Experimental Study on the Autogenic Acid Fluid System of a High-Temperature Carbonate Reservoir by Acid Fracturing

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ABSTRACT: As an important part of the acid fracturing process of carbonate reservoir, the performance of acid fracturing working fluid directly affects the stimulation effect of oil wells. In this paper, formaldehyde (agent A) and ammonium chloride (agent B) were used as the matrix. Several aldehydes with different volume ratios were prepared. The acid ratio with the highest acid yield was selected by the sodium hydroxide titration experiment. The results show that when the volume ratio of agent A to agent B is 1:1.3, the acid production capacity is the strongest. The pH values at several time points in the process of acid reaction were measured by a pen pH meter. The relationship curve between acid production capacity and time was obtained. The acid production capacity increased with time. It tends to be stable after a certain time. The experiment of acid rock reaction kinetics shows that the reaction rate between acid and rock decreases with the extension of time. The reaction time can reach 6 h. The reaction rate of autogenic acid under different temperatures and concentrations ranges from $6.61 \times 10^{-7}$ to $9.49 \times 10^{-7}$ mol/(s·cm$^2$) within 6 h. Therefore, it indicates that the reaction time between autogenic acid and carbonate rock is long and the reaction rate is low. It is beneficial to improve the acid treatment effect of the carbonate reservoir. The conductivity experiments show that at different temperatures, with the increase of sealing pressure, the etching ability of autogenic acid decreases. The etching effect is better at 338 K. After etching, the permeability and conductivity of the rock slab of 5 MPa closure pressure are 227 D and 72.62 D·cm, respectively. To sum up, this autogenic acid is an effective working fluid in the acid fracturing process of the carbonate reservoir. It can obviously reduce the reaction rate of acid rock and has certain conductivity.

1. INTRODUCTION

Carbonate reservoirs worldwide are complex in structure, diverse in form, and highly heterogeneous, which is one of the key and hot areas in current oil and gas exploration and development.1 Stimulation technology for the carbonate reservoir is the key technology for exploration and development of the carbonate reservoir. Acid fracturing is one of the main measures to increase production of carbonate reservoirs with strong heterogeneity. As the acid flows into natural fractures that intersect hydraulic fractures (main fractures), it etches the walls of the natural fractures, which then increases the natural fractures’ width and generates conductivity.2 Among them, the performance of acid pressing working fluid and acid additives directly affects the acid pressing effect, especially in high-temperature deep Wells.3,4 Due to high reservoir temperature and fast acid rock reaction, the effective length of acid-etched fracture after acid compression is short.5 At the same time, the reservoir temperature is high. It will cause serious acid corrosion of downhole string and easy to cause equipment damage.5

In order to solve these difficulties, technicians at home and abroad have carried out in-depth research on the unconventional acid system. The thickener and crosslinking agent in crosslinking acid can generate high strength stereoscopic network gel through crosslinking, which can effectively reduce the reaction speed of acid rock, improve the penetration depth and the conductivity of acid erosion fracture, and prolong the validity period of acid compression.7–10 Emulsified acid is a multiphase system composed of an oil phase and acid phase. It has high viscosity, good filtration reduction, slow speed effect, strong corrosion ability, and small corrosion and does little damage to the strength of pipe string. Emulsified acid is widely used in repeated acid pressure or high sulfur gas well acid pressure, and the use of emulsified acid in matrix acidification is also significantly increased.11–15 Gelled acid can reduce the filtration loss of acid solution, form a colloidal network structure, and reduce the diffusion of H+. Thickened acid can form wide cracks, small filtration loss, and low friction and
show good performance of suspended solid particles in the process of acid pressing.\textsuperscript{16–18} Autogenic acid is an acid product produced in situ by chemical dissociation or reaction of fluid injected into the formation. It has no acidity or weak acidity on the surface, but acid is produced gradually at the bottom of the hole temperature, and acid production is carried out gradually, which can effectively reduce the acid rock reaction rate, prolong the acid action distance, and reduce the corrosion effect on the underground pipe string.\textsuperscript{19–23}

