Investigation on the Interaction of Alkaline Chemical Stimulation with the Hot Dry Rock (HDR) with Quartz-rich Minerals

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ABSTRACT
Hot Dry Rock (HDR) is a kind of high temperature rock, with low porosity and permeability, which is mostly composed of metamorphic rock or granite. Enhanced Geothermal System (EGS) is an effective method for exploiting HDR geothermal resources, which stimulates the rock matrix artificially for improving the production performance. Efforts have been made to create fracture networks and open the existed fractures to improve performance of EGS. As a consequence, chemical stimulation, in addition to hydraulic/thermal fracturing, has been proposed and employed as an important method for the reservoir stimulation. In 2017, huge potential of HDR resources was found by drilling in Gonghe Basin of Qinghai Province, Northwest China. The temperature reached 236°C at the depth of 3706m. Consequently, the first EGS demonstration project of China will be developed in the basin. The lithology of drilling core samples in Gonghe Basin is mainly feldspar and quartz minerals. Alkaline chemical stimulation may be the best choice for improving permeability of HDR. However, complex chemical composition of lithology in the actual stratum resulted in the formation of secondary minerals. This study explored the interaction mechanism of alkaline agents on feldspar and quartz minerals. Based on laboratory experiments, the effective components of alkaline agents are proposed to promote dissociation of specified minerals and avoid serious formation of secondary minerals. Laboratory experiments results show that solution ratio is more than 20%. The components of scale inhibitors and masking agents can effectively extend the reaction time and increase penetration distance by reducing the formation of secondary minerals. The results of this study can provide theoretical support for the construction of EGS demonstration projects in the Gonghe Basin, and provide a corresponding scientific basis for the development of similar types of HDR in the future.

1. INTRODUCTION
With global resource shortage, the constant deterioration of the ecological environment, survived and brought a series of influence and challenge for the mankind. Geothermal resources, as a kind of clean energy with stable operation and wide spatial distribution, have gradually become the focus of attention of all countries in the world. Geothermal resources include hydrothermal energy and hot dry rock energy (Wallroth T et al, 1999). Hydrothermal geothermal resources account for only a very small part of them. Hot Dry Rock (HDR) is a kind of rock mass with economic development value with a temperature of 180 °C or higher, which generally refers to 3-10 km underground and no water. It is conservatively estimated that the energy of hot dry rock in the earth's crust is equivalent to 30 times the energy of all oil, natural gas and coal in the world (Xu T, Yuan Y et al, 2016). According to the latest data from the China Geological Survey, the total amount of hot dry rock resources in China is equivalent to 860 trillion tons of standard coal. If 2% of that is extracted, it is equivalent to 4,400 times the total national disposable energy consumption in 2015(Wang J, Hu S, Pang Z, et al, 2012). It is foreseen that the development of dry and hot rock resources will make a major contribution to China's energy conservation and emission reduction and new round of energy structure adjustment with the advancement of science and technology.

Enhanced Geothermal Systems (EGS) is an artificial geothermal system that forms artificially geothermal reservoirs to economically extract deep thermal energy from low-permeability rock masses. In other words, it is geothermal projects from hot dry rocks (Benato and Taron, 2016). The key technology of successful EGS is the transformation of hot dry rock thermal reservoirs, that is, artificially expanding the original natural fissures in the low permeability rock mass or generating new fissures to form a fracture network and increase the contact area between water and rock mass, to enhance the hydraulic connection between production and injection wells and artificial geothermal reservoir fracture networks and meet capacity needs. At present, the hot reservoir excitation methods commonly used in the world mainly include hydraulic fracturing, chemical stimulation and thermal stimulation. The hydraulic fracturing method can crush the rock mass by high-pressure mass and form a new artificial heat storage fissure, which is widely used in the transformation of large-volume thermal reservoirs (Portier, Vuataz et al, 2009). The thermal stimulation method can produce cracks, which caused by the thermal cracking of the rock components (Zhao Y., Wan Z., et al, 2010). The chemical stimulation inject chemical stimulants into the thermal reservoir fractures near the well with injection pressure lower than the fracture pressure of the formation, and dissolve the thermal reservoir fracture channel plugs by its chemical dissolution to increase the vicinity of the wellbore and the permeability of the distant formation. Due to the advantages of low risk and well penetrating performance of chemical stimulation, it has gradually got more attention.

