Experimental study on microscopic formation damage of low permeability reservoir caused by HPG fracturing fluid

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A B S T R A C T

Hydraulic fracturing has become an important stimulation technique for low/ultra-low permeability reservoirs. Research on formation damage caused by fracturing fluid has mainly focused on permeability, sensitivity, fracturing fluid and clay minerals. However, little attention has been devoted to the microscopic changes in pore structure and properties. In this paper, nitrogen gas-adsorption techniques were introduced to characterize the microscopic changes in pore structure. Meanwhile, contact angle testing and Scanning Electron Microscope (SEM) observations were also used to show the changes in wettability and surface morphology of cores, respectively. The results showed that the pore size distributions (PSDs) of low permeability cores were wide, with approximately 75% macropore volume. The obvious changes in PSDs of damaged samples occurred in the range of 2–5 nm and 30–80 nm. The specific surface area decreased, and the adsorbability of damaged samples declined, as well. Concentrated gel and solid residues were confirmed to be the main damage mechanisms for gel breaking liquids, which resulted in changes in composition and roughness, making the cores more hydrophilic. Based on the results of the analysis, the N2 adsorption technique is deemed appropriate for the study of reservoir formation damage when a certain amount of mesopores are present. Additionally, a new method of determining contact angles for porous media is also recommended.

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1. Introduction

Hydroxypropyl Gum (HPG) cross-lined with borax (HPG gel) is widely used in hydraulic fracturing operations due to the following advantages: high cross-linking velocity, good rheological properties, strong sand-carrying capacity and low price. However, in the flow-back process, due to factors such as incomplete gel breaking, a low flow-back rate and high residue retention, the fracturing effect is often lower than expected, causing reservoir damage. Although new types of fracturing fluids such as viscoelastic surfactant (VES) and CO2 have been introduced to boost hydrocarbon production and decrease formation damage (Lv et al., 2015; Ribeiro et al., 2015; Chen et al., 2014), liner or cross-linked guards are still the most commonly used method in fracturing operations (Barati and Liang, 2014). Additionally, it is worth noting that low permeability reservoirs with low formation pressure and small pore throat radius usually contain a high concentration of clay minerals and are more sensitive to water-based fracturing fluids. Therefore, it is essential to investigate formation damage with an emphasis on the microscopic changes that occur in small pores as a result of the invasion of fracturing fluids.

The main causes of formation damage and their remediation measures are well understood and documented. The primary mechanism of formation damage is fluid loss during fracturing operations. To mitigate this problem, fluid-loss agents (Yoshimura et al., 2015) and fluid loss control technologies (Lin et al., 2015; Kang et al., 2014b) have been suggested in hydraulic fracturing operation. Another mechanism that leads to formation damage is retention of fracturing fluids during the flow-back process. Zhou et al. (2016) reported that fracturing fluids caused serious reduction in both matrix and open fracture permeabilities but increased the permeability of micro-fractures due to lubrication effect. Wang et al. (2012) noted that fracture fluid cleanup was affected by static yield stress, flowing yield stress, the amount of polymer residue, filter cake on the walls of the fracture, proppant crushing as well as

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non-Darcy flow effects. Lastly, the surfactants added to fracturing fluids could have different effects on the adsorption capacity and wettability (You et al., 2015).