According to the mechanism of acid-rock reaction, acid-rock reaction speed is closely related to the ability of acid to release hydrogen ions and reaction kinetic parameters. In recent years, many scholars have conducted a lot of research and summarized the acid-rock reaction behavior. Yoo used the apparatus repeatedly to investigate the reaction kinetics of dolomite rock under the various concentrations of fresh acid and spent acid. It was revealed that the dissolution rate and diffusion coefficient for spent acid were higher than those of fresh acid due to the higher kinematic viscosity and the lower pH of spent acid.\textsuperscript{24} Mahmoud used a new synthetic Gemini surfactant as a fracturing fluid additive to stabilize the clay in the fracturing of unconventional dense sandstone.\textsuperscript{25} Kamal proposed to use the polyoxyethylene quaternary ammonium gemini surfactants with different types of spacers as clay swelling additives in completion fluids to mitigate the formation damage in unconventional reservoirs.\textsuperscript{26} Kalam reviewed several waterless technologies for improving shale and ultratight rocks conductivity and introduced some available simulation techniques for monitoring the performance of these techniques.\textsuperscript{27} Gomaa used an in situ-generated hydrofluoric acid (HF) for sandstone acidizing, where an acid precursor (ammonium fluoride NH\textsubscript{4}F) reacted with a suitable oxidizer (sodium bromates NaBrO\textsubscript{3}) in an exothermic reaction. Upon application of this new simulation technology, the true production potential of sandstone reservoirs can be achieved, well tubular corrosion will be minimized, and handling hazardous chemicals such as HF will be avoided.\textsuperscript{28} Zhao synthesized a series of cationic Gemini surfactants with different hydrophobic chain lengths (C\textsubscript{n}=12, 14, 16). The surface tension, adhesion work, and AFM are used to evaluate the performance of these techniques.\textsuperscript{29} Tarig investigated the performance of the chelating agents, namely, ethylenediaminetetraacetic acid (EDTA) and glutamic acid N,N-diabetic acid (GLDA), in creating sufficient fracture conductivity. Several experiments/measurements were performed, the lab-scale outcomes were reproduced numerically, and field-scale simulations were carried out.\textsuperscript{30}

Therefore, the current research on the acid rock reaction behavior of carbonate reservoir. There are a large number of studies, both on-site acid rock jet experiment and indoor experimental research, such as acid rock reaction law, optimization of conventional acid system, synthesis of surfactants.\textsuperscript{31,32} However, there are few studies on the true acid system of a carbonate reservoir. Especially under the background of increasing exploration and development of carbonate reservoirs in China, the study of the autogenous acid system should be accelerated. This paper compares the acid production capacity of agent A and agent B under different ratios. The acid system with strong acid production capacity was selected. The reaction law of acid was evaluated by laboratory experiments.

### 2. EXPERIMENTAL SECTION

#### 2.1. Material

2.1.1. Carbonate Cores and Plates. In this paper, the three rocks shown in Figure 1 are used in the reaction kinetics experiment. The three rock slabs shown in Figure 2 are used for the conductivity test experiment. We take some rock samples and grind them into powder. Then we make a very flat sample. Next, we analyze the mineral composition of the carbonate rock by the Rigaku Smartlab9K X-ray diffractometer (with Cu Ko radiation at 40 kV and 40 mA); the test angle is 5–140°. Table 1 shows the test results.

The results show that the mineral composition of the six rock samples is mainly dolomite. The content of dolomite is the highest, up to 98%. The second is calcite. Therefore, the core (plate) used in the experiment is a typical rock sample of dolomite and calcite in a carbonate reservoir.

2.1.2. Potion. The potions used in titration experiments are NaOH solution (Chengdu Cologne Chemicals Co., Ltd.; Analytical purity) and potassium hydrogen phthalate (Chengdu Kelon Chemical Reagent Factory; Analytical purity).

The autogenic acid system studied in this paper mainly consists of two parts: formaldehyde (Chengdu Cologne Chemical Co., Ltd.; Analytical purity) and ammonium chloride (Chengdu Jinshan Chemical Reagent Co., Ltd.; Analytical purity). Formaldehyde and ammonium salt can produce H\textsuperscript{+}; this reaction is a characteristic reaction, as shown in eq (1). As the H\textsuperscript{+} is consumed, the reaction moves to the right and achieves a slow speed effect. This reaction can be carried out at room temperature, with the increase of temperature reaction speed.

\[
6\text{CH}_3\text{O} + 4\text{NH}_4\text{Cl} \rightarrow \text{N}_6\text{(CH}_3\text{)}_4 + 4\text{HCl} + 6\text{H}_2\text{O}
\]  \hspace{1cm} (1)