Chemical stimulation includes acidic chemical stimulation and alkaline chemical stimulation. In acid chemical stimulation, mud acid is widely used in existing EGS demonstration projects due to its low price and strong dissolution effect (Na, Xu et al, 2016). For example, the Soulzt EGS site in France is mainly filled with carbonate minerals such as calcite. After the acid conversion of the reservoir, the injection rate of the well GPK4 increased by 35% (Gerard, Genter et al, 2006, Cuenot, Faucher et al, 2008). However, the reaction rate between mud acid and rock is too fast to penetrate deep into the rock mass. Zhuang shows that the acid-stimulated rock mass will cause precipitation of potassium fluorophosphates (K3AlF6), potassium fluorosilicate (K2SiF6) and amorphous dioxide silicon (SiO2), blocking the fracture channel (Zhuang, Zhang et al, 2017). In 1977, Fenton Hill EGS used Na2CO3 and NaOH solution to dissolve quartz minerals in rock mass fissures. The experimental results show that the alkaline dissolution effect is well, and the dissolution effect increases with the increase of concentration and stimulation time. Rose (Rose Peter, 2007) proposed the use of NaOH and the chelating agent NTA to form an alkaline chemical stimulator, NaOH dissolve silicate and...
aluminosilicate minerals in the fracture channel, and the high pH chelating agent NTA is used to dissolve calcite, SiO₂ and feldspar, and form a chelate with metal ions in water to avoid the formation of secondary precipitation (Xu, Rose et al, 2009). Another commonly used chelating agent is EDTA. Malate studied the applicability to the dissolution of calcite minerals in rock formations, concluding that EDTA is a very effective mineral solubilize and the solubility increases with increasing temperature. In view of the fact that the reservoir fissures in the Gonghe Basin are quartz-type hot-dry rocks such as quartz and aluminosilicate materials, acid chemical stimulation cannot achieve satisfactory corrosion effects. Laboratory experimental studies of alkaline chemical stimulators and rocks are not sufficient. In order to further study the reaction mechanism between alkaline chemical stimulator and granite hot dry rock mass, this paper selects granite samples from Gonghe Basin as the research object, and conducts alkaline chemical stimulation research of granite with different reaction duration under high temperature and high pressure conditions. The dissolution of granite minerals and the formation of secondary minerals before and after the reaction, combined with the change of chemical composition of the solution, which reveal the reaction mechanism of alkaline chemical stimulator and rock.

2. GEOLOGICAL CONDITIONS ON RESERVOIR
The Gonghe Basin is located in Gonghe County, Qinghai Province, China, which is between the Kunlun Mountains and the Qinling Mountains. The total area of the basin is 13,800 km². The intrusive rock lithology is dominated by granite, granodiorite, quartz diorite and porphyritic granite. The basin has a high heat flow value, the average temperature gradient is greater than 5°C/100 m. Gonghe Basin has successfully constructed 5 hot dry rock exploration holes with depth of 3000-3705 m and a bottom hole temperature of 180~236°C at present (Xue, Gan et al, 2013; Zhang et al, 2018). The GR1 hot dry rock exploration hole has a depth of 3705 m, which reaches 236 °C at bottom. This is the hottest dry rock that has been drilled in China so far, and has achieved a major breakthrough in the exploration of hot dry rock in China.

