

## Article

# Development and Performance Evaluation of Scale-Inhibiting Fracturing Fluid System

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**Abstract:** The injection water and formation water in the Mahu oil field have high salinity and poor compatibility, which leads to scaling and blockage in the formation or fracture propping zone during production. In this paper, a scale-inhibiting fracturing fluid system is developed which can prevent the formation of scale in the reservoir and solves the problem of scaling in the fracture propping zone at the Mahu oil field. Firstly, based on scale-inhibition rate, the performances of six commercial scale inhibitors were evaluated, including their acid and alkali resistance and temperature resistance. Then, the optimal scale inhibitors were combined with the fracturing fluid to obtain a scale-inhibiting fracturing fluid system. Its compatibility with other additives and scale-inhibition performance were evaluated. Finally, the system's drag-reduction ability was tested through the loop friction tester. The results showed that, among the six scale inhibitors, the organic phosphonic acid scale inhibitor SC-1 has the best performance regardless of high-temperature, alkaline, and mixed scale conditions. In addition, SC-1 has good compatibility with the fracturing fluid. The scale-inhibiting fracturing fluid system can effectively prevent scaling inside the large pores in the propping zone, and a scale-inhibiting efficiency of 96.29% was obtained. The new fracture system maintained a drag-reduction efficiency of about 75%, indicating that the addition of the scale inhibitor did not cause a significant influence on the drag-reduction efficiency of the fracturing fluid.

**Keywords:** scale inhibitor; fracturing fluid; scaling in propping zone; compatibility; drag-reduction rate



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## 1. Introduction

In recent years, conventional oil and gas resources have been gradually drying up, and their development has become increasingly difficult [1]. The exploration and development of unconventional oil and gas resources have shown a rapid rise [2]. Large-scale hydraulic fracturing is the most widely used and technically mature means to increase the production of unconventional oil and gas, which is the key to realizing the low-cost development of oil fields [3,4]. However, the rapid change in the temperature and pressure near the wellbore area after fracturing has already led to scaling and formation damage, especially using high-salinity fracturing fluid in dry areas. The scaling in the formation after fracturing can reduce reservoir permeability [5], severe skin damage [6], and ultimately reduced oil well production [7,8]. The Samotlor field in West Siberia of the former Soviet Union, the Foster oil field in Texas, the oil field in Louisiana, the Ujin and Retibai oil fields in the Mangyshlak region, the Changtan oil field in California, and the Burbank and Drumright oil fields in Oklahoma were all subject to scaling with various degrees, mostly of calcium carbonate and calcium sulfate [9]. In China, Daqing oil field, Zhongyuan oil field, Jilin oil field, Gaskule oil field in Qinghai, Tuha oil field, Tarim oil field, and Bohai offshore oil field had different degrees of scaling problems, which even caused them to be shut down and scrapped [10,11]. Therefore, oil field scaling can seriously affect oil and gas field development, and oil field scale prevention has attracted great attention all over the world [12,13].

In the fracturing process, there are various sources of scaling. High-salinity fracturing fluid, acid corrosion, and water–rock reaction (ion exchange between the liquid phase and solid phase) can increase the total salinity of the liquid phase at the reservoir and cause potential scaling hazards [14,15]. At present, there are various scale-inhibiting methods, mainly divided into physical and chemical methods. Although physical scale removal methods such as high-intensity shock waves have a high scale removal rate, their action area is small, mostly in the near the well zone, such as wellbore. In addition, they cannot be applied to the fracture and propping zone and their cost is high, which makes it difficult for large-scale application [16]. In contrast, the chemical scale-inhibiting method is highly effective and highly cost-effective. After the scale inhibitor is combined with fracturing fluid, it can penetrate deeply into the formation and act on the fractures, rock pores, and propping zones. If slow-release technology is used, it can achieve a long-lasting scale-inhibiting effect during the fracturing process. In addition, the operation cost is low [17].

