Research Article

Alkali Solution Erodes Shale: Influencing Factors and Structural Damage Characteristics

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High-pH drilling fluids are often used for drilling shale gas wells. Alkali erosion of shale is one of the important factors of wellbore instability. Alkali erosion experiments of different kinds of minerals and shale were conducted in this paper. Experimental results show that the corrosion rate of kaolinite is the highest when the pH is 9, the corrosion rate of smectite is the highest when the pH is 10 or 11, and the corrosion rate of the quartz is the highest when the pH is 12. Both shale particle size and concentration of hydroxide ion all affect the reaction rate, and the former has a negative correlation with the reaction rate, and the latter has a positive correlation with the reaction rate. In addition, alkaline erosion can lead to the fracture propagation along the bedding planes of shale, which can easily result in wellbore instability. This study may offer some theoretical basis for wellbore instability induced by high-pH drilling fluids.

1. Introduction

Wellbore instability is common in the process of shale formation drilling and completion. It not only increases nonproduction time and cost, but also becomes a serious challenge to drill safely and efficiently. Wellbore instability is primarily a function of rock response to the stress concentration induced around the wellbore during drilling. If the strength of the rock is higher than these stresses, the borehole will be stable; otherwise, rock will yield and may collapse, detach, or converge according to factors such as fluid properties, strength, and the failure behavior of rock [1, 2].

The strength of the shale will be reduced due to the interaction between the drilling fluid and shale. Water molecules of the drilling fluid enter the pores of shale by means of displacing pressure, infiltration, diffusion, and so on [3, 4]. Clay minerals such as smectite swell when water goes in, which will produce swelling stress. This stress can lead to the shale dispersion and bedding propagation, which decreases the strength of shale sharply [5]. To prevent clay minerals from hydrating swelling, some inhibitory agents such as KCl are generally added into the drilling fluid. But, for some kinds of shale, these agents do not have the inhibitive effect. Instead, it increases the shale’s dispersion. For example, the strength of kaolinite-rich shale will lose strength when exposed to KCl due to chemical transformation of the kaolinite minerals [6, 7]. The oil-based drilling fluid greatly solves the problem of clay minerals hydration swelling. However, the wellbore instability is still unable to be avoided by using this fluid. On the one hand, the oil-based drilling fluid contains a little water, which leads to a small swelling and reduces the strength of the shale. On the other hand, in order to keep good emulsifying properties, the oil-based drilling fluid generally has strong alkaline. Some minerals of shale are easily eroded by alkali, which also leads to wellbore instability [7–9].

In addition, the wellbore instability is also concerned with the structural integrity of the rock mass. On the one hand, if the rock has many weak bedding planes and fractures, the wellbore instability is easy to happen when the weak bedding plane destructs or slides [10]. On the other hand, the bedding planes and natural fractures can propagate due to lost circulation. Lost circulation can cause the
decrease of borehole pressure and the damage of wall surrounding rock and then induces the collapse of wellbore [11–15].

This paper took the LMX shale formation in Sichuan Basin as the object of study. Wellbore instability had been the main downhole complex problem in the process of drilling (Figure 1) and unable to be avoided even if using a strong inhibitory water-based or oil-based drilling fluid. According to the analysis, the instability was mainly caused by high pH (pH = 11–12) of drilling fluids (Table 1). In this paper, a new insight was proposed on why wellbore instability can be induced by high-pH drilling fluids, in terms of some chemical reaction experiments on both high-pH solution and shale.

2. Samples and Experimental Methods

2.1. Samples Used

2.1.1. Single Mineral. Five types of single mineral were used in the experiments, which were quartz, smectite, kaolinite, illite, and chlorite (Figure 2). These single mineral were from geological specimens company of Hangzhou.

2.1.2. Shale. In this study, LMX shale was used in the experiments. The mineralogical composition and other parameters of shale are listed in Table 2. It contains 39.3% clay, which included illite (84.9%), illite/smectite (2.2%), kaolinite (10.3%), and chlorite (2.6%).

2.1.3. Fluids. In order to eliminate the interference of bentonite and treatment agents in drilling fluids, alkali solutions with different pH were used instead of the high-pH drilling fluid in the experiments. Two types of alkaline solutions were used in this study. The pH of alkali solutions is 9 to 12.

2.2. Experimental Methods

2.2.1. Alkaline Erosion Experiment of Mineral. Dry mineral powder (particle size is 1 to 10 μm) is soaked in alkali solutions for 24 hours under 70°C. In this reaction, the weight of the mineral powder sample is 10 g, and the solid-liquid ratio is 1:30. After the reaction, the solid phase is filtered and dried. The weight of the solid phase after the reaction is recorded as W. The erosion rate is calculated as shown in the following equation:

\[
\text{erosion rate} = \frac{10.00 - W}{10.00} \times 100\%.
\]

2.2.2. Alkaline Erosion Experiment of Shale Particles. Shale particles were evaluated by alkaline erosion experiment. Shale particles were crushed into particles with three different particle sizes (1~10 μm, 25~60 μm, and 75~100 μm, resp.) and then soaked in the different pH alkali solutions under the 70°C condition. After 24 h, the samples were filtered, dried, and weighed.