Most scholars studied the degree of formation damage by testing and calculating permeability recovery. (Tang et al., 2015; Kang et al., 2014a; Jin-Gang et al., 2013; Cheng et al., 2012; Potter et al., 2011). Rapid-Gel-Damage (RGD) and API conductivity cell methods were used to obtain similar regained permeability for gel breaking liquids with different break-times (Weaver et al., 2015). Fang et al. (2016) proposed the use of nuclear magnetic resonance (NMR) as a new experimental method for quantitative evaluation of sensitive clay minerals. Meanwhile, some other scholars have investigated formation damage microscopically and recommended improvements in working fluids design. Guo and He (2012) studied the gel breaking process of HPG gel and noted that the oxide gel breaker could effectively reduce the viscosity of the fracturing fluid but contributed little to the degradation of molecular size and weight. Additionally, the degradation rate of galactose in the side chain of the HPG molecule was much higher than that of the mannose in the main chain, which led to lower water solubility. These two attributes were the main reasons for the production of residues in the gel breaking process. Chen et al. (2010) studied the filtration of gel breaking liquids cross-linked in different pH conditions by atomic force microscope (AFM). They noted that dense network structures could be observed in the filtrate that cross-linked in conventional alkaline conditions while no residue and a loose gathering of particles were observed in the filtrate that cross-linked in acidic conditions. This, according to the authors, implied that HPG/Borate gel, which is commonly used in alkaline conditions, caused greater damage to reservoirs. Wilson et al. (2014) reviewed the various mechanisms involved in formation damage as well as the physicochemical properties of individual clay minerals. They concluded that the swelling of smectitic clays, dispersion and migration of a variety of clay minerals and transformation of clay minerals into other mineral phases were responsible for formation damage in sandstones. To facilitate a better understanding of the factors involved in the above processes, the diffuse double electric layer (DDL) and hydration pressure, which varied with solution salinity and pH, were also discussed for each mineral.

Most of the research available focused on fracturing fluids, clay minerals, changes in core sensitivity and permeability; but very little research has been conducted on the changes in pore structure and properties of the pore wall. Four problems were investigated and discussed in this paper: (1) microscopic properties of undamaged samples, including pore shape, pore volume, pore size distributions (PSDs), specific surface area (SSA) and adsorbability; (2) changes in the aforementioned properties after damage by HPG fracturing fluid; (3) changes in wettability and surface morphology of core samples; and (4) improved methods in data processing and analysis.

### 2. Experimental fluids

Mineralized water was prepared according to the fracturing fluid composition as used in the field. This same mineralized water was used to prepare the HPG gel and the gel breaking liquids with different break-times of 1 h, 2 h, 4 h, 8 h and 12 h. The viscosity of the base fluid was 45 mPa·s, and the HPG gel was a pseudoplastic fluid with a smooth appearance and suitable viscoelasticity (Fig. 1). It performed well as a static sand-carrying agent (the average settlement rate was 0.0032 cm/min in 12 h with proppant concentration of 25%). At 60 °C and for over 2 h the gel breaking liquids had a low stable viscosity and showed no elasticity (Fig. 2). These properties met the requirements for field operation applications.

### 3. Methods

#### 3.1. N2 adsorption measurements

The experimental cores came from a typical low-permeability sandstone reservoir in Y oilfield.

Parts of the cores were crushed into 20–60 mesh particles. The particles were then separated into 7 groups. Each sample was measured by an N2 adsorption-desorption analysis instrument. Since this was performed before damage was effected, these samples are referred to as undamaged. The damage process was then carried out by placing each sample into mineralized water and HPG gel for 12 h. The remaining 5 samples were each placed into gel breaking liquids over different break times of 1 h, 2 h, 4 h, 8 h and 12 h, respectively. N2 adsorption-desorption analysis was then carried out again on these damaged samples to investigate the degree of damage.

The static volumetric method was used to represent the changes in microscopic parameters of samples damaged by HPG fracturing fluid. The adsorbance was measured at different relative pressures and at a temperature of 77 K by N2 to obtain the adsorption–desorption isotherm. Parameters such as SSA, PSDs and pore volume were calculated on the basis of reasonable models and theories. Isotherm characteristics were used to describe the morphology of pores qualitatively. The SSA was analyzed by the BET.
model in a relative pressure range of 0.05–0.35. The PSDs were calculated by the BJH–adsorption model, and the pore volume was obtained from adsorbance at \( p/p_0 = 0.98 \) combined with the density difference between liquid nitrogen and nitrogen at standard conditions. All of these parameters were critical indicators of the microstructure and microscopic pore properties.

3.2. Contact angle test

Parts of the cores were cut into 7 slices and each slice had two planar surfaces. Contact angle measurements were carried out at two different points for each slice and these points were recorded. The slices were similarly damaged as described in section 3.1. Contact angle measurements were conducted at the same points on the damaged samples as on the undamaged slices.