However, as the pH, temperature, and pressure on the reservoir are unstable during the oil production process, the performance of the scale inhibitor under various conditions is different [18,19]. At present, scale inhibitors are mostly acidic and weakly acidic, which can also affect the drag-reduction or crosslinking performance of the alkaline fracturing fluid [20]. As early as the 1990s, researchers found that most scale inhibitors have poor compatibility with fracturing fluids. After adding the scale inhibitors, the fracturing fluids are either precipitation with fluids or not thermally stable at high temperatures. They proposed that qualified scale inhibitors should have features such as good compatibility, thermal stability, and acid and alkali resistance [21]. In addition, scale inhibitors need as little impact as possible on the performance of fracturing fluids [22]. Yue (2014) et al. conducted a study on the compatibility of nine commercially available scale inhibitors with fracturing fluids and concluded that only two of them could be added to the fracturing fluid [23,24].

At present, the temperature resistance and compatibility of scale inhibitors is poor, and they also have a narrow range of acid and alkali resistance. Therefore, the selection of scale inhibitors is crucial for scale-inhibiting fracturing fluids. At present, the scale inhibitors used in the Mahu oil field have poor performance in the formation environment. When combined with fracturing fluid, the stability, drag reduction, and other performance of fracturing fluid was also affected. Therefore, a new scale inhibitor should be optimized to achieve the purpose of scale inhibition while fracturing.

In this paper, an optimal scale inhibitor SC-1 was found and was combined with the fracturing fluid. Various performance indicators of scale inhibitors were evaluated, including the temperature and acid/alkali resistance as well as the mixed scale-inhibiting ability. After adding the scale inhibitor SC-1 with fracturing fluid, the scale inhibiting and the drag reduction of the new fracturing fluid on the fracturing propping zone of the scale inhibitor were studied. The results showed that the fracturing fluid system had high inhibition efficiency and high drag-reduction rate in a wide acid and alkali and temperature range. This is of great significance for improving the fracturing effect and increasing oil and gas production.

## 2. Materials and Methods

This section discloses the experimental details. The main experimental design ideas are: (1) first, temperature and pH resistance of scale inhibitors were evaluated, and the optimal scale inhibitor was selected; (2) then, compatibility experiments were carried out to form the new fracturing fluid formula; (3) finally, the performance of the new fracturing fluid was evaluated comprehensively, and its scale-inhibition mechanism was characterized by nuclear magnetism.

### 2.1. Experimental Materials

A scale inhibitor [13] has the advantages of powerful chelating ability as well as low dosage and low cost, which is the current main scale-inhibition method [6,25]. However,

the existing scale inhibitors in the Mahu oil field have poor performance, and most of them have no temperature and alkali resistance. Therefore, the scaling phenomenon at the reservoir is becoming more and more serious. Here, six commercial scale inhibitors were optimized in this study. They are organic phosphoric acids and included: SC-1 (pH: 2.0–3.0, 8500 RMB/t, Hengkang Environmental Protection Technology Co., Ltd., Linyi, China), polyaspartic acid SC-5 (pH: 3.0–5.0, 8300 RMB/t Xiongguan Technology Development Co., Ltd., Tianjin, China), and composite scale inhibitors SC-2 (pH: 3.0–4.5, 8700 RMB/t Gansu Heima Petrochemical Engineering Co., Ltd., Lanzhou, China), SC-3 (pH 3.0–4.5 8200 RMB/t Gansu Heima Petrochemical Engineering Co., Ltd., Lanzhou, China), SC-4 (pH: 5.0–6.0, Xiongguan Technology Development Co., Ltd., Tianjin, China), and SC-6 (5.0–7.0, 8000 RMB/t Dongfang Chemical Co., Ltd., Yantai, China).

The formulation of the scale inhibitor fracturing fluid system is 0.08% drag-reduction agent DR800 + 0.3% scale inhibitor (preferred scale inhibitor) + 4% autogenic acid SEG-C + 0.2% clay stabilizer. The scale inhibitor fracturing fluid system is a combination of the fracturing fluid currently used at the Mahu site and the preferred scale inhibitor. DR800 is the current drag-reducing agent used in the Mahu oil field. A 0.08% proportion of drag-reducing agents is the best choice in terms of cost and effect. The reason for adding 4% the autogenic acid SEG-C is to maintain a low-pH environment in the reservoir over the long term. The autogenic acid is the organic ester, and it can slowly hydrolyze in the formation to produce the organic acid, which can be helpful for inhibiting scale precipitation [6].