#### 2.2. Experiment Content

2.2.1. Formula Ratio Optimized in Aldehydes and Ammonium Salt. Through the NaOH titration experiment, the ratio of the formula can be optimized in aldehyde and ammonium salt. Before the experiment is performed, the concentration of the standard configured fluid needs to be corrected. We use potassium hydrogen phthalate for correction and record the volume of...
standard liquid consumed by four groups of solutions. Equation 2 calculates the concentrations of the four groups of standard fluids and takes the average value to obtain $0.10\text{--}1\text{ mol/L}$ standard fluid after correction.

$$C(\text{NaOH}) = \frac{m(\text{KHC}_2\text{H}_3\text{O}_4)}{M(\text{KHC}_2\text{H}_3\text{O}_4)V(\text{NaOH})} = \frac{m(\text{KHC}_2\text{H}_3\text{O}_4)}{204.22 \times V(\text{NaOH})}$$ \hspace{1cm} (2)

In order to find the best ratio of agent A and agent B in the autogenic acid system and optimize the autogenic acid formula. We fix 1 wt % formaldehyde and change the concentration of ammonium chloride from 0.8 to 1.4 wt %. After standing for 2 h at room temperature, we obtain 0.061 in.$^3$ autogenic acid and correct NaOH standard solution for multiple titration experiments. Then, we record the average volume of sodium hydroxide consumed to obtain the total amount of hydrochloric acid released by autogenous acid under different volumes.

2.2.2. Ability of Autogenic Acid to Produce Acid. The ability of autogenic acid to produce acid can be expressed by the hydrogen ion concentration during an acid reaction. The pen pH meter (Beekman Biotechnology Co., Ltd.; operating temperature 273--323 K) is used to measure pH in the process of acid reaction. Equation 3 can calculate the concentration of hydrogen ions in solution and make the curve of acid concentration in 3 h.

$$C(H^+) = 1/(10^{\text{pH}})$$ \hspace{1cm} (3)

Then, on the one hand, we test the effects of different temperatures (298, 313, and 323 K) on acid production capacity with concentration unchanged; on the other hand, we test the effects of different concentrations ($C_{0.5}$, $C_9$, $C_{10}$, $C_7$, $C_8$, $C_9$, and $C_{11}$) on acid production capacity with temperature unchanged.

2.2.3. Kinetics of Acid and Rock Reaction. Due to the limitation of pen pH meter’s operating temperature, it cannot accurately measure the pH in the process of autogenic acid reaction above 323 K. Therefore, according to the acid rock reaction kinetics experiment, the ability of autogenic acid to react with the core at higher temperature is tested.

We need to prepare three groups ($C_5$, $C_{10}$, and $C_{15}$) of 12.2 in.$^3$ autogenic acid. Carbonate cores are wrapped in thermoplastic tubes. Only the bottom of the core is left in contact with autogenic acid. After sealing them, we should place them successively in an oil bath at a speed of 20 rpm. Each concentration of autogenic acid reacts with the core at different temperatures (313, 338, and 363 K). 1.22 in.$^3$ acid samples are taken at certain intervals (0.5, 1, 2, 4, and 6 h), diluted 1000 times, and filtered with an $8.668 \times 10^{-6}$ needle filter. The spectrophotometer shown in Figure 3 (Beijing East West Instrument Co., Ltd.) can measure the calcium ion concentration in the solution, which tests the reaction ability of autogenic acid to carbonate rocks. Then, the reaction rate between acid and rock can be calculated according to eq 4.

$$J = -\left(\frac{\partial C}{\partial t}\right)\frac{V}{S}$$ \hspace{1cm} (4)

where $J$ refers to the reaction rate between acid and rock, mol/(s·cm$^2$); $C$ refers to the acid concentration at time $T$, mol/L; and $S/V$ refers to the area--volume ratio, that is, the ratio of the reaction area of the rock to the volume of the acid involved in the reaction, cm$^2$/cm$^3$.

2.2.4. Conductivity Test. We use the acid erosion conductivity evaluation device (Chengdu Core Technology Co., Ltd.) to test conductivity. The experiment adopts the sequence of etching first and conductivity later. The conductivity of $C_{10}$ autogenic acid to acid etching cracks of rock plates was tested at 313, 338, and 363 K.

Etching ability test is to place two iron wires between a pair of rock plates to form an acid etching channel. Before etching, the rock plate should be fixed in the gripper and placed in the water bath at the set temperature of preheat. Then, we should configure 61 in.$^3$. $C_{10}$ autogenic acid and open the advection pump. The carbonate rock plate is etched slowly at a flow rate of 0.18 in.$^3$/min. Five and a half hours later, the etching is finished. The etched plates are taken out, and the morphologic changes of the plates are observed with naked eyes or a 3D scanner.