2.2.3. Alkaline Erosion Experiment of Shale. For the shale pieces, the experimental procedures were as follows:

1. Cut shale pieces with the diameter of 25 mm and the thickness of 4 mm from the same shale core plug.
2. Select one piece of the shale sample to soak into distilled water and solutions with the pH of 9, 10, 11, and 12, respectively.
3. Put the different solutions with shale pieces into different aging cells of a roller furnace.
4. Set the temperature of the roller furnace to 70°C and run the roller furnace.
5. After 1 day, 3 days, and 7 days, open the roller furnace to take photos for shale pieces, respectively.

3. Results and Discussion

3.1. Effect of Mineral Types on Alkaline Erosion. For the reaction mechanism of rock minerals and alkaline fluids, researchers showed that common minerals (including quartz, feldspar, and clay minerals) can react with alkaline fluids. The reaction of common minerals with sodium hydroxide solution is shown in Table 3.

According to the reaction formula in Table 3, if minerals are exposed to alkaline fluids, minerals will be lost and some new products will be generated. As shown in Figure 3, alkali erosion experiments of minerals show that both quartz and clay minerals can react with the alkaline solution. When the pH was 9, the corrosion rate of kaolinite was 6.9%, and the corrosion rates of quartz and smectite were similar, which were 4.2% and 3.9%, respectively. The corrosion rates of illite and chlorite were 1.9% and 1.6%, respectively. The corrosion rates of the five minerals are as follows: kaolinite > smectite > quartz > illite > chlorite. When the pH was 10, the corrosion rates of quartz, montmorillonite, illite, kaolinite, and chlorite are 9.5%, 10.8%, 7.0%, 1.5%, and 0.5%, respectively. The corrosion rates of the five minerals are as follows: smectite > quartz > kaolinite > illite > chlorite. When the pH increased to 11, the corrosion rates of quartz, smectite, illite, kaolinite, and chlorite further increased, and the corrosion rates were 7.8%, 11.8%, 7.2%, 1.7% and 1.0%, respectively. The corrosion rates of the five minerals are as follows: smectite > quartz > kaolinite > illite > chlorite. When the pH reached 12, the corrosion rate of illite
### Table 1: Downhole problems during drilling shale wells in Sichuan Basin and Ordos Basin.

<table>
<thead>
<tr>
<th>Wells</th>
<th>Basins</th>
<th>Formations</th>
<th>pH of drilling fluids</th>
<th>Downhole problems</th>
</tr>
</thead>
<tbody>
<tr>
<td>W-H1</td>
<td>Sichuan</td>
<td>Longmaxi</td>
<td>11.0–11.5</td>
<td>Borehole collapse occurred and a large amount of black collapsed debris with a size of 5–8 cm returned from the well head when drilling shale formations (1856–2611 m)</td>
</tr>
<tr>
<td>W-H3</td>
<td>Sichuan</td>
<td>Qiongzhusi</td>
<td>11.0–11.5</td>
<td>Serious shale collapse caused pipe sticking at 3642.24 m so drilling finished in advance</td>
</tr>
<tr>
<td>N-H1</td>
<td>Sichuan</td>
<td>Longmaxi</td>
<td>11.0–11.5</td>
<td>Shale sloughing often occurred, and a large amount of black collapsed shale debris returned from the well head during drilling; pipe stuck happened when picking out drilling tools</td>
</tr>
<tr>
<td>Y1</td>
<td>Sichuan</td>
<td>Longmaxi</td>
<td>11.0–11.5</td>
<td>Serious lost circulation and shale collapse occurred when drilling a horizontal zone</td>
</tr>
<tr>
<td>Z101</td>
<td>Sichuan</td>
<td>Niutitang</td>
<td>11.0–12.0</td>
<td>Serious wellbore diameter enlargement</td>
</tr>
<tr>
<td>DP1</td>
<td>Ordos</td>
<td>Yanchang</td>
<td>11.0–12.0</td>
<td>Serious lost circulation (leakage volume was 177 m³) and shale collapse occurred when drilling from 1960 to 2100 m</td>
</tr>
<tr>
<td>JH-x2</td>
<td>Ordos</td>
<td>Yanchang</td>
<td>10.0–11.0</td>
<td>Ratio of wellbore diameter enlargement ranging from 38% to 60%</td>
</tr>
</tbody>
</table>