#### 2.1.1. Effect of Temperature on CaSO<sub>4</sub> Scale Inhibition

The performances of scale inhibitors on CaSO<sub>4</sub> were determined according to methods of the literature [26], which came from the China National Petroleum Corporation method (SY/T5673-93). The experimental process was as follows: prepare solution A (7.5 g/L NaCl, 11.1 g/L CaCl<sub>2</sub>·H<sub>2</sub>O), solution B (7.5 g/L NaCl, 10.66 g/L Na<sub>2</sub>SO<sub>4</sub>), and solution C (0.5% scale inhibitor). Mix 50 mL solution A, 50 mL solution B, 0.8 mL solution C to obtain sample 1. Mix 50 mL solution A, 50 mL solution B to obtain sample 2. Mix 50 mL solution A, 50 mL distilled water to obtain sample 3. Put the three samples in a 90 °C water bath for 24 h and filter them separately. Then, 2 mL is taken out and diluted to 100 mL. The appropriate amount of 0.1 wt% NaOH solution is added to the solution to adjust the pH between 12 and 13. Next, a little calcium indicator is added to make the solution system appear light red.

The titration was performed with 0.01 mol/L EDTA, and the finish of titration was based on the color change from red to blue. The scale-inhibition rate was calculated by Equation (1) [27]. The water bath temperature was adjusted to 70 °C, 50 °C, and 30 °C, and the above process was repeated.

$$E_f = \frac{V_1 - V_0}{V - V_0} \times 100 \quad (1)$$

where  $E_f$  is the scale-inhibition rate in %,  $V_0$  is the volume of EDTA consumed by sample 2 in mL,  $V$  is the volume of EDTA consumed by sample 3 in mL, and  $V_1$  is the volume of EDTA consumed by sample 1 in mL.

In order to ensure the accuracy of the experiment, each group of scale-inhibition rates was tested three times. The average value and the error were calculated, and the error bars are added in the figures.

#### 2.1.2. Effect of Temperature on CaCO<sub>3</sub> Scale Inhibition

Prepare solution A (33.00 g/L NaCl, 12.15 g/L CaCl<sub>2</sub>·H<sub>2</sub>O, 3.68 g/L MgCl<sub>2</sub>·6H<sub>2</sub>O), B (33.00 g/L NaCl, 0.03 g/L Na<sub>2</sub>SO<sub>4</sub>, 7.38 g/L NaHCO<sub>3</sub>), and C (0.5% scale inhibitor). The test method is the same as the test method in Section 2.1.1.

### 2.1.3. Effect of pH on CaSO<sub>4</sub> Scale Inhibition

Sample 1, sample 2, and sample 3 were prepared according to Section 2.1.2. The pH of the three solutions was adjusted to 5, 6, 7, 8, 9, 10, and 11 by 0.1 wt% HCl or 0.1 wt% NaOH solutions. Then, they were placed in a water bath at 50 °C for 24 h, and the subsequent filtration titration test was the same as Section 2.1.1.

### 2.1.4. Effect of pH on CaCO<sub>3</sub> Scale Inhibition

Sample 1, sample 2, and sample 3 were prepared according to Section 2.1.2. Their pH was adjusted to 5, 6, 7, 8, 9, 10, and 11. Then, they were placed in a water bath at 50 °C for 24 h, and the subsequent filtration titration test was the same as Section 2.1.1.

### 2.1.5. Mixed-Scale Preparation, Scale-Inhibition Ability Test, and Optimal Test of Scale Inhibitor Concentration

Prepare solution A (20.25 g/L NaCl, 11.63 g/L CaCl<sub>2</sub>·H<sub>2</sub>O, 84 g/L MgCl<sub>2</sub>·6H<sub>2</sub>O), solution B (20.25 g/L NaCl, 5.33 g/L Na<sub>2</sub>SO<sub>4</sub>, 3.69 g/L Na<sub>2</sub>CO<sub>3</sub>), and solution C (0.5% scale inhibitor). The choice of scale inhibitor is the three best performers among the above 6 types of scale inhibitors. These three samples are mixed according to Section 2.1.1 and placed in a 90 °C water bath for 24 h. The subsequent filtration titration test is the same as Section 2.1.2.