Evaluation of conductivity is to test the permeability and conductivity of etched plates of water. The etched plates are loaded into the gripper and sealed. After adding a certain confining pressure, we need to open the advection pump and empty the gas in the pipeline at a flow rate of 0.61 in.$^3$/min. After preparation, we use the standard acid diversion software to set the closure pressure from 5 to 60 MPa and the...
acquisition cycle to 30 s. Finally, we test the permeability and conductivity of rock plates of water under different pressures. Figure 4 shows the flow of the specific experimental device.

3. RESULTS AND DISCUSSION

3.1. Formula Ratio Optimized in Aldehydes and Ammonium Salt. Figure 5 shows the amount of NaOH consumed by autogenic acids with multiple groups of volume ratios. The results show that ammonium chloride has the highest acid production efficiency at 1.3. Therefore, autogenic acid with a volume ratio of 1:1.3 will be used in subsequent experiments. 0.5 wt % CH₂O + 0.65 wt % NH₄Cl as C₀.5, 3 wt % CH₂O + 3.9 wt % NH₄Cl as C₃, and 10 wt % CH₂O + 13 wt % NH₄Cl at C₁₀ are defined.

Figure 5. Titration results of ammonium salt at different volume ratios.

3.2. Acid Production Capacities are Tested in Autogenic Acid. According to the experimental scheme of acid production capacity of autogenic acid, the dynamic process of hydrogen ion release of autogenic acid in the reaction process can be described. We tested the pH of autogenous acid at different acid concentrations and temperatures within 3 h. The ability curves of autogenous acid to release hydrogen ions in different environments were obtained. The results are as follows.

3.2.1. Acid Production Capacity is Tested at 298, 313, and 323 K. Autogenic acids can react to produce hydrogen ions at room temperature and under heating conditions. We use a pen pH meter to measure pH at different stages (0, 0.5, 1, 1.5, 2, 2.5, and 3 h) during the acid reaction process. Then, we calculate the concentration of releasing hydrogen ions by eq 3. Figure 6 shows the change of hydrogen ion released from the initial contact between formaldehyde and ammonium chloride to 3 h after the reaction. The results show that the capacity of acid production increased rapidly with time and tended to be stable after a certain time. At 298 K, C₃ reached a stable value of 3.8 × 10⁻² mol/L at 1.5 h. At 323 K, C₆ reached a stable value of 0.269 mol/L at 1 h. At 333 K, C₉ reached a stable value of 0.588 mol/L at 1 h.

3.2.2. Treatment with Temperature at Constant Concentration. The content of hydrogen ions in the solution of autogenic acid is fixed after the acid reacts for 1.5 h. Acid formation ability under this condition is affected by concentration and temperature. Figure 7 shows the change of treatment with temperature at constant concentration of autogenic acid. The results show that the hydrogen ion content in solution increases with the increase of temperature at the...
Figure 6. Changes in the amount of hydrogen ions released during 3 h of autogenic acid reaction: (a) C₃, (b) C₆, and (c) C₉.

Figure 7. Treatment with temperature at constant concentration.

Figure 8. Treatment with concentration at constant temperature.
same concentration. After multi-temperature treating, the increment of hydrogen ion content of high concentration autogenic acid is obviously larger than that of low concentration autogenic acid.

3.2.3. Treatment with Concentration at Constant Temperature. Figure 8 shows the change of the concentration of hydrogen ions released during the process of increasing the autogenic acid concentration from C₅ to C₁₀ at fixed temperature. The results show that the hydrogen ion content in solution increases with the increase of concentration at constant temperature. The effect of temperature on high concentration autogenic acid is greater than that on low concentration autogenic acid. In the process of increasing the temperature from 298 to 323 K, the concentration of hydrogen ions in C₉ solution increased by 12 times as much as that in C₃ solution.

3.3. Ability of Autogenic Acid to React with Calcium Carbonate. According to the experimental scheme of acid rock reaction kinetics, we can judge the reaction ability of acid and calcium carbonate. We measure the concentration of Ca²⁺ in solution by flame absorption with an atomic spectrophotometer and obtain the hydrogen ion concentration of self-generated acid consumed by the core within a certain period of time. The reaction rate of acid rock is calculated by eq 4.