An optical projection instrument was used to measure the contact angle in this paper. The experiment was conducted with distilled water at room temperature. Dissimilar to glass slides, porous media showed dynamic contact angles with increasing time. Choosing a reasonable value for the contact angle was considered in the data processing. Changes in the equilibrium contact angles were direct indicators of changes in wettability.

3.3. SEM and microscopic morphology

Parts of the cores were drilled off and trimmed to an approximate size of 10 mm \( \times 10 \text{ mm} \times 5 \text{ mm} \). Seven stubs were prepared from these samples and 6 were damaged as described in section 3.1. Both damaged and undamaged samples were then dried and coated with a gold film.

The microscopic morphology was observed using SEM. Photographs were taken at 500 \( \times \) and 1000 \( \times \) magnification to show the direct changes in samples. These data were also used as secondary evidence to explain other phenomena. Multiple points were observed and statistical characters were selected as general results.

3.4. Air permeability test

Samples 006-2# and 009-3# were standard cores with \( \phi = 25.4 \times 50 \text{ mm} \). Air permeability tests were conducted before damage. To simulate the fluid loss process, the cores were placed into the HPG fracturing fluid with breakers at 60 °C and 15 MPa for 4 h to effect damage to the cores. Air permeability measurements were then carried out again.

4. Results and discussions

4.1. Microstructure and microscopic pore properties

4.1.1. Characteristics of nitrogen adsorption isotherms and qualitative description of pore morphology

Samples show similar isotherms and a typical example is shown in Fig. 3. The shape of the curves indicates primarily Type II isotherms with H3 hysteresis loop according to International Union of Pure and Applied Chemistry (IUPAC) nomenclature (Sing, 1985). The main characteristics are described as follows. Firstly, the convex curve with point B (Fig. 3, insert 1) over a range of low \( p/p_0 \) showed that there is a fairly strong interaction between the adsorbent (core samples) and adsorbate \((N_2)\). Point B is the inflection point between monolayer and multilayer adsorption processes. Secondly, adsorbance continues to increase and there is no ‘limiting platform’ over a range of high \( p/p_0 \), demonstrating the existence of numerous macropores. Thirdly, due to capillary condensation, adsorbance sharply increases and the curves show obvious hysteresis loop over a range of moderate to high \( p/p_0 \).

An obvious hysteresis loop over a range of moderate to high \( p/p_0 \) provides significant proof of the presence of macropores, and the wide hysteresis loop indicates heterogeneity of pore/throat distributions. This is proved quantitatively by pore volume analysis in sub-section 4.1.6.

4.1.2. Changes in nitrogen adsorption isotherms

Obvious variations in isotherms were found in the damaged samples (Fig. 4). The damaged sample with break-times of 2 h, 4 h, 8 h, and 12 h all showed similar variations. Isotherms for a break-time of 2 h are shown in Fig. 4(b).

There is a rightward shift in the hysteresis loop of the isotherms. Minimal variation of curves is observed for samples damaged by mineralized water. This could be due to small differences in inorganic mineral properties after some soluble minerals dissolved. The shapes of the curves for the samples damaged by gel breaking liquids exhibit the most variation. Solid residues and concentrated gel in gel breaking liquids inevitably cover the surfaces, changing the composition and structure of the pore walls. The samples damaged by HPG gel show intermediate variation. This could be due to the high viscosity and large networks of HPG gel, which precluded deep invasion. Another characteristic observed in the isotherms is variation of maximum adsorbance. Firstly, samples damaged by gel breaking liquid with a break-time of 1 h show a decrement in adsorbance (Fig. 4(a)). It suggests this gel breaking liquid invaded more deeply and blocked more throats and pores, engendering a strong ‘viscous blocking effect’. Secondly, samples damaged by gel breaking liquids over 2–12 h show little variation in maximum adsorbance compared to the undamaged samples, suggesting that

![Fig. 3. Type II isotherms with H3 hysteresis loop (sample: 009#; 77 K).](image-url)
most pore volumes are detected by N2 molecule (Fig. 4, b). Lastly, samples damaged by HPG gel and mineralized water show higher maximum adsorbance than undamaged samples (Fig. 4c and d). This behavior is further explained at the end of sub-section 4.1.6.

