Research and Evaluation of a New Autogenic Acid System Suitable for Acid Fracturing of a High-Temperature Reservoir

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ABSTRACT: An organic ester p-nitrobenzyl acetate (PNBA) was synthesized and used to establish a kind of autogenic acid system through the hydrolysis of ester to acetic acid in situ. The autogenic acid system can form a homogeneous solution by adding an organic solvent. The autogenic acid system possesses the desired characteristic in which hydrolysis can generate a small amount of acetic acid below 120 °C and a large amount of acid above 140 °C in 2 h. The acid-generated ability at different time and temperature was studied in detail. The dissolution of solid calcium carbonate and carbonate rocks by the autogenic acid system was investigated. The autogenic acid displayed lower dissolution ability on a carbonate rock and weak corrosion of a N80 steel sheet at 150 °C. The autogenic acid is especially suitable for acid fracturing and dissolution of rocks in a high-temperature carbonate reservoir.

1. INTRODUCTION

A deep carbonate reservoir is a very important field for oil and gas exploration and development. In recent years, a number of deep carbonate reservoirs have been found in Tarim, Ordos, and Sichuan basins in China. The main characteristics of deep carbonate reservoirs in China include the following aspects: the reservoirs are mainly concentrated in 6000−7000 m, porosity is between 2 and 6%, and most of them belong to ultralow porosity and permeability reservoirs. The newly discovered oil and gas reservoirs have more buried depth and complex geological conditions than before, which bring many difficulties for reservoir acid fracturing.

The buried depth of deep oil and gas reservoirs in the Sichuan Basin is generally 7000 m, the formation temperature is 160 °C, the formation pressure is 70 MPa, and the fracture and karst cave in the fault zone are relatively developed. Under the action of high temperature in a deep layer, the effective distance of an acid system in a conventional acid fracturing process is short, and it cannot form a long-distance and large-scale acid solution volume, which seriously restricts the effect of acid fracturing.

Scholars at home and abroad have developed a variety of retarded acid systems to increase the effective action distance of acid solution. For example, gelling acid can delay the reaction rate of an acid rock and reduce the filtration of acid solution by increasing the viscosity of acid solution, reducing the diffusion speed of H+ to the rock surface and retarding the reaction rate of the acid rock through increasing the viscosity of acid solution. Emulsified acid can block the contact between acid solution and the rock surface through the form of oil-in-acid emulsion and retard the reaction rate of the acid rock. Autogenic acid can slow down the reaction rate of the acid rock with the help of the characteristics of gradual acid generation at high temperature.

According to the acid rock reaction mechanism, the acid rock reaction rate is closely related to hydrogen ion concentration and mass transfer speed. Therefore, due to the dissociation characteristics of organic acids, it can slow down the acid rock reaction rate and increase the effective action distance of acid solution. Organic acids have been successfully used in acid fracturing and plug the removal at home and abroad. In the past 10 years, scholars have also done a lot of research on the reaction mechanism and law of organic acids. Marten et al. established an acid rock reaction model suitable for the mixing of strong and weak acids and used it to calculate the effective action distance of acid solution in acid fracturing. Li et al. compared the reaction rule of organic acid and the chelating agent in the process of matrix acidification. Chang et al. obtained the reaction law of organic acid and the carbonate rock by Gibbs free energy analysis. Al-Douri et al. tested the reaction rate of 10% organic acid and calcite by rotating the disc experiment and obtained the acid rock reaction and dissolution law.
reaction rule of organic acid (formic acid and acetic acid) and the chelating agent with a dolomite core by rotating the disc experiment.25

To sum up, at present, the research work of autogenic acid to acid fracturing carbonate rocks mainly focuses on the recognition of an acid rock reaction law and the establishment of an acid rock reaction model, while the research and development work for the organic acid liquid system is less. Especially at present, China has strengthened the exploration and development of deep carbonate reservoirs. It is urgent to develop a new organic acid system suitable for high-temperature formation. In this paper, a new type of an organic acid system was developed and its acid reaction characterization was evaluated.

2. RESULTS AND DISCUSSION

2.1. Comparison of Ability of the Acid Generated for Various Organic Autogenic Acid Systems. Acid fracturing of carbonate reservoirs is accomplished by injecting treatment fluids at a downhole pressure. Organic esters can be hydrolyzed to organic acids. Inorganic acids, such as hydrochloric acid, corrode mineral rocks too fast and result in a short effective distance and low depth penetration. An alternative method is to replace inorganic acid with organic acid fracturing fluids. Typical organic esters such as methyl formate and ethyl acetate can be hydrolyzed into formic and acetic acid. These organic acids can corrode and dissolve carbonate rocks. However, the hydrolysis of many organic esters is fast, and they are often hydrolyzed in large quantities at a relatively low temperature (T < 80 °C). At present, the temperature of a carbonate reservoir to be exploited is generally higher than 100 °C. Therefore, finding a system that generates little acid at low temperature and a large amount of acid at high temperature is a challenging task for the acidification of carbonate rocks in high-temperature reservoirs.