3. EXPERIMENTAL MATERIALS AND METHODS
3.1 Alkaline chemical stimulation test material
The rock samples in this experiment are from the Qabqa Valley of the Gonghe Basin. The lithology of this area is altered granite, which is a typical granite-type hot dry rock reservoir with a reservoir temperature of 150°C. The altered granite with a drilling depth of 3200m in the GR1 well was selected as the experimental object. The systematic mineral composition analysis test (XRD) was carried out on the collected granite samples before the experiment. The analysis results are shown in Table 1. It is shown that the main minerals in granite rock samples are quartz, plagioclase, chlorite, potassium feldspar, muscovite and biotite. The content of quartz is 44%, the content of plagioclase is 36%, green. The content of mudstone is 8%, the content of potassium feldspar is 5%, the content of muscovite is 5%, and the content of biotite is 2%.

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Mineral composition of Qinghai Gonghe hot-dry rock granite samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mineral</td>
<td>quartz</td>
</tr>
<tr>
<td>Volume fraction (vol. %)</td>
<td>44</td>
</tr>
</tbody>
</table>

3.2 Experiment schemes of alkaline chemical stimulation
As one of the common methods of reservoir stimulation, chemical stimulant can dissolve the primary minerals in the fractures of hot dry rock reservoirs effectively, increase the permeability of hot dry rock mass, and form a good fracture network. The chemical stimulating effect is mainly controlled by the type of chemical stimulant and the reaction rate of chemical stimulant and rock. Therefore, it is especially important to select the appropriate chemical stimulant for improving the reservoir stimulation effect for different reservoirs. NaOH can dissolve feldspar minerals such as quartz and plagioclase, and the corrosion capacity increases with the increase of temperature, which can be effectively applied to HDR reservoirs. In addition, NaOH has a slower dissolution rate than the acidic chemical stimulator such as mud acid, and has good penetrating performance, which can achieve the purpose of deep reformation of hot dry rock reservoir. However, some of the dissolved components of NaOH alkaline solution reacts with the rock sample to form amorphous SiO₂ or amorphous aluminosilicate altered minerals. For example, Na⁺ combines with Si³⁺ and Al³⁺ to form albite, and these secondary minerals are attached on the surface of the rock. Some new cracks are blocked, which makes the rock mass permeability relatively lower, and affects the reservoir transformation effect. The primary minerals in the fractures of the reservoir rock (calcite, amphibole, etc.) release metal ions such as Ca²⁺ and Mg²⁺, which will precipitate with Ca(OH)₂ and Mg(OH)₂ on the fracture channel. Not only will block the fissure channel, but also prevent the contact between the rock mass in the deep part of the reservoir and the alkaline stimulation, and hinder the further dissolution of the alkaline stimulation. Therefore, a single alkaline chemical stimulant cannot meet the requirements for the transformation of hot dry rock thermal reservoirs in the study area. The chelating agent can chelate with the metal ions (K⁺, Al³⁺, Ca²⁺, Mg²⁺) released by the dissolution of the primary mineral to form a stable water-soluble chelate, thereby blocking the metal ions to participate in the secondary precipitation formation process and reducing the secondary precipitation. The chelating agents currently used mainly are: NTA and EDTA. Therefore, this experiment selected 10% NaOH, 10% NaOH + 3% EDTA, 10% NaOH + 3% NTA as chemical stimulant to explore the mechanism of action of alkaline chemical stimulator and rock mass, which reveal the law of secondary precipitation formation.

The ground temperature of the buried depth of 3200 m in the reference study area is about 150°C. Therefore, the design temperature of this experiment is 150°C and the pressure is 10MPa. In order to ensure that the stimulating fluid and rock react fully, the ratio of alkaline chemical stimulator and rock is 20:1, and the reaction time is 2h, 4h, 6h, 8h, 12h, 24h.
### Table 2 Experiment schemes of alkaline chemical stimulation

<table>
<thead>
<tr>
<th>Number</th>
<th>Component</th>
<th>Temperature (°C)</th>
<th>Pressure (MPa)</th>
<th>Reaction duration (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10%NaOH</td>
<td>150</td>
<td>10</td>
<td>2, 4, 6, 8, 12, 24</td>
</tr>
<tr>
<td>2</td>
<td>10%NaOH+3%EDTA</td>
<td>150</td>
<td>10</td>
<td>2, 4, 6, 8, 12, 24</td>
</tr>
<tr>
<td>3</td>
<td>10%NaOH+3%NTA</td>
<td>150</td>
<td>10</td>
<td>2, 4, 6, 8, 12, 24</td>
</tr>
</tbody>
</table>

