Development and evaluation of authigenic acid system in high-temperature carbonate reservoirs

Zhipeng Xu, Ning Qi *, Zehui Zhang, Zizhao Han and Xuhang Su
College of Petroleum Engineering, China University of Petroleum (East China), Qingdao, China
*Corresponding author e-mail: qining@upc.edu.cn

Abstract. Acidizing the carbonate reservoirs with the conventional acidizing liquid system always causes fast acid-rock reaction and short acidizing distance, and the productivity of oil wells is not significantly improved. The key to improve the acidizing effect in the deep carbonate reservoirs is to optimize the retardation performance of the acid system. The authigenic acid system provides the excellent retardation performance and long acid-rock reaction due to its characteristics of slow and continuous acid generation. Here, an authigenic acid system with the performance of stable and continuous acid generation at high temperature was developed with halide salt, carbonyl compounds and esters. The authigenic acid system provides the excellent acid generation performance, with 12.9% hydrochloric acid generated after reaction at 90°C for 6 hours and 18.9% hydrochloric acid generated after reaction at 150°C for 6 hours. Comparison of hydrochloric acid, viscous acid and authigenic acid by experiments of static corrosion in rock cores shows the longer acid-rock reaction time of the authigenic acid than that of the conventional acids. At 150°C, N80 steel sheet is corroded in the authigenic acid system at the rate of 0.984 g·m⁻²·h⁻¹, which is lower than the industrial first-class standard and indicates excellent corrosion inhibition performance. Comparison of the acid-rock reaction kinetic equation of hydrochloric acid, authigenic acid in the carbonate rocks shows that the authigenic acid has the acid-rock reaction rate which is an order of magnitude lower than that of the conventional acid and has the better retardation performance, and it can be used to solve the difficulties in the deep acidizing of high-temperature reservoirs.

1. Introduction
Acidizing is a key technology in the development of both conventional and unconventional oil and gas resources. Currently, deep acidizing of carbonate reservoirs has been considered an international difficult problem. Deep acidizing is always operated with the retarded acid systems [1-4] such as viscous acid and foamed acid, which are always deficient in deep acidizing of carbonate high-temperature reservoirs. Authigenic acid, also known as latent acid [5], refers to a system that has no obvious strong acid characteristics on the ground and slowly reacts to generate hydrogen ions under the catalytic action of temperature or inducer after mixing in the reservoirs. According to study of three low-molecular-weight organic acid esters [6] by Moajil (2007), the acid generation rate is affected by the ester type and the ambient temperature. Generally, the medium and low temperatures are favorable for hydrolysis of
esters. An authigenic acid system with a corrosion ratio of up to 70% was developed by Chen Dajun et al. (2015) by using the carboxylate LYSY [7] as the acid-generation parent and the formic acid as the proton donor. Nevertheless, it is only applicable in the lower temperature reservoirs and cannot be used in acidizing of high temperature reservoirs. Liu Youquan et al. (2015) used a combination of organic acid esters and chloroacetate, which generates an acid system with the concentration up to 12%-14%, showing the weak acid-generation ability [8]. Deep acidizing at high temperature is increasingly needed in the oil and gas development. Considering this situation, an authigenic acid system with 12% HCHO+12% NH₄Cl+15% C₅H₁₀O₃ as the effective ingredient was developed to meet the requirements of long-term deep acidizing of high temperature reservoir with the high acid concentration.

2. Experiment

2.1. Materials and instruments

2.1.1. Experimental materials. The experiment was performed with the materials such as paraformaldehyde, ammonium chloride, ethyl lactate, and hydrochloric acid, and corrosion inhibitor HSJ. The generated acid reacted with the limestone rock powder and outcrop core and the dolomite rock powder and outcrop core.

2.1.2. Instruments. The experiment was performed with the instruments such as BSA423S precision electronic balance, DF-101S heat-collecting constant temperature heating magnetic stirrer, 101-2A electric blast drying oven, ZDJ-4A automatic potentiometric titrator, high-temperature and high-pressure rotating rock plate apparatus.

2.2. Experimental method

2.2.1. Evaluation of acid generation performance. (1) Final acid generation concentration. The authigenic acid system was prepared according to the designed formula and was placed in the three-necked flasks. The heating stirrer temperature was set at 90°C, 120°C and 150°C respectively. Five milliliter of authigenic acid and 2-3 drops of phenolphthalein reagent were added to the beaker per 1h. The solution was titrated with 1mol/L NaOH standard solution, and the authigenic acid concentration was calculated according to the end point of the titration. (2) Effective acid generation concentration [9]. The dried calcium carbonate powder mCaCO₃ was weighed and divided into several portions. The authigenic acid system was prepared in proportion and placed in the three-necked flask. The heating stirrer temperature was set at 90°C and 150°C respectively, and 20ml of authigenic acid solution was placed in the beaker, and its mass msolution was weighed in a millimeter balance. The excess calcium carbonate mCaCO₃ was poured into the beaker filled with the acid solution, and the breaker was continuously stirred with an electric stirrer to allow escape of CO₂. The total mass of the beaker after the acid-calcium carbonate reaction was weighed and was recorded as m₁. Then, the effective acid concentration was obtained. The mass of the emitted CO₂ is expressed as:

\[ m₂ = m_{\text{solution}} + m_{\text{CaCO₃}} - m₁ \]  (1)