The optimal concentration of the preferred scale inhibitor is then screened. The experimental procedure is as follows: prepare solution A (33.00 g/L NaCl, 12.15 g/L CaCl<sub>2</sub>·H<sub>2</sub>O, 3.68 g/L MgCl<sub>2</sub>·6H<sub>2</sub>O) and solution B (33.00 g/L NaCl, 0.03 g/L Na<sub>2</sub>SO<sub>4</sub>, 7.38 g/L NaHCO<sub>3</sub>). Mix solution A, solution B, and scale inhibitor. The concentrations of the scale inhibitor are: 0.01%, 0.03%, 0.05%, 0.07%, 0.09%, and they are placed at 90 °C for 24 h. The subsequent experimental procedure is the same as Section 2.1.2. Prepare solution C (7.5 g/L NaCl, 11.1 g/L CaCl<sub>2</sub>·H<sub>2</sub>O) and solution D (7.5 g/L NaCl, 10.66 g/L Na<sub>2</sub>SO<sub>4</sub>); Mix solution C, solution D, and scale inhibitor. The concentrations of the scale inhibitor are 0.1%, 0.3%, 0.5%, 0.7%, and they are placed at 90 °C for 24 h. The subsequent experimental procedure is the same as Section 2.1.2.

## 2.2. Fracturing Fluid and Its Compatibility with Scale Inhibitor

The scale inhibitor fracturing fluid was prepared according to the formula: 0.08% drag-reducing agent DR800 + 0.3% scale inhibitor (preferred scale inhibitor) + 4% autogenous acid SEG-C + 0.2% clay stabilizer. The dosed water was from Mahu injection water, and its ionic composition is shown in Table 1. The fracturing fluid system was placed in a 90 °C water bath and it was observed whether there was flocculation or precipitation in the fracturing fluid system after heating for 15 min, 1 h, 3 h, 12 h, 24 h, and 48 h.

**Table 1.** Ion components of Mahu injection water.

| Ionic Types           | CO <sub>3</sub> <sup>2−</sup> | HCO <sub>3</sub> <sup>−</sup> | Cl <sup>−</sup> | SO <sub>4</sub> <sup>2−</sup> | Ca <sup>2+</sup> | Mg <sup>2+</sup> | pH |
|-----------------------|-------------------------------|-------------------------------|-----------------|-------------------------------|------------------|------------------|----|
| Injected water (mg/L) | 8                             | 287.3                         | 11,574          | 540                           | 320              | 67               | 8  |

## 2.3. Performance Evaluation of Scale Inhibition

### 2.3.1. Rock Sample Preparation

The sandstone core with fracture and proppants was manufactured manually. Firstly, a natural tight sandstone was processed in advance, and it was split from the middle by Brazilian splitting methods. Then, a layer of 100/140 mesh quartz sand was evenly laid inside the splitting surface of the core. A porous metal screen was pasted on the upper and lower end surfaces, which can prevent the proppant in the fracture from slipping out of the fracture. Finally, it was wrapped with thermoplastic tube to form a complete core, and a strip of artificial propping fracture through the whole was formed. Two cores, named b-1 and b-2, were made according to the above methods. Table 2 shows the basic information of the cores used in the later evaluation experiment.

**Table 2.** Core data for the study of scale-inhibition performance.

| Core No. | Length/cm | Diameter/cm | Weight/g | Porosity /% | Pore Volume /cm <sup>3</sup> | Quartz/% | Potash Feldspar/% | Plagioclase/% | Dolomite/% | Clay/% |
|----------|-----------|-------------|----------|-------------|------------------------------|----------|-------------------|---------------|------------|--------|
| b-1      | 5.71      | 2.38        | 58.11    | 8.22        | 2.09                         | 17.23    | 1.10              | 13.20         | 67.20      | 1.27   |
| b-2      | 5.42      | 2.31        | 57.68    | 8.17        | 1.85                         | 18.57    | 2.13              | 11.80         | 65.90      | 1.60   |