4.1.3. Changes in SSA based on BET model

Compared with the undamaged samples, samples damaged by HPG fracturing fluid show a 30% decline in SSA but samples damaged by mineralized water show a decline of 16% (Table 1). The main reasons for these phenomena could be decreases in roughness, reductions in the number of pores, and increments in pore diameter, among others. Concentrated gel and solid residues covered the original surfaces and this decreased the surface roughness, causing a decline in the SSA. The SEM micrographs also indicate that the roughness of gel-coated minerals is much smoother than that of the original minerals (Fig. 9, e–f). The PSDs are discussed in the sub-section 4.1.5.

4.1.4. Changes in adsorbability based on BET model

The BET equation displays a good linear relationship when \( p/p_0 \) ranges from 0.05 to 0.35 and the constants \( V_m \) and \( C \) can be calculated from Equation (1). Some of the volumes of adsorbed gas \( (V) \) measured from the experiment were less than the \( V_m \) computed from the BET equation. These \( V \) values are considered unreasonable data points and are therefore ignored. The adsorbance at any \( p/p_0 \) can then be calculated by the BET equation (Equation (1)) (Fu et al., 2005). The saturated amount of monomolecular layer, represented by \( V_m \) is the maximum adsorbance when the solid surface is covered with one layer of gas molecules. The constant \( C \) is related to the isothermal heat of adsorption (Equation (2)). The first-layer heat of adsorption, represented by \( Q_1 \) is an important parameter in determining the adsorbability of the solid surface. The heat of adsorption and adsorbance are both used to characterize the changes in adsorbability as well as microscopic properties of the pore walls.

\[
V = V_m \frac{C p}{(p_0 - p) \left( 1 + (C - 1) \frac{p}{p_0} \right)} = V_m \left( \frac{C p}{p_0} \right) \left( 1 + (C - 1) \frac{p}{p_0} \right) \left( \frac{p_0}{p} (1 - p/p_0) \right) \tag{1}
\]

\[
Q_1 = Q_L + RT \ln C \tag{2}
\]

Where, \( Q_L \) —— heat of adsorption for the first layer, J/mol;
4.1.5. Changes in PSDs based on BJH model

To determine the population of pores as a function of the pore width, the BJH model based on adsorption isotherms (BJH-adsorption method) was selected for this study because of the tensile strength effect (TSE) (Groen et al., 2003), which frequently leads to extra contributions to PSDs according to the desorption isotherms.

Obvious variations in PSDs are observed for damaged samples in two ranges. One is the mesopores ranging from 2 to 5 nm and the other is the meso-macro pores ranging from 30 to 80 nm (Fig. 5, typical curve (b) represented samples damaged over 2–12 h). The peak value of differential pore volume evidently declines and pore size increases slightly in the range of 2–5 nm. Peak values of samples damaged by mineralized water decline by approximately 15%, whereas other samples declined by 30%. The ranges of these declines are in accordance with SSA although the values are a bit lower. It can be inferred that the decrement of these pores is the main reason for the decrement in adsorbance. A more in-depth reason is discussed in sub-section 4.1.6.

### Table 2

<table>
<thead>
<tr>
<th>Samples</th>
<th>Before damage</th>
<th>After damage</th>
<th>Rate of change for Qe (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Qe</td>
<td>Qe</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7.71</td>
<td>7.56</td>
<td>–1.95</td>
<td></td>
</tr>
<tr>
<td>7.77</td>
<td>7.58</td>
<td>–2.45</td>
<td></td>
</tr>
<tr>
<td>7.76</td>
<td>7.70</td>
<td>–0.77</td>
<td></td>
</tr>
<tr>
<td>7.77</td>
<td>7.69</td>
<td>–1.03</td>
<td></td>
</tr>
<tr>
<td>7.76</td>
<td>7.70</td>
<td>–0.77</td>
<td></td>
</tr>
<tr>
<td>7.74</td>
<td>7.68</td>
<td>–0.78</td>
<td></td>
</tr>
<tr>
<td>7.77</td>
<td>7.69</td>
<td>–1.03</td>
<td></td>
</tr>
</tbody>
</table>