### 3.3 Experimental equipment and analytical instruments

This experiment used ML-0.3 high temperature and high pressure reactor (Fig. 1). The standard capacity of the reaction vessel of the high temperature and high pressure reactor is 300ml; the material is Hastelloy, which has a higher corrosion resistance. The maximum working temperature is 400°C and the highest pressure is 12 MPa. The reactor is equipped with a magnetic stirring rod to adjust the stirring speed. At the same time, in order to maintain the temperature required for the experiment, the reaction kettle is placed in a heating jacket and the temperature is controlled by a thermal sensor. The nitrogen bottle provided for the reactor can provide a maximum pressure of 25 MPa to the reactor, and the pressure in the kettle increases correspondingly with an increase in temperature. Adjust the nitrogen gas inlet valve, set the nitrogen bottle outlet pressure to 1.5 MPa, increase the inlet pressure to 10 MPa through the air pressurization system, the pressure after the reactor is stable is 10 MPa, and the temperature of the temperature controller is set to 150°C. The experimental analysis is: X-ray fluorescence spectrometer, JSM-6700F field emission scanning electron microscope.

![Figure 1: ML-0.3 high temperature and high pressure reactor structure diagram](image)

### 3.4 Experimental methods

Firstly, determine the mineral composition and proportion of granite rock samples (including XRD and scanning electron microscopy analysis), then treat the rock sample into particles with a particle size of 5 mm-10 mm, soak the rock block with ultrapure water, rinse, and remove the surface adhesion ions, after drying, are divided into several equal parts. In order to observe the scanning electron micrograph of the rock after the reaction facilitate easily, a rock piece of 1cm×1cm×0.1mm is added to each reaction rock block, and the total mass of the rock block and rock piece is 10g; Measure 200g of alkaline stimulation with (mass concentrations) 10% NaOH, 10% NaOH + 3% EDTA, 10% NaOH + 3% NTA, transfer to the reaction vessel, insert the granite sample, seal the reaction kettle, and pass into the reaction kettle. Nitrogen pressurization, after the pressure in the autoclave is stabilized; the heating switch is turned on. As the temperature increases, the pressure in the autoclave gradually rises until the temperature stabilizes to 150 °C, the pressure stabilizes at 10 MPa, Reaction reacts at a fixed temperature and pressure for different periods of time, and then the power is turned off to naturally cool to room temperature; when the room temperature condition is reached, the residual gas is released, the reaction kettle is opened, the sample and the reaction liquid are taken out; the sample is taken out, repeatedly washed with distilled water, and then weighed. The dissolution rate of the rock was calculated; the reaction solution was taken out with a disposable needle tube, concentrated in a PET bottle for filtration, and the chemical reaction composition of the filtered reaction solution was analyzed; the rock fragments after the reaction were subjected to scanning electron microscope analysis.
4. RESULTS AND DISCUSSION

4.1 Change of solution rate of granite samples after reaction

The chemical stimulator can dissolve the granite sample, which causes the quality of the granite sample change. The change in the quality of the granite sample can reflect the strength of the chemical stimulant dissolution. The dissolution rate, is the percentage of mass loss of granite samples before and after the reaction, which is an important indicator reflecting the dissolution of granite samples. The calculation formula of rock dissolution rate is:

$$SR = \frac{M_0 - M_1}{M_0} \times 100\%$$ (1)

Where SR is the solution rate of rocks; $M_0$ and $M_1$ is the rock mass before reaction and after reaction respectively.

Table 3, 4, 5 show that solution rate of three different chemical stimulators (10% NaOH, 10% NaOH + 3% EDTA, 10% NaOH + 3% NTA). And Figure 2 show that solution rate curve of three different chemical stimulators reacting with rock for different durations.

