permeability damage of the core is calculated by Abou Kassem (2000) and sulfur deposition phenomenon is simulated, however, due to the high temperature of sulfur sublimation, the experimental program and data should be carefully investigated. Guo and Du (2006) have executed some experimental researches on sulfur deposition in carbonate reservoir. The influences of initial gas velocity, H2S concentration and core permeability on sulfur deposition were analyzed. To make sure that experimental environment are close to actual reservoir. Yang (2008) has executed some researches on dry core depletion type of experiments. The experimental results show that elemental sulfur may deposit and block pores. Under the condition that temperature is a constant, the permeability declines while the pressure decreases. The higher the initial pressure is, the worse the permeability is damaged when initial pressure is constant. However, the effect of non-movable water was not considered...
in Yang (2008) researches. In order to simulate sulfur deposition under high temperature and pressure accurately with taking consideration of the effect of non-movable water, a depletion type damage experiment was carried out to observe sulfur precipitation and plugging in core.

2. Experiment device and method

2.1. Experiment device and material

(1) Core flow experimental devices: 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: reservoir carbonate core, normal saline and saturated sour gas.

2.2. Basic data of experimental core

The permeability of dried carbonatite core samples (from Sichuan gas reservoir) is measured and shown in Tables 1 and 2. In order to compare with sulfur deposition experimental results of dry reservoir core by Yang (2008), the physical characters of the chosen experimental cores should be as close to those of the reservoir dry cores as possible. To compare the effect of different non-movable water on sulfur deposition, the depletion types of experiments are carried out on two chosen cores.

2.3. Experimental fluid medium preparation

The data for Table 3 is a reservoir gas sample from Sichuan gas field, with enough sulfur powder mixed in, supersaturated sour gas is formed. Cores are taken from the same reservoir. In order to reach the biggest similarity between the experiment condition and actual reservoir, cores are extracted from the well when gas reservoir pressure is above the saturation pressure so that there is no sulfur deposition in core. Furthermore, core is also dried for 8 h in oven under the temperature of 100 °C to secure the adequate dryness.

After dried cores are immersed in normal saline for 24 h, a certain non-movable water saturation, which is 10.8% in reservoir core \( \Phi_1 \) and 6.29% in core \( \Phi_2 \), is established by a normal displacement method under a displacement pressure of 1.0 MPa.

2.4. Experimental methods

(1) Mixed with sulfur and sour gas under a high pressure and temperature in a sample preparation tank to form the over-saturated sour gas. When the experiment begins, elemental sulfur may precipitate as pressure decreasing. So a filter screen is used in the outflow point to separate sulfur particles.

(2) In favor of the safety for executing this experiment through the fluid medium of sour gas, sealing function tests must be conducted in the whole experimental program to ensure no gas leakage under a high pressure and temperature before experiment. The test pressure is set at 45 MPa. If the pressure can stay stable for half an hour, the sealing property is safe.

(3) The non-movable water is established under normal temperature and pressure. During this process, the differential pressure of core inlet and outlet is controlled within 1 MPa.

(4) Set the initial pressure of saturated sour gas at 40 MPa and control core temperature at 70 °C to conduct the depletion type experiment. The effective stress is maintained at 5 MPa to lower the impact as much as possible. In consideration of collecting stable data and safety during experiment, the back pressure valve is adopted and the differential pressure of core inlet and outlet is controlled within 1 MPa.

(5) In order to collect enough experimental data, parameters are recorded every half an hour, and then time for reaching every cumulative flow of 100 ml is recorded. The pressure of core inlet and outlet is also recorded. Core permeability is calculated in accordance with Darcy-law.

(6) To prevent air pollution, the tail gas is chemically treated.

(7) The duration for an experiment will last 4–5 days and the experiment is completed when the core average pressure for inlet and outlet is 8 MPa.

2.5. Experiments conditions and set-up diagram

In order to compare with dry core depletion type of experiments, the experimental theories and conditions adopted in this paper are kept the most possibly biggest similarity to the experiments mentioned. The initial pressure is set at 40 MPa and the temperature is set at 70 °C. For the actual flow chart and set-up diagram refer to Fig. 1.