### Table 3

<table>
<thead>
<tr>
<th>Samples</th>
<th>Adsorbance of the first layer, Vfo</th>
<th>Adsorbance of multi layers, Vfo,35</th>
<th>Contribution of multilayers (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Before damage</td>
<td>After damage</td>
<td>Rate of change (%)</td>
</tr>
<tr>
<td></td>
<td>(mL/g)</td>
<td>(mL/g)</td>
<td></td>
</tr>
<tr>
<td>Breaking-1h</td>
<td>1.1324</td>
<td>0.7798</td>
<td>–31.14</td>
</tr>
<tr>
<td>Breaking-2h</td>
<td>1.1418</td>
<td>0.8214</td>
<td>–28.06</td>
</tr>
<tr>
<td>Breaking-4h</td>
<td>1.1748</td>
<td>0.8406</td>
<td>–28.45</td>
</tr>
<tr>
<td>Breaking-8h</td>
<td>1.1543</td>
<td>0.8024</td>
<td>–30.49</td>
</tr>
<tr>
<td>Breaking-12 h</td>
<td>1.136</td>
<td>0.787</td>
<td>–30.72</td>
</tr>
<tr>
<td>HPG gel-12 h</td>
<td>1.1637</td>
<td>0.8486</td>
<td>–26.99</td>
</tr>
<tr>
<td>Mineralized water-12 h</td>
<td>1.1447</td>
<td>0.9824</td>
<td>–14.18</td>
</tr>
</tbody>
</table>

* Contraction of multi layers was defined as absolute value of difference between rate of changes in multi layers and the first layer. It referred to the reduction of adsorbance except the first layer (see Table 3).
are defined to describe their contribution to total porosity. In the studied range, mesopores are 60–70% while macropores are 30–40%. This indicates that mesopores make up the majority of the pore volume. Considering that mesopores have smaller diameters, it can be inferred that the number of mesopores is more numerous than macropores, which is consistent with the PSDs. The results also indicate that the studied pores only contributed 35–40% to the total pores. In other words, some macropores with 60–65% pore volume of samples are out of the study range. That is why there is no 'limiting platform' over a range of high p/p₀ on isotherm curves (Fig. 3).

The pore volumes for both undamaged and damaged samples are shown in Table 6. In the series of gel breaking liquids, samples with 1 h break-time show different variation from all others. A strong 'viscous blocking' effect exists, evidenced by the decreasing volume of macropores and the total pores. A small amount of

Table 4

Diameters of the most probable pores (BJH-adsorption method, nm).

<table>
<thead>
<tr>
<th>Samples</th>
<th>HPG gel before damage</th>
<th>Breaking before damage</th>
<th>Breaking before damage</th>
<th>Breaking before damage</th>
<th>Breaking before damage</th>
<th>Breaking before damage</th>
<th>Mineralized water before damage</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>0.62</td>
<td>2.02</td>
<td>2.63</td>
<td>1.14</td>
<td>2.64</td>
<td>1.25</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.64</td>
<td>2.26</td>
<td>2.64</td>
<td>2.13</td>
<td>2.64</td>
<td>2.25</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.68</td>
<td>2.14</td>
<td>2.64</td>
<td>2.13</td>
<td>2.64</td>
<td>2.25</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.70</td>
<td>2.14</td>
<td>2.64</td>
<td>2.13</td>
<td>2.64</td>
<td>2.25</td>
</tr>
</tbody>
</table>