Table 3 Solution rate of granite rock reacted with 10% NaOH for different durations

<table>
<thead>
<tr>
<th>Reaction duration (h)</th>
<th>$M_0$/g</th>
<th>$M_1$/g</th>
<th>Solution rate (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>9.990</td>
<td>9.880</td>
<td>1.10</td>
</tr>
<tr>
<td>4</td>
<td>10.050</td>
<td>9.696</td>
<td>3.52</td>
</tr>
<tr>
<td>6</td>
<td>10.011</td>
<td>9.485</td>
<td>5.54</td>
</tr>
<tr>
<td>8</td>
<td>10.010</td>
<td>9.638</td>
<td>3.72</td>
</tr>
<tr>
<td>12</td>
<td>10.004</td>
<td>8.757</td>
<td>12.47</td>
</tr>
<tr>
<td>24</td>
<td>9.796</td>
<td>7.405</td>
<td>24.40</td>
</tr>
</tbody>
</table>

Table 4 Solution rate of granite rock reacted with 10% NaOH+3%EDTA for different durations

<table>
<thead>
<tr>
<th>Reaction duration (h)</th>
<th>$M_0$/g</th>
<th>$M_1$/g</th>
<th>Solution rate (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>10.010</td>
<td>9.920</td>
<td>0.90</td>
</tr>
<tr>
<td>4</td>
<td>10.030</td>
<td>9.847</td>
<td>1.82</td>
</tr>
<tr>
<td>6</td>
<td>9.990</td>
<td>9.293</td>
<td>6.98</td>
</tr>
<tr>
<td>8</td>
<td>10.030</td>
<td>9.487</td>
<td>5.41</td>
</tr>
<tr>
<td>12</td>
<td>10.004</td>
<td>8.873</td>
<td>11.31</td>
</tr>
<tr>
<td>24</td>
<td>10.087</td>
<td>7.9531</td>
<td>21.15</td>
</tr>
</tbody>
</table>

Table 5 Solution rate of granite rock reacted with 10% NaOH+3%NTA for different durations

<table>
<thead>
<tr>
<th>Reaction duration (h)</th>
<th>$M_0$/g</th>
<th>$M_1$/g</th>
<th>Solution rate (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>9.980</td>
<td>9.690</td>
<td>2.91</td>
</tr>
<tr>
<td>4</td>
<td>10.050</td>
<td>9.681</td>
<td>3.67</td>
</tr>
<tr>
<td>6</td>
<td>9.989</td>
<td>9.324</td>
<td>6.66</td>
</tr>
<tr>
<td>8</td>
<td>10.030</td>
<td>9.083</td>
<td>9.44</td>
</tr>
<tr>
<td>12</td>
<td>10.015</td>
<td>8.792</td>
<td>12.21</td>
</tr>
<tr>
<td>24</td>
<td>9.960</td>
<td>8.043</td>
<td>19.25</td>
</tr>
</tbody>
</table>
As shown in Figure 2, the alkaline chemical stimulator can effectively dissolve the granite sample. As the reaction time increases, the rock dissolution rate also increases. When the reaction time is 24h, the 10% NaOH has the highest degree of dissolution of rock, and the dissolution rate can reach 24.4%; 10% NaOH + 3% EDTA, the dissolution rate is 21.15%; 10% NaOH + 3% NTA is the lowest, the dissolution rate was 19.25%. However, when the reaction time arrives 6h, the dissolution rate of rock by 10% NaOH and 10% NaOH + 3% EDTA solution suddenly decreased. After 8h, the dissolution rate increased again, while 10% NaOH + 3% NTA dissolved the rock. The rate is on a continuous upward trend. This is because 10% NaOH and 10% NaOH + 3% EDTA two chemical stimulants generate more secondary precipitation, the negative effect of secondary precipitation is greater than the positive influence of dissolved minerals, so the dissolution rate shows a downward trend (The generation of secondary sediments will be detailed in 4.3). In order to analyze the dissolution of granite samples, the scanning electron microscopy and energy spectrum analysis of the rock fragments were carried out after the chemical stimulation was completed, as shown in, Fig. 4 and Fig. 6. The results show that the rock minerals have been dissolved to different extents, and irregular dissolution cracks and dissolution pores appear on the surface of quartz and plagioclase.