As can be seen from Figure 1, the hydrolysis rates of different organic esters vary greatly. Methyl formate cannot tolerate high temperature, and it is easily hydrolyzed below 50 °C and almost completely hydrolyzed in 2 h above 70 °C. Similarly, the hydrolysis of p-nitrophenyl acetate was also faster, and the hydrolysis almost finishes within 2 h at 80 °C. So, the p-nitrophenyl acetate is not suitable for acidification of carbonate rocks in high-temperature reservoirs, too. Interestingly, it can be observed from Figure 1 that organic ester PNBA possesses the desired characteristic in which hydrolysis can generate a small amount of acetic acid below 120 °C and a large amount of acid above 140 °C in 2 h. The hydrolysis is very slow below 120 °C, and the amount of acid in 2 h is very small, but it starts to produce more acetic acid obviously above 130 °C. The excellent performance of acid generation is very suitable for acid fracturing of high-temperature reservoirs. Therefore, it was selected as the main research object in this work.

2.2. Kinetics of Acid Generated for the PNBA Autogenic Acid System. To investigate the process of acid generation, the reaction was carried out for a different reaction time at 140 °C. The amount of generated acid by hydrolysis of ester PNBA was analyzed, and the results are illustrated in Figure 2. From Figure 2, we can observe that this reaction seems to have an induction period since there is less acetic acid generation in the first hour and it reaches an equilibrium at about 7 h. It is worth pointing out that the acid concentration at equilibrium increases with the increase of the water content of the autogenic acid system.

2.3. Dissolution of Carbonate Rock by Acid. To study the practicability of the autogenic acid system, the carbonate rock was excavated from high-temperature reservoirs, its surface electronic image and the composition were analyzed by energy-dispersive spectroscopy (EDS) analysis, and the results are shown in Figure 3 and Table 1. From the EDS analysis, we can find that the rock from a high-temperature reservoir is a carbonate-based rock. The dissolution of the carbonate rock taken from high-temperature reservoirs by autogenic acid of PNBA was also investigated.

First, we measured the weight (N1) of the rock before the reaction with acid, then we put the rock into a different solution for the reaction for 60 min, we recorded the weight (N2) of rock after the reaction, and we defined the dissolved fraction of the rock after 60 min as equal to (N1 − N2)/N1 × 100%. It can be seen from Figure 4 that the dissolved fraction of the rock with HCl is the largest at 95 or 150 °C, and it is much larger than other acids. The dissolved fraction of the rock with autogenic acid is much lower than those of gelled

![Figure 1. Plots of hydrolysis of organic ester versus a reaction temperature of 2 h; ester:H2O = 1:4; 1, Methyl formate; 2, p-nitrophenyl acetate; 3, PNBA.](image1)

![Figure 2. Plot of hydrolysis of PNBA versus reaction time at 140 °C.](image2)
and cross-linked acid; especially at 150 °C, the advantage of the slow reaction rate of autogenic acid is obvious, which shows that the lower reaction rate of autogenic acid can not only effectively dissolve the rock but also greatly improve the effective action time of acid in the fracture.

The reaction rate of autogenic acid is very low. It can be used to dissolve near the wellbore with gelled acid and dissolve the far well with autogenic acid so as to improve the overall conductivity of the fracture.

2.4. Dynamic Corrosion Rate of Autogenic Acid on a N80 Steel Sheet at 150 °C. First, we measure the surface area (ΔA) of a N80 steel sheet, weigh the N80 steel sheet and record the initial weight (m1) of the steel sheet, and then put the N80 steel sheet into a dynamic corrosion rate tester filled with acid. Second, we adjust the temperature of the dynamic corrosion rate tester to 150 °C, taking the N80 steel sheet in a dynamic corrosion rate tester for 4 h and recording the weight (m2) of the steel sheet after the reaction. It can be found that the corrosion rate of autogenic acid is much lower than that of gelled acid at high temperature, which is equivalent to that of acetic acid, and the test results are shown below in Table 2.

\[ v = \frac{10^6(m1 - m2)}{\Delta A \cdot t} \]

where \( v \) is the corrosion rate (g/m²-h), \( t \) is the reaction time (h), \( \Delta A \) is the surface area of the steel (mm²), and \( m1 \) and \( m2 \) are the weights of the steel sheet before and after corrosion (g), respectively.