Table 5

Relative amount of pore volume with different diameters.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Based on studied pores</th>
<th>Based on total pores</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mesopores (%)</td>
<td>Macropores (%)</td>
</tr>
<tr>
<td>009–1</td>
<td>60.53</td>
<td>39.47</td>
</tr>
<tr>
<td>009–2</td>
<td>68.84</td>
<td>31.16</td>
</tr>
<tr>
<td>009–3</td>
<td>69.27</td>
<td>30.73</td>
</tr>
<tr>
<td>009–4</td>
<td>68.81</td>
<td>31.19</td>
</tr>
<tr>
<td>009–5</td>
<td>69.19</td>
<td>30.81</td>
</tr>
<tr>
<td>009–6</td>
<td>69.70</td>
<td>30.30</td>
</tr>
</tbody>
</table>
concentrated gel deposited on key throats could render open pores blocked, causing an abrupt decrease in pore volume. The other samples have almost the same pore volume with little change due to the low viscosity and little viscous blocking effect. The volume of mesopores, macropores and total pores all increase for samples damaged by both mineralized water and HPG gel.

Notably, samples damaged by mineralized water and HPG gel show the same trends in many aspects such as higher maximum adsorbance (section 4.1.2), increasing PSDs in the range of 30–80 nm (section 4.1.5) and larger pore volumes. However, the reasons behind these trends are believed to be totally different. Some soluble minerals were dissolved and dispersed in the mineralized water and then the diameters and the pore volumes increased. Conversely, the HPG gel had numerous microscopic networks which may have increased the extra pores that the N2 molecules could detect, as well as high viscosity which prevented deep invasion. Therefore, samples damaged by HPG gel showed more meso-macro pores, larger pore volumes and a smaller degree of blocking effect than that of gel breaking liquid with 1 h. The other concentrated gel deposited on key throats could render open pores blocked, causing an abrupt decrease in pore volume. The other samples have almost the same pore volume with little change due to the low viscosity and little ‘viscous blocking’ effect. The volume of mesopores, macropores and total pores all increase for samples damaged by both mineralized water and HPG gel.

Notably, samples damaged by mineralized water and HPG gel show the same trends in many aspects such as higher maximum adsorbance (section 4.1.2), increasing PSDs in the range of 30–80 nm (section 4.1.5) and larger pore volumes. However, the reasons behind these trends are believed to be totally different. Some soluble minerals were dissolved and dispersed in the mineralized water and then the diameters and the pore volumes increased. Conversely, the HPG gel had numerous microscopic networks which may have increased the extra pores that the N2 molecules could detect, as well as high viscosity which prevented deep invasion. Therefore, samples damaged by HPG gel showed more meso-macro pores, larger pore volumes and a smaller degree of blocking effect than that of gel breaking liquid with 1 h.

Furthermore, both HPG gel and mineralized water are considered to cause formation damage despite the fact that their pore volume increased. The increased pore volume, which is due to the networks, is evidence of HPG gel invasion. The greater increment noticed in pore volume, the deeper the HPG gel invaded the sample. These increased pore volumes are temporary and contribute no improvement to permeability. While the mineralized water may increase pore volume because of the dissolution of some clays, the dissolved clay minerals weaken the cementation among the matrixes and then increase the risk of stress sensitivity. Therefore, the contradictory effects of increment in pore size and susceptibility to stress should also be estimated comprehensively.

4.2. Wettability of core surface

Contact angle tests were used in this paper to measure the wettability of samples. The left and the right contact angles usually show different values because of surface roughness, heterogeneity, etc. To obtain the average contact angle of a particular local surface, the D-H algorithm was used to process the data with the assumption that the droplets were ideally spherical (Equation (3)), where height and chord of droplets are represented by h and D, respectively.

\[
\tan \theta = \frac{2h}{D}
\]

4.2.1. Determination of contact angles

Unlike the stable values obtained from using glass slides, the contact angle measured on the surface of porous media decreased with time due most significantly to permeation as well as spreading and wetting. The velocity of permeation is related to porosity and permeability. The spreading, which occurred not only on the surface but also into the insides of the cores, is affected by wettability.

In Fig. 6, two stages can be observed clearly in each contact angle test curve. In the first stage, the contact angle decreases rapidly. It is assumed that the droplet balance process primarily occurs on the surface in approximately 3–5 s. In the second stage, the contact angle decreases relatively slowly as the spreading on the surface and permeation into the insides of the samples occurs, which continues for a long time until the droplets disappear on the surface. The inflection point of the curves is believed to be the

Table 6

Changes in pore volume for damaged samples (range from 2 to 100 nm).