### 4.2 Corrosion of main minerals in granite samples after reaction

#### 4.2.1 Quartz dissolution

It can be seen from Fig. 3 that as the reaction time increases, the content of quartz decreases gradually, which is dissolved by NaOH, and finally remains stable. When the reaction time is 24h, the 10% NaOH has the highest degree of dissolution of quartz, the content of quartz is 8%; 10% NaOH + 3% NTA, the content of quartz is 12%; 10% NaOH + 3% EDTA is the lowest, the content of quartz is 23%. Similar to Similar to figure 2:Solution rate curve of three different chemical stimulators reacting with rock for different durations, when the reaction proceeds to 6h, the corresponding quartz content of 10% NaOH and 10% NaOH+3% EDTA solution decreases suddenly. After 8h, the content of quartz increased again, while the dissolution rate of 10% NaOH+3% NTA on the rock showed an inflection point when the reaction was 4h, and the change range was smooth. Because the secondary precipitation (Si<sup>2+</sup> released by quartz and other metal ions in the solution form secondary precipitates such as chlorite and montmorillonite.) by 10% NaOH and 10% NaOH+3% EDTA is more than 10% NaOH + 3% NTA (the formation of secondary precipitation will be detailed in 4.3).

<table>
<thead>
<tr>
<th>Reaction duration (h)</th>
<th>10% NaOH</th>
<th>10% NaOH+3% EDTA</th>
<th>10% NaOH+3% NTA</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>44.00%</td>
<td>44.00%</td>
<td>44.00%</td>
</tr>
<tr>
<td>2</td>
<td>26.00%</td>
<td>24.00%</td>
<td>25.00%</td>
</tr>
<tr>
<td>4</td>
<td>25.00%</td>
<td>25.00%</td>
<td>10.00%</td>
</tr>
<tr>
<td>6</td>
<td>18.00%</td>
<td>19.00%</td>
<td>12.00%</td>
</tr>
<tr>
<td>8</td>
<td>22.00%</td>
<td>25.00%</td>
<td>13.00%</td>
</tr>
<tr>
<td>12</td>
<td>15.00%</td>
<td>22.00%</td>
<td>13.00%</td>
</tr>
<tr>
<td>24</td>
<td>8.00%</td>
<td>23.00%</td>
<td>12.00%</td>
</tr>
</tbody>
</table>
Figure 3: Content of quartz variation curves of three different chemical stimulators reacting with rock at different durations.

Scanning electron micrograph shows that the originally smooth quartz surface is eroded by chemical stimulants to form many tiny cracks and holes. As time goes on, the cracks become deeper and the pores expand gradually.
4.2.2 Plagioclase dissolution

Fig. 3 shows that as the reaction time increases, the content of plagioclase present a certain fluctuation, but the trends of the three chemical stimulations on the content of plagioclase are consistent. Before 4h, the plagioclase was dissolved by NaOH, and the content of plagioclase decreased gradually. When the reaction at 6h, the quartz was dissolved by NaOH, and the content of plagioclase increased indicating that the quartz was converted to plagioclase; after 8h, the plagioclase continued to be dissolved by NaOH. The content of plagioclase continues to decrease accompanied by the formation of plagioclase (plagioclase is secondary precipitation). As the reaction continues, the content of secondary precipitated plagioclase increases gradually and eventually remains stable relatively. The change of plagioclase content indicates that plagioclase is not only dissolved, but a dynamic process of dissolution-precipitation, which reaches a certain dynamic equilibrium as the reaction time increases.
Table 7 Plagioclase content of three different chemical stimulators reacting with rock at different durations