<table>
<thead>
<tr>
<th>Components</th>
<th>Mol fraction (mol%)</th>
<th>Components</th>
<th>Mol fraction (mol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{H}_2\text{S} )</td>
<td>6.86</td>
<td>( \text{C}_1 )</td>
<td>89.63</td>
</tr>
<tr>
<td>( \text{N}_2 )</td>
<td>0.5</td>
<td>( \text{C}_2 )</td>
<td>0.21</td>
</tr>
<tr>
<td>( \text{He} )</td>
<td>0.02</td>
<td>( \text{C}_3 )</td>
<td>0.02</td>
</tr>
<tr>
<td>( \text{CO}_2 )</td>
<td>2.76</td>
<td>( \text{C}_4-\text{C}_7 )</td>
<td>0</td>
</tr>
</tbody>
</table>
3. Experiment conclusion analysis

3.1. Sulfur deposition experiments with non-movable water

Figs. 2 and 3 show the relationship between average pressure reciprocal and permeability when the initial pressure is set as 40 MPa and temperature is set as 70 °C. The established initial non-movable water saturation of core 1 is bigger than core 2. It can show that the permeability is increasing while pressure is decreasing.

Figs. 4 and 5 show the relationship between permeability and volume flow. It can be seen that core permeability is increasing while the cumulative volume flow is increasing (cumulative experiment time increasing). This shows an obvious slippage effect.

3.2. Discussion of elemental sulfur deposition experiments

In order to illustrate the effect of non-movable water on core, the core depletion type of experiments with non-movable water is executed. The permeability rates are shown in Table 4. The results show that wet sample’s permeability is improved after the experiments. The higher initial non-movable water saturation is, the more the permeability is improved. The core flow capacity is improved due to the occurrence of chemical reaction between the core and the acid environment formed by H₂S dissolution in water.

It will not be easy to measure the variation of non-movable water, because the saturation of the preliminary non-movable water is considered to be low. Furthermore, the poisonous fluid medium and high pressure and temperature experimental environment also adds the difficulties to the measurement. With the decreasing of pressure and temperature, precipitated sulfur

Table 4
The change of core permeability with non-movable water considered.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Permeability (mD)</th>
<th>Before experiment</th>
<th>Non-movable water established</th>
<th>After experiment</th>
<th>Damage rate (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wet sample 1</td>
<td>1.50</td>
<td>1.28</td>
<td>1.72</td>
<td>−14.7</td>
<td></td>
</tr>
<tr>
<td>Wet sample 2</td>
<td>1.26</td>
<td>1.06</td>
<td>1.39</td>
<td>−10.3</td>
<td></td>
</tr>
</tbody>
</table>
decreases core permeability, but the change of core porosity is so small that it can be ignored. Thin sections and SEM analysis are made by Yang (2008). And elemental sulfur is observed in pore surface. However, gas may carry some deposited sulfur and the extent of damage is not too serious. This paper enters into some researches of the effects of non-movable water on sulfur deposition experiment. One is that elemental sulfur may decline core permeability, precipitated sulfur may be cemented together due to the effect of liquid bridge force and they cannot be carried over by gas (Hu et al., 2011), and the other is that feeble sour environment may improve core permeability. The results show that the effects of precipitated sulfur on core permeability are limited in dynamic experiments.

4. Conclusion

With the decreasing of pressure, elemental sulfur may deposit and block pore, thus declining permeability. However, when the factor of non-movable water is considered and core samples are reservoir carbonate core, hydrogen sulfide may dissolves in water and acid environment may be formed so that the permeability of cores is improved and flow capacity is enhanced. The extent of damage sulfur deposition has done to core permeability is limited under a dynamic condition.

Acknowledgment

This acknowledge is to the support provided by National Science and technology Major Project (2011ZX05009-006) and the Fundamental Research Funds for the Central Universities (2–9-2012-52).

References