<table>
<thead>
<tr>
<th>Samples</th>
<th>Rate of changes&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Rate of changes&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Rate of changes&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Before damage (μL/g)</td>
<td>After damage (μL/g)</td>
<td>Before damage (μL/g)</td>
</tr>
<tr>
<td>Breaking-1h</td>
<td>13.8</td>
<td>11.4</td>
<td>–17.39</td>
</tr>
<tr>
<td>Breaking-2h</td>
<td>13.7</td>
<td>12.0</td>
<td>–12.41</td>
</tr>
<tr>
<td>Breaking-4h</td>
<td>14.2</td>
<td>11.9</td>
<td>–16.20</td>
</tr>
<tr>
<td>Breaking-8h</td>
<td>13.9</td>
<td>11.9</td>
<td>–14.39</td>
</tr>
<tr>
<td>Breaking-12h</td>
<td>13.7</td>
<td>11.6</td>
<td>–15.33</td>
</tr>
<tr>
<td>HPG gel-12h</td>
<td>14.0</td>
<td>14.6</td>
<td>4.29</td>
</tr>
<tr>
<td>Mineralized water-12 h</td>
<td>13.8</td>
<td>14.9</td>
<td>7.97</td>
</tr>
</tbody>
</table>

<sup>a</sup> Positive values mean the pore volume increased after being damaged; While negative values mean decrement (see Table 6).

![Fig. 6. Two decrement stages of contact angle (50 frames – 6 s).](image-url)
equilibrium contact angle that can characterize the wettability of a particular surface of the porous media.

4.2.2. Changes in wettability

The contact angles of pre- and post-damaged samples are shown in Fig. 7. Due to the heterogeneity and pollution on the surface, the values of contact angles of undamaged samples vary in a comparatively large range. Nonetheless, some conclusions can be drawn from the statistical data.

(1) Contact angles of undamaged samples

Half of the contact angles of 006# undamaged samples are greater than 75° because of different degrees of pollution, while the rest of the contact angles belonging to fresh sections range from 55° to 75°. This demonstrates that sections of core 006# are weak water-wetting. Most of the contact angles measured on undamaged samples of core 009# range from 40° to 65°. This means that 009# shows slightly stronger hydrophilicity than 006#. The reason for this phenomenon may be that core 009# contains more clay minerals.

(2) Contact angles of damaged samples

The contact angles of surfaces damaged by gel breaking liquids range from 30° to 55° for both core 006# and core 009# samples. Compared with the undamaged samples, the values indicate that the hydrophilicity for damaged cores increases and is unrelated to the original sections. It is believed that the primary damage mechanisms for gel breaking liquids are concentrated gel and solid residue. More hydroxyl groups make their hydrophilicity stronger than SiO2 and clay minerals and then lead to smaller values of contact angles. Their remains on the original surface result in the wettability not attributed to the original surface.

(3) Contact angles in different liquids

Contact angles of the surfaces damaged by low viscosity liquids are roughly the same and unrelated to the break-times. However, the contact angles of the surfaces damaged by HPG gel are relatively minimal. The contact angles of the surfaces damaged by the mineralized water seemed to be the same value, 55°. The reason for this phenomenon may be due to the surface properties tending to be consistent after the dissolution of soluble minerals.

(4) The influence of the original porosity and permeability of cores

The contact angle decrement is mainly related to permeation, which is a function of the original porosity and permeability. Two experimental phenomena are obviously displayed in the figures. Firstly, in the second stage of the decrement process, the contact angles of sample 006# decrease faster than sample 009# irrespective of whether they are undamaged or damaged (Fig. 6). Secondly, the contact angles of samples 006# damaged by HPG gel are smaller than those of samples 009# (Fig. 7, Δ). The reason for the first phenomenon is better permeation on the 006# surface, and for the latter is deeper invasion of gel in sample 006#. Both reasons positively correlate with the higher porosity and permeability of 006#.