<table>
<thead>
<tr>
<th>Reaction duration (h)</th>
<th>10%NaOH</th>
<th>10%NaOH+3%EDTA</th>
<th>10%NaOH+3%NTA</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>36.00%</td>
<td>36.00%</td>
<td>36.00%</td>
</tr>
<tr>
<td>2</td>
<td>12.00%</td>
<td>11.00%</td>
<td>12.00%</td>
</tr>
<tr>
<td>4</td>
<td>10.00%</td>
<td>17.00%</td>
<td>16.00%</td>
</tr>
<tr>
<td>6</td>
<td>36.00%</td>
<td>39.00%</td>
<td>51.00%</td>
</tr>
<tr>
<td>8</td>
<td>15.00%</td>
<td>15.00%</td>
<td>22.00%</td>
</tr>
<tr>
<td>12</td>
<td>36.00%</td>
<td>39.00%</td>
<td>48.00%</td>
</tr>
<tr>
<td>24</td>
<td>30.00%</td>
<td>38.00%</td>
<td>48.00%</td>
</tr>
</tbody>
</table>

Figure 5: Content of plagioclase variation curves of three different chemical stimulators reacting with rock at different durations

Scanning electron micrograph pictured that the surface of the originally smooth plagioclase is eroded by chemical stimulants to form many tiny cracks and holes, and the surface of the plagioclase has a book-like kaolinite secondary precipitate.
4.3 Formation of secondary minerals after reaction

Since the dissolution rate curve and the quartz curve showed an inflection point at the reaction time of 6h under the 10% NaOH and 10% NaOH+3% EDTA stimulation. For this reason, the secondary minerals of the reaction for 4h, 6h and 8h were studied specially. At 4h, secondary precipitation began to form, 10% NaOH produced spherical SiO2, 10% NaOH + 3% EDTA produced albite, 10% NaOH + 3% NTA produced plagioclase, and the number of secondary precipitates attached to the surface of quartz and cracks was small.
When the reaction was carried out for 6 hours, the content of secondary precipitates increased and it had specific morphological characteristics. 10% NaOH produced chlorite, montmorillonite, 10% NaOH + 3% EDTA produced anorthite, 10% NaOH + 3% NTA produced less secondary precipitates, and secondary precipitation was not observed by scanning electron microscopy. During this period, the large amount of secondary precipitation promoted the dissolution of quartz, but the amount of secondary precipitation was larger than that of quartz. Therefore, the solution rate of rock decreased, and the curve of quartz content and the curve of dissolution rate showed an inflection point. In addition, due to the scale inhibition effect of the chelating agent, 10% NaOH + 3% EDTA and 10% NaOH + 3% NTA produced less secondary precipitates, and 10% NaOH produced the most secondary precipitates, so during this period, 10% NaOH has the lowest solution rate.
Figure 8 Formation of secondary precipitation of three different chemical stimulators reacted with rock for 6h

When the reaction was carried out for 8 hours, 10% NaOH continued to form secondary precipitates, and the clay mineral chlorite developed into a regular spherical shape, and the solution rate of 10% NaOH was the lowest at this time point. As the reaction continues, the secondary mineral sodium feldspar and the like are dissolved, and the dissolution rate rises again. Due to the scale inhibition effect of the chelating agents EDTA and NTA, secondary minerals were not found at this time point, and it was also possible that the secondary mineral content was small and difficult to detect.
5. CONCLUSION

Based on the alkaline chemical stimulation result, the following conclusions are obtained:

(1) Compared with mud acid, the alkaline chemical stimulator has a low solution rate because the reaction rate of the alkaline chemical stimulation is slow. As time goes on, the solution rate increases to 24.4% (the highest) gradually.

(2) Although 10% NaOH has a high solution rate, it will produce more secondary precipitation. The chelating agents EDTA and NTA inhibit the formation of secondary precipitates.

(3) NTA has better solution effect than EDTA chelating agent, produces the less secondary precipitation and has good scale inhibition.

(4) The altered minerals produced by the reaction of alkaline chemical stimulation with rock are mainly clay minerals (such as chlorite, montmorillonite, anorthite, etc.), which are intermediate products and decrease with increasing reaction time.

(5) When plagioclase is dissolved, it also produces secondary precipitation of feldspar, which is a dissolution-precipitation dynamic equilibrium process.

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