3. CONCLUSIONS

1. The autogenic acid generates little acid below 120 °C but rapidly generates acid above 140 °C, and the reaction rate is far less than hydrochloric acid at high temperature, which is conducive to improve the fracturing effect of high-temperature carbonate reservoirs.

2. The dissolved fraction of the rock with PNBA is significantly lower than other acid systems in the same time, which means that the autogenic acid has a lower acid rock reaction rate at high temperatures.

3. The corrosion rate of autogenic acid to steel is low, which is beneficial to the safety of the downhole string during the acid fracturing construction.

4. EXPERIMENTAL SECTION

4.1. Materials. Methyl formate, \( p \)-nitrophenyl acetate, \( p \)-nitrobenzyl acetate (PNBA), methanol, acetone, \( p \)-nitrobenzyl alcohol, sodium bisulfate, sodium citrate, and hexadecanethiol were analytical grade and purchased from commercial sources and used without further purification.

4.2. Synthesis of \( p \)-Nitrobenzyl Acetate (PNBA). The synthesis of \( p \)-nitrobenzyl acetate was carried out as follows: 5.1 g of acetic anhydride and 10 g of \( p \)-nitrobenzyl alcohol were poured into a 250 mL flask. Sodium bisulfate (1 g) was added and stirred. Then, the mixture was heated to 80 °C and reacted for 5 h. The solution was cooled and kept at room temperature for 2 h. The white crystals of \( p \)-nitrobenzoate acetate were obtained by vacuum distillation, washed with saturated salt water and ether, and recrystallized in hot water.

Figure 3. The surface electronic image.

Table 1. Content of Various Elements of the Carbonate Rock by EDS Analysis

| elements | apparent concentration | k ratio | wt % | wt % sigma | standard sample label |
|----------|------------------------|---------|------|------------|----------------------|
| C        | 7.71                   | 0.07713 | 17.92 | 0.25       | C Vit                |
| O        | 28.14                  | 0.09468 | 46.91 | 0.24       | SiO₂                 |
| Mg       | 2.23                   | 0.01477 | 2.67  | 0.05       | MgO                  |
| Al       | 0.48                   | 0.00345 | 0.55  | 0.03       | Al₂O₃                |

| elements | apparent concentration | k ratio | wt % | wt % sigma | standard sample label |
|----------|------------------------|---------|------|------------|----------------------|
| Si       | 1.62                   | 0.01281 | 1.74  | 0.04       | SiO₂                 |
| S        | 0.13                   | 0.00112 | 0.14  | 0.03       | FeS₂                 |
| K        | 0.32                   | 0.00272 | 0.30  | 0.04       | KBr                  |
| Ca       | 28.36                  | 0.25337 | 29.52 | 0.17       | wollastonite          |
| Fe       | 0.19                   | 0.00190 | 0.25  | 0.08       | Fe                   |

Figure 4. Dissolved fraction of the carbonate rock by different acid solution for a reaction of 60 min at 95 and 150 °C.
4.3. Preparation of Autogenic Acid. An autogenic organic acid system was prepared by mixing a certain amount of organic esters with water, organic solvents, and other reagents such as a ferric ion stabilizer and corrosion inhibitor. In a typical procedure, 30 mL of methyl formate was added into 40 mL of H$_2$O, and then, a ferric ion stabilizer sodium citrate of 1% and a corrosion inhibitor hexamercaptan of 0.5% were added. Consequently, the solvents methanol and acetone were added and stirred to obtain a homogeneous autogenic acid system.

4.4. Experimental Methods. A typical reaction solution containing homogeneous autogenic acid was added to a 150 mL elevated pressure reactor vessel, and a theoretical amount of the rock was added. The solution was sealed, heated to a desired temperature for a certain time, and stopped reacting. The unreacted solid rock was filtered and weighed to obtain the dissolved fraction of the rock. The content of acid generated in the solution was determined quantitatively by acid–base titration, and the content of ester was determined by HPLC.

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| Table 2. Dynamic Corrosion Rate of Different Acid on a N80 Steel Sheet at 150 °C |

| acid          | temperature (°C) | reaction time (h) | surface area of the steel sheet (mm$^2$) | weight before corrosion (g) | weight after corrosion (g) | corrosion rate (g/m$^2$·h) |
|---------------|-----------------|-------------------|------------------------------------------|-----------------------------|---------------------------|----------------------------|
| autogenic acid| 150 °C          | 4 h               | 13.654                                   | 10.918                      | 10.902                    | 3.057                      |
| gelled acid   | 150 °C          | 4 h               | 15.190                                   | 6.3128                      | 4.9804                    | 219.30                     |
| acetic acid   | 150 °C          | 4 h               | 13.390                                   | 10.687                      | 10.673                    | 2.483                      |
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