2.2.2. Corrosion test. The rock powder was dried in an oven at 100°C to a constant weight, and 10g of limestone rock powder and 10g of dolomite rock powder were placed in the small beaker. The autogenous hydrochloric acid and 20% hydrochloric acid were poured into the small beaker, which was placed in the water bath at 150°C. The beaker was manually shaken per 10 min and taken from the water bath after 120 min of acid-rock reaction. The left solids were filtered, dried and weighed.

2.2.3. Corrosion inhibition test. The N-80 tubing steel was polished and cleaned with petroleum ether or acetone, and it was placed in the oven for 30 min and then weighed [10]. The dried steel sheet was
hanged up in the high-temperature and high-pressure rotating rock plate reactor, and the authigenic acid and hydrochloric acid were added to the reactor. The temperature and time for reaction were set.

2.2.4. Retardation experiment. The limestone core with a diameter of 2.54 cm was treated with static acid-rock reaction with authigenic acid, hydrochloric acid and viscous acid of the same concentration, and the core was excessive. The acid retardation performance was evaluated with the time for the same effective corrosion ratio.

2.2.5. Acid-rock reaction kinetics test. The dolomite and limestone cores were dried and weighed. 300 ml of authigenic acid and 300 ml of hydrochloric acid with a mass fraction of 20% were prepared and placed in the preheating kettle of the rotating rock plate reactor [11]. The reactor temperature was set at 150 ℃, and the booster valve was opened to adjust the pressure to 7-8 MPa. The core was fixed on the rotating rod of the reactor, and the rotating speed of the rotating rod was set as 500r/min. When the temperature reaches the set value, the acid in the preheating kettle was hydraulically injected into the reactor for reaction with the core for 5 min. The acid concentration after reaction was measured with an automatic potentiometric titrator. The reacted core was washed, dried and weighed, and the acid-rock reaction rate was calculated.

3. Results and discussion

3.1. Evaluation of acid generation performance

3.1.1. Final acid generation concentration. The final acid concentration of the authigenic acid system of 12% HCHO+12%NH₄Cl+15%C₅H₁₀O₃ at different temperature was measured, as shown in Fig.1.

![Final acid concentration](image)

**Figure 1.** Final acid concentration of the authigenic acid system at different temperature.

Comparison of the final acid generation concentration of the authigenic acid at 90℃, 120℃ and 150℃ shows that the final acid generation concentration of the authigenic acid system increases with the
increase of temperature and reaches the maximum of 18.9% at 150℃, which meets the needs of the oil field production. The acid generation rate of the authigenic acid system also increases with the increase of temperature, which meets the requirements of deep acidizing of high-temperature reservoirs.

3.1.2. Effective acid generation concentration. The authigenic acid system was tested at 90℃ and 150℃ with the CO₂ weight loss method. The experimental data are listed in Fig.2.

![Figure 2](image.png)

**Figure 2.** Test of the acid generation performance of the authigenic acid system with the CO₂ weight loss method.

According to Fig.2, the effective acid concentration gradually increases to be stable, indicating a gradual acid generation process. Comparison of CO₂ emission at 90℃ and 150℃ shows that the reaction is an endothermic process. As the temperature rises, the reaction limit moves to the right until the saturated acid concentration at this temperature is reached.

3.2. Corrosion test
The corrosion of limestone and dolomite with the authigenic acid system was carried out at 150℃ for 2 hours, and the result was compared with that of 20% hydrochloric acid, as shown in Table 1.

| Acid types      | Lithology | Rock powder mass/g | Filter paper mass/g | Filter paper mass after reaction/g | Corrosion ratio/% |
|-----------------|-----------|--------------------|---------------------|-----------------------------------|-------------------|
| Authigenic acid | Dolomite  | 10.127             | 2.054               | 5.954                             | 61.49             |
|                 | Limestone | 10.104             | 2.063               | 3.672                             | 84.08             |
| Hydrochloric acid| Dolomite | 10.054             | 2.042               | 5.037                             | 70.21             |
|                 | Limestone | 10.982             | 2.048               | 3.142                             | 90.04             |
According to Table 1, the authigenic acid causes a higher corrosion ratio to limestone than that to dolomite, and its corrosion ratio close to 20% hydrochloric acid, indicating the good corrosion ability of the authigenic acid.