### Figure 2: Quartz and clay minerals.

### Table 2: Basic parameters of LMX formation of Sichuan Basin.

<table>
<thead>
<tr>
<th>X-ray: whole sample, wt.%</th>
<th>X-ray: clay mineral relative percentage, wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz 45.9</td>
<td>Dolomite 1.4</td>
</tr>
<tr>
<td>Feldspar 7.2</td>
<td>Dolomite 3.5</td>
</tr>
<tr>
<td>Dolomite 2.7</td>
<td>Pyrite 2.7</td>
</tr>
<tr>
<td>Total clay 39.3</td>
<td>Illite 84.9</td>
</tr>
<tr>
<td>Illite/smectite 2.2</td>
<td>Kaolinite 10.3</td>
</tr>
<tr>
<td>Chlorite 2.6</td>
<td></td>
</tr>
</tbody>
</table>

### Table 3: Chemical reaction formula of minerals and sodium hydroxide solution.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Chemical reaction formula</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz</td>
<td>SiO₂(s) + NaOH + H₂O = NaH₂SiO₄</td>
<td>[17, 18]</td>
</tr>
<tr>
<td>Feldspar</td>
<td>SiO₂ + 2NaOH = Na₂SiO₃ + H₂O</td>
<td>[8, 19]</td>
</tr>
<tr>
<td>Dolomite</td>
<td>CaMg(CO₃)₂ + 2Na⁺ + 2OH⁻ = CaCO₃ + Mg(OH)₂ + Na₂CO₃</td>
<td>[8, 20]</td>
</tr>
<tr>
<td>Smectite</td>
<td>5Al₂Si₄O₁₀(OH)₂ + 12H₂O = 2Al(OH)₃ + 2Si(OH)₄</td>
<td>[21]</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>(OH)₄ = 2NaAlSiO₄ + 1H₂O</td>
<td>[22, 23]</td>
</tr>
<tr>
<td>Illite</td>
<td>(K, H₂O⁺)(Al, Mg, Fe₃⁺)[(Si, Al)O₁₀(OH)] + OH⁻ → Al(OH)₃ + K⁺ + Fe³⁺ + Mg²⁺ + SiO₃²⁻</td>
<td>[19]</td>
</tr>
<tr>
<td>Chlorite</td>
<td>Y₃<a href="OH">Zr(PO₄)₃</a>₂ + 3OH⁻ → Al(OH)₃ + Fe³⁺ + Fe²⁺ + Mg²⁺ + Zr⁴⁺</td>
<td>[19]</td>
</tr>
<tr>
<td>Pyrite</td>
<td>FeS₂ + 2OH⁻ → Fe(OH)₂ + SO₄²⁻ + 14e</td>
<td>[24]</td>
</tr>
</tbody>
</table>

(electrochemical reaction)
significantly increased, while the corrosion rate of smectite showed a decreasing trend. So, the corrosion rates of the quartz, smectite, illite, kaolinite, and chlorite were 11.9%, 8.4%, 7.7%, 10.0%, and 1.2%, respectively. The corrosion rates of the five minerals are as follows: quartz > illite > smectite > kaolinite > chlorite.

So, when the pH of the alkaline solution is low, such as 9, the reaction rate of kaolinite and the alkali solution is the fastest. The content of kaolinite controls the reaction rate. When the pH of the alkaline solution is 10 or 11, the reaction rate of quartz and montmorillonite rapidly increases, and even exceeds the reaction rate of kaolinite, while the reaction rate of illite and chlorite with the alkali solution is slow. Therefore, the content of quartz, montmorillonite, and kaolinite controls the reaction rate when the pH of the alkaline solution is 10 or 11. When the pH of the alkaline solution is 12, the chlorite reaction rate is the slowest. The reaction rate is determined by the contents of four minerals: quartz, montmorillonite, illite, and kaolinite.

The experimental results show that there are great differences in the reaction rates of minerals in different concentrations of alkaline solutions. The higher the concentration of the alkali solution is, the more the kinds of minerals participate in the reaction.

3.2. Effect of Particle Size of Shale on Reaction Rate. As shown in Figure 4, the reaction between shale powder and alkali solutions shows that the alkaline erosion rate increases with the decrease of particle size. The experimental results show that the smaller the particle size, the larger the specific surface area. Therefore, the erosion effect is also stronger for the shale powder with smaller particle size. In addition, the experimental results also showed that the higher the hydroxide ion, the greater the erosion rate. It can be seen that the higher the concentration of hydroxide ions, the more severe the reaction of the shale and alkali solution.

As shown in Figure 5, the experimental results show that the smaller the size of the shale powder, the higher the concentration of silica in the alkali solution after the reaction. It can be seen that shale powder with smaller particle size can react more quickly with the alkaline solution.
In addition, when the pH is 9 to 12, the concentration of silica in the alkali solution tends to increase slowly as the pH increases, but when the pH is more than 12, the concentration of silica in the alkali solution rapidly increases. And the data fitting results show that the silica concentration and pH accord with the power function. So, the experimental results also show that increased concentration of hydroxide ions can induce more intense reactions. Especially, when the pH exceeds 12, the reaction rate increases faster.