3.3.1. Calcium Ion Content in Solution. Figure 9 shows the Ca²⁺ concentration in the solution during the reaction of autogenic acid with carbonate rock. Thus, Ca²⁺ concentration increases with time and the solution did not stop reacting until 6 h later. It shows that autogenic acid has good retarding performance and can prolong the reaction time of acid rock. The results show that the temperature has a great influence on the calcium content of the solution. The higher the temperature, the higher will be the concentration of Ca²⁺ in the autogenic acid solution. Concentration also has a certain effect on the content of calcium in the solution. The higher the concentration, the higher will be the calcium concentration. However, its effect is weaker than temperature.

Figure 10 shows the increase in Ca²⁺ concentration in solution during the reaction of autogenic acid with carbonate rock at 313 K. As can be seen from the figure, the change trend of Ca²⁺ increment over time in the acid reaction process is as follows: decrease first and reach a stable value after 2 h. Among them, the stable increment of calcium ions in C₅ solution is 3.77 × 10⁻² mol/L, that in C₁₀ is 4.49 × 10⁻² mol/L, and that in C₁₅ is 4.58 × 10⁻² mol/L. This indicates that autogenic acid has been releasing hydrogen ions within 6 h of reaction. It has strong release ability in the first 2 h. Hydrogen ions can also be released stably in the process of 2 to 6 h.

3.3.2. Rate of Acid Reaction with Rock. The Ca²⁺ concentration increases in a certain time during the reaction of autogenic acid with carbonate rock. It can reflect the hydrogen ion concentration consumed by acid generation in this time period so as to calculate the acid rock reaction rate. Because 1.22 in.³ samples are taken at each time point of the experiment, the area volume ratio in eq 4 varies with time.

Table 2. Reaction Rates of Autogenic Acid Rocks at Different Temperatures

| autogenic acid type | temp, K | reaction time, h | area volume ratio, cm²/cm³ | Ca²⁺ concentration, mol/L | reaction rate, mol/(s·cm²) |
|---------------------|---------|------------------|-----------------------------|--------------------------|---------------------------|
| C₅                  | 313     | 6                | 4.25 × 10⁻²                 | 0.304                    | 6.61 × 10⁻⁷               |
| C₁₀                 | 313     | 6                | 4.25 × 10⁻²                 | 0.325                    | 7.07 × 10⁻⁷               |
| C₁₅                 | 313     | 6                | 4.25 × 10⁻²                 | 0.344                    | 7.54 × 10⁻⁷               |
| C₅                  | 338     | 6                | 4.25 × 10⁻²                 | 0.394                    | 8.57 × 10⁻⁷               |
| C₁₀                 | 338     | 6                | 4.25 × 10⁻²                 | 0.409                    | 8.89 × 10⁻⁷               |
| C₁₅                 | 338     | 6                | 4.25 × 10⁻²                 | 0.421                    | 9.17 × 10⁻⁷               |
| C₅                  | 363     | 6                | 4.25 × 10⁻²                 | 0.416                    | 9.05 × 10⁻⁷               |
| C₁₀                 | 363     | 6                | 4.25 × 10⁻²                 | 0.426                    | 9.28 × 10⁻⁷               |
| C₁₅                 | 363     | 6                | 4.25 × 10⁻²                 | 0.439                    | 9.49 × 10⁻⁷               |

Figure 9. Ca²⁺ concentration in the reaction between autogenic acid and carbonate rock.

Figure 10. Increase in Ca²⁺ concentration during acid rock reaction at 313 K.
Table 2 shows the acid-rock reaction rates of autogenic acids at different temperatures and concentrations within 6 h. The reaction rate of acid rock is $6.61 \times 10^{-7}$ mol/(s·cm²) to $9.49 \times 10^{-7}$ mol/(s·cm²). The results show that the reaction rate between autogenic acid and carbonate rock is very low. It is beneficial to improve the acid treatment effect of the carbonate reservoir.

Table 3 shows the reaction kinetics experiments of autogenic acids used in this paper and those used previously. It can be seen that the reaction rates of used autogenic acid A, B, and C are lower than those used previously.

| autogenic acid type | temp, K | reaction time, h | acid formula | reaction rate, mol/(s·cm²) |
|--------------------|---------|------------------|--------------|---------------------------|
| autogenic acid A    | 393     | 6                | 30% (ammonium salt A2 + carbonyl compound G) + 3% HCl + 1% SA1-7 + 3% SA-3-2 + 0.3% HW-10 | $3.68 \times 10^{-6}$ |
| autogenic acid B    | 423     | 6                | 25% carboxylate I + 3% HCl + 1% SA1-7 + 3% SA-3-2 + 0.3% HW-10 | $3.83 \times 10^{-6}$ |
| autogenic acid C    | 443     | 6                | 30% acetate D + 3% HCl + 1% SA1-7 + 3% SA-3-2 + 0.3% HW-10 | $3.61 \times 10^{-6}$ |
| autogenic acid      | 363     | 6                | 15% formaldehyde + 19.5% ammonium chloride | $9.49 \times 10^{-7}$ |

Figure 11. Comparison of the front and rear faces of the lithographic plate etching at different temperatures: (a) 313 K etched plates 1, (b) 338 K etched plates 2, and (c) 363 K etched plates 3.