4.3. Microscopic morphology of samples

The surface morphology was studied using scanning electron microscopy (SEM) imaging. The results not only show intuitive changes in surface structure but also contribute to better understanding of other experimental phenomena such as SSA, PSDs and so on. In this experiment, the original morphology of HPG gel has changed because the samples are initially dehydrated. However, the smooth surface and the arc-shaped slice (Fig. 9, b–d) are considered to represent the changed morphology of the concentrated gel and solid residue.

The inter-crystalline pores (ICP) and a few inter-particle pores (IPP) are clearly observed on undamaged surfaces. The edges and corners of the minerals are sharp and clear, which denotes that these minerals are naturally crystallized (Fig. 8, a; Fig. 9, a). This is congruent with the H3 hysteresis loops in Fig. 3. Samples damaged by mineralized water show relatively loose structure and some grain dissolution pores (GDP) (Fig. 8, b), which confirms dissolution of soluble minerals. HPG gel renders the matrix surfaces to be covered with gel (Fig. 9, c) and the IPP are figures.

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These organic residuals, as well as the smooth gel, cause decrement in contact angles. However, a few viscous residuals can still be observed among the grains (Fig. 8, e–h), indicating that HPG gel could not break completely.

4.4. Air permeability test

Air permeability measurements were carried out on pre- and post-damaged cores as the most direct indicator of damage with fluid invasion. As shown in Fig. 10, the Klinkenberg permeability of

![Fig. 8. Surface morphology of undamaged and damaged samples by SEM micrograph at 500 magnification.](image)

![Fig. 9. Surface morphology of undamaged and damaged samples by SEM micrograph at 1000 magnification.](image)

![Fig. 10. Decrements in Klinkenberg permeability for pre- and post-damaged samples at 2 MPa.](image)
006-2# is $5.7551 \times 10^{-3}$ m$^2$ and $4.4704 \times 10^{-3}$ m$^2$ for pre- and post-damaged cores, respectively. This amounts to a decrement of 22.32%. That of 009-3# is $0.1129 \times 10^{-3}$ m$^2$ and $0.0947 \times 10^{-3}$ m$^2$ with a decrement of 16.12%. These data fully indicate that HPG fracturing fluids have adverse effects on the formation because of fluid loss and residues.

5. Conclusions

The pore structures, wettability and microscopic morphology are studied with N$_2$ adsorption method, contact angle measurement and SEM for undamaged and HPG-damaged samples. The conclusions can be summarized as follows.

1) Both undamaged and damaged samples show Type II isotherms with H3 hysteresis loop. The isotherms, the PSDs and SEM results indicate there are slit-shaped mesopores with an average diameter of 10–15 nm and ink-bottle-shaped pores with throat diameter of 2–5 nm as well as numerous macropores making up 75% of pore volume. For damaged samples, the decrement of pores in the range of 2–5 nm is the main reason for the decrement of SSA and adsorbance.

2) Mineralized water is mainly responsible for water sensitivity according to the PSDs. The swelling process causes pore diameter decrement in the range of 2–5 nm while dissolution processes result in increment in PSDs (30–80 nm) as well as the total pore volume. Grain dissolution pores are also observed in SEM micrographs.

3) The concentrated gel and solid residue are confirmed to be the main damage mechanisms for gel breaking liquids. The PSDs show different damage effects during different phases of the HPG gel breaking procedure. The most sensitive range of pore damage is 2–5 nm. The microscopic damage results in the decrement in Klinkenber permeability by 16–23%.

4) The higher the original porosity and permeability, the greater the changes in contact angles. The surfaces damaged by HPG fracturing fluid are much more hydrophilic, while the surfaces damaged by mineralized water tend to have the same hydrophilicity.

5) The N$_2$ adsorption method could be used to study formation damage from a new perspective. This method could be used in reservoirs which have a certain amount mesopores. Pore shape, PSDs, SSA, adsorbance, heat of adsorption and other parameters could also be obtained to study the microscopic pore structure, both qualitatively and quantitatively.

6) The changes in contact angle could be divided into the balance process and then the spreading and permeation process. The inflection point of the two stages is the equilibrium contact angle. This method of contact angle determination is recommended for the study of the wettability of low permeability reservoirs.

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