According to the theory of chemical reaction kinetics, the reaction rate between the shale and alkaline solution can be expressed by the following equation [25]:

\[ J = KC^m. \]  

(2)

In (2), \( J \) is the reaction rate (mol/(Ls)); \( K \) is the reaction rate constant \((\text{mol/L})^{1-m} \text{s}^{-1})\); \( C \) is the concentration of fluid (mol/L); and \( m \) is the reaction order (dimensionless).

According to the data fitting results (Figure 5), the relationship between the concentration of silicon and pH is in accordance with the expression of (2). In addition, the reaction between rock minerals and alkali solution can produce aluminosilicate products (Table 3). So, the silicon element concentration can reflect the degree of reaction between the shale and alkali solution. Based on the above analysis, the reaction kinetics equations of shale with different particle sizes and alkaline solution can be obtained (Table 4).

As shown in Table 3, for the shale with three particle sizes, the reaction constant is 0.008 to 0.048. And the reaction order is 0.970 to 1.155. A small reaction rate constant indicates that the reaction between shale and alkali solution occurs slowly, and a large reaction order indicates that the pH has a significant influence on the reaction rate [25, 26]. So, it can be seen that both shale particle size and concentration of hydroxide ion all affect the reaction rate, and the former has a negative correlation with the reaction rate, and the latter has a positive correlation with the reaction rate.

3.3. Effect of Alkaline Erosion on Shale Structure. As Figure 6 shows, soaking experiments of shale show that there were no obvious fractures seen on the shale surface before soaking into an alkaline solution. With the increasing of soaking time and pH, the alkaline erosion caused the fracture propagation along the bedding planes of shale. When the pH was 11 to 12, the alkali erosion effect for shale was reflected remarkably. The longer the soaking time was, the more obvious the fracture propagation became.

In addition, when the pH of the alkaline solution is 11 or 12, it can be observed that the fracture on the shale surface was filled with brown and white sediments. In order to further confirm the above experimental phenomena, scanning electron microscopy (SEM) analysis and energy dispersive spectroscopy (EDS) analysis were used to determine the erosion degree and reaction products on the shale surface. As shown in Figures 7(a) and 7(b), because of the alkali erosion effect, the shale surface appeared with a large amount of dissolution pores. Hexagon thin sheet minerals were further eroded into tiny flocules and small particles. Some products attached in the dissolution pore and presented a loose structure. As shown in Figures 7(c) and 7(e), the EDS of particles on the shale surface shows that the main component of these products are \( \text{CaCO}_3 \) and \( \text{Fe}_2\text{O}_3 \), respectively, which shows that the pyrite and dolomite in the shale have reacted with the alkali solution.

The aforementioned experimental results show that the alkaline erosion effect on shale can lead to the fracture propagation along the bedding plane, which may easily result in collapse along the fractures intersecting a wellbore.

4. Conclusion

(1) For alkaline solutions with different pH, the corrosion rate of minerals is not the same. The corrosion rates are as follows: kaolinite > smectite > quartz > quartz > illite > chlorite when the pH is 9; smectite > quartz > kaolinite > illite > chlorite when the pH is 10.
Table 4: Reaction kinetics equation of shale with different particle sizes.

<table>
<thead>
<tr>
<th>Particle size of shale (μm)</th>
<th>$K$ (mol/(L·s))</th>
<th>$m ((mol/L)^{1-m}·s^{-1})$</th>
<th>Reaction kinetic equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1~10</td>
<td>0.048</td>
<td>0.970</td>
<td>$J = 0.048C^{0.970}_{NaOH}$</td>
</tr>
<tr>
<td>25~60</td>
<td>0.015</td>
<td>0.993</td>
<td>$J = 0.015C_{NaOH}$</td>
</tr>
<tr>
<td>75~100</td>
<td>0.008</td>
<td>1.155</td>
<td>$J = 0.008C^{1.155}_{NaOH}$</td>
</tr>
</tbody>
</table>

Figure 6: The results of shale fracture development rolling into different pH solutions at different times.

Figure 7: Continued.
or 11; quartz > illite > smectite > kaolinite > chlorite when the pH is 12.

(2) Reaction kinetics experiments show that both shale particle size and concentration of hydroxide ion all affect the reaction rate, and the former has a negative correlation with the reaction rate, and the latter has a positive correlation with the reaction rate.

(3) The alkaline erosion effect on shale can lead to the fracture propagation along the bedding plane, which can easily result in collapse along the fractures intersecting a wellbore.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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