Figure 12. 3D scanning of the rock plate face.
are all on the dot product of $10^{-6}$. However, the quantitative product of the reaction rate of autogenic acid prepared from formaldehyde and ammonium chloride is $10^{-7}$, which is significantly lower than other types of autogenic acids.

### 3.4. Autogenic Acid Conductivity Tests

The conductivity test of acid etched fracture is one of the important indexes for calculating the effective action distance of acid and evaluating the effect of acid compression. Through this test, we can understand the fracture diversion morphology of artificial fracture and natural fracture after acid rock reaction under high temperature and high pressure. According to the experimental scheme of diversion, the three plates were first etched with $C_{10}$ autogenic acid at different temperatures to establish artificial fracture channels. Figure 11 shows the change of face morphology before and after etching of each pair of plates.

![Figure 11](image1.png)

**Figure 11.** The change of face morphology before and after etching of each pair of plates.

Table 4 shows the scanning results of autogenic acid etched rock slabs before and after scanning with 3D scanner at 363 K.

The results show that $C_{10}$ autogenic acid has a certain etching effect on the three plates at different temperatures. However, the etching morphology is not ideal. It can be observed from the plate change of the face before and after the plate etching that the acid solution at 313 K has poor etching effect on the rock plate and there are only a few etching marks on the end face of the rock plate. The acid solution at 338 K had a better etching effect on the plate, and several short crack channels were produced on the end face. The etching effect of acid solution at 363 K on the injection end of rock plate is better.

3D scans show that the slabs are intact before the acid etching. At 363 K, the color of slab inlet end turns yellow. It shows that the autogenic acid has a certain etching ability at the slab injection end. The blackening of the etched part is disturbed by the iron wire between the two plates. The color of the rest remains unchanged. It shows that the etching effect of autogenic acid on the rest of slate is poor.

Table 4 and Figure 13 show the conductivity test results of etching slabs. When the closure pressure is 5 MPa, the temperature is 338 and 363 K. The permeability of the etched plate is $210.16\text{ D}$. The conductivity is $67.23\text{ D} \cdot \text{cm}$. The permeability and conductivity of rock slab etched at 313 K at the same condition are only $36.77\text{ D}$ and $11.76\text{ D} \cdot \text{cm}$, respectively. The conductivity of the plate decreases with the increase of the closure pressure. When etched at 338 and 363 K, the conductivity decreases significantly between 20 and 40 MPa. The decrease of etching at 313 K is the largest at 10 MPa, and then, it becomes smaller.

### 4. CONCLUSIONS

(1) When the volume ratio of formaldehyde to ammonium chloride is 1:1.3, the acid production efficiency is the highest. Autogenic acid can release hydrogen ions at room temperature and under heating conditions. The amount of hydrogen ions released increases with time and tends to be stable after a
certain time. Several groups of experiments confirmed that the higher the acid concentration and temperature, the lower the pH of the autogenic acid, and the stronger the acid generating capacity.  

(2) Acid rock reaction kinetics experiments show that the reaction rate of acid and rock decreases with time. The reaction time can reach 6 h. Acid-rock reaction rates of autogenic acids at different temperatures and concentrations within the 6 h range from $6.61 \times 10^{-2}$ mol/(s·cm$^2$) to $9.49 \times 10^{-2}$ mol/(s·cm$^2$). It shows that the reaction time of autogenic acid and carbonate rock is long and the reaction speed is slow, which is beneficial to improve the acid treatment effect of the carbonate reservoir.

(3) The conductivity experiment shows that the etching ability of autogenic acid decreases with the increase of closure pressure at different temperatures, among which 338 and 363 K have a better etching effect. The permeability and conductivity of etched slabs are 210.16–226.99 D and 67.23–72.62 D·cm at 5 MPa closure pressure. At 313 K, the etching effect is poor, and the permeability and conductivity are only 36.77 D and 11.76 D·cm.

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Notes
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