3.3. Corrosion inhibition test
The authigenic acid system of 12% HCHO+12%NH$_4$Cl+15%C$_5$H$_{10}$O$_3$+1% HSJ-1 was prepared, and its corrosion inhibition performance was compared with that of 20% hydrochloric acid added with 1% HSJ-1. Two sets of parallel experiments of reaction for 4h at 150°C were planned, and the corrosion rate of two acid solutions to N80 steel sheet was measured.

| Temperature/°C | Time/h | Acid type          | Weight before corrosion/g | Weight after corrosion/g | Weight loss/g | Corrosion rate/(g·m$^{-2}$·h$^{-1}$) |
|----------------|--------|--------------------|---------------------------|-------------------------|---------------|---------------------------------|
| 150            | 4      | hydrochloric acid  | 19.845                    | 19.697                  | 0.148         | 18.548                          |
|                |        | authigenic acid    | 19.765                    | 19.757                  | 0.008         | 0.984                           |

According to Table 2, the authigenic acid system has a very low corrosion rate, which is about 20 times lower than of hydrochloric acid, and the corrosion rate of the authigenic acid system is only 0.984 g·m$^{-2}$·h$^{-1}$, which is lower than the industry first class standard and shows the excellent corrosion inhibition performance.

3.4. Retardation performance
The corrosion is complete when the effective corrosion ratio reaches 70%. The time of completing corrosion by each acid type is recorded, as shown in Fig.3.

Figure 3. Reaction time of different types of acid to reach the effective corrosion ratio.

According to Fig.3, the time for corrosion ratio of 70% by the hydrochloric acid is about 2h, and it is much shorter than those by authigenic acid and viscous acid, which are 4.5h and 5h respectively. This
indicates that the reaction rate of viscous acid and authigenic acid is much slower than hydrochloric acid and meets the requirement of retarded acidizing. Compared with the viscous acid, the authigenic acid requires a longer action time, and shows the relatively stable upward trend of corrosion ratio. The authigenic acid has a slower corrosion rate than hydrochloric acid and viscous acid in the early stage of the acid-rock reaction, a constant corrosion rate in the middle stage, and a higher corrosion rate corrosion rate than hydrochloric acid and viscous acid in the late stage. This is due to that during consumption of the authigenic acid hydrogen ions by reaction with the core, the hydrogen ions generated constantly by the authigenic acid supplements the hydrogen ion concentration in the reaction system, which balances dynamically the hydrogen ion concentration in the system and ensures the stable reaction rate. This avoids ineffective reservoir stimulation due to that the acid liquid is almost consumed when the conventional acid and the viscous acid reach the target reservoir.

3.5. Acid-rock reaction rate

The authigenic acid, hydrochloric acid and viscous acid with the mass fraction of 20% were prepared and reacted with limestone and dolomite respectively at 150°C. The reaction rate was observed. The results are listed in Table 3.

| Acid types     | Sample  | Acid solution/ (mol/L) | Difference of concentration/(mol/L) | Reaction rate J/(mol·cm⁻²·s⁻¹) | lgC   | lgJ   |
|----------------|---------|------------------------|-------------------------------------|--------------------------------|-------|-------|
| Authigenic acid | Dolomite| 6.02                   | 0.003                               | 4.26E-07                       | 0.78  | -6.371|
| Authigenic acid | Limestone| 6.02                   | 0.0524                              | 7.35E-06                       | 0.78  | -5.134|
| Hydrochloric acid | Dolomite| 6.02                   | 0.01                                | 1.40E-06                       | 0.78  | -5.904|
| Hydrochloric acid | Limestone| 6.02                   | 0.2393                              | 3.36E-05                       | 0.78  | -4.474|

According to Table 3, the reaction rate of authigenic acid with limestone and dolomite acid rock is one order of magnitude lower than that of hydrochloric acid. This is due to both reaction and generation of hydrogen ions in the acid-rock reaction process of authigenic acid, and the relatively stable value of H⁺. In the test of the acid-rock reaction rate, the hydrogen ions of the authigenic acid are not completely released due to the short reaction time. The authigenic acid shows a slower trend of lower reaction rate in a short time and the declined reaction rate in long time than that of hydrochloric acid.

4. Conclusion

(1) The maximum acid generation concentration of the authigenic acid system at 150°C reached 18.9%, which is close to the corrosion performance of 20% hydrochloric acid and meets the requirements for deep acidizing of high-temperature reservoirs. Moreover, the acid generation rate of the authigenic acid system increases with the increase of temperature, which proves that the acid generation is a process endothermic reaction, and temperature has a great influence on the acid generation performance of the authigenic acid.

(2) The acid-rock reaction rate of the authigenic acid with limestone and dolomite at 150°C is an order of magnitude lower than that of the hydrochloric acid of same concentration. The corrosion rate of the authigenic acid system is only 0.984 g·m⁻²·h⁻¹, which is lower than the industry first class standard and shows the excellent retardation performance. The authigenic acid reduces the corrosion to pipe string and meets the requirements for deep acidizing of high-temperature reservoirs.

(3) Compared with conventional acids, the authigenic acid system has a longer acid-rock reaction time, and during the reaction between authigenic acid and core, H⁺ is continuously generated, which causes the dynamic balance of H⁺ and a relatively high reaction rate, and achieves deep acidizing.
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