### 2.3.2. Performance Evaluation of Scale-Inhibiting Fracturing Fluid

The scale formation process in the propping zone was characterized and described by using an online low-field NMR device in the laboratory. Under conditions of 5 MPa and room temperature, a 2 wt% KCl solution with flow rate of 0.2 mL/min was inject into core b-1. When the flow rate was stable at the exit end, an NMR T2 spectrum scanning was performed. Then, 1 wt% Na<sub>2</sub>CO<sub>3</sub> and 1 wt% CaCl<sub>2</sub> + 0.08% DR800 were injected into core b-1 at a rate of 0.2 mL/min, and the injection time was set to 2 h. After the injection was completed, a large amount of CaCO<sub>3</sub> scale appeared in the core propping zone. Finally, all switches of the core holder were turned off and left for 6 h. The cores were scanned again by NMR T2 spectra. The relaxation times in the experimental data were collected and converted to pore size, and the formula of pore size conversion is shown in Equation (2) [28].

$$\frac{1}{T_{2s}} = \rho_2^2 \frac{s}{v} \quad (2)$$

where  $T_{2s}$  is the transverse relaxation time;  $\frac{s}{v}$  is the ratio of the internal surface pore volume to the sample volume;  $\rho_2$  is the transverse relaxation, which characterizes the relaxation strength of solid–fluid interactions.

The scale-inhibiting process in the propping zone was also characterized by NMR T2 spectrum. First, three solutions were prepared, including 2 wt% KCl, 1 wt% Na<sub>2</sub>CO<sub>3</sub>, and 1 wt% CaCl<sub>2</sub> + scale-inhibiting fracturing fluid system. Under conditions of 5 MPa and room temperature, a 2 wt% KCl solution with flow rate of 0.2 mL/min was injected into core b-2. When the flow rate was stable at the exit end, an NMR T2 spectrum scanning was performed. Then, three solutions were simultaneously injected into core b-2 at a rate of 0.2 mL/min, and the injection time was set to 2 h. After the injection was completed, all switches of the core holder were turned off and left for 6 h. Finally, the core was scanned for NMR T2 spectra, and the relaxation time in the experimental data was collected and converted into the pore size in the same way as Equation (2).

The integral area of relaxation signal has a linear dependence with the pore volume, and the change in semaphores can reflect the amount of scaling in the pore. Therefore, the core scaling rate can be calculated by Equation (3), and the scale-inhibition rate of the scale-inhibiting fracturing fluid can be calculated by using Equation (4).

$$\delta = (S_1 - S'_1) \div S_1 \times 100 \quad (3)$$

$$\varnothing = [(S_1 - S'_1) - (S_2 - S'_2)] \div (S_1 - S'_1) \times 100 \quad (4)$$

where  $\delta$  is the scaling rate in %,  $\varnothing$  is the scale-inhibiting rate in %;  $S_1$  is the integral area of relaxation signal after core b-1 is saturated with 2 wt% KCl;  $S'_1$  is the integral area of the relaxation signal after scaling;  $S_2$  is the integral area of the relaxation signal after core b-2 is saturated with 2 wt% KCl;  $S'_2$  is the integral area of relaxation signal after the new fracturing fluid system.

According to accuracy parameters from the equipment manufacturer, the magnet of the equipment is a permanent magnet, the magnetic field strength is  $0.3T \pm 0.05T$ , the magnetic field uniformity is  $\leq 30$  pm ( $\varphi 110$  sphere), and the magnetic field stability is  $\leq 300$  Hz/h, so the accuracy of this equipment test is quite high.

## 2.4. Drag-Reduction Test of Scale-Inhibiting Fracturing Fluid

### 2.4.1. Loop Friction Test Device

Figure 1 shows the loop friction test device, which consists of three parts, namely, the tank part, the pipe parts, and the data processing parts. The main body of the pipe parts consists of three stainless steel test tubes with different diameters, 6 mm, 8 mm, and 10 mm from top to bottom, and a mixer. The pressure difference, flow rate, and temperature of this system are automatically monitored by the computer.



**Figure 1.** Picture of the loop friction test device.

### 2.4.2. Drag-Reduction Test

The scale-inhibiting fracturing fluid is made of slick water fracturing fluid and a scale inhibitor. Its formulation is: 0.08% scale inhibitor DR800 + 0.3% scale inhibitor SC-1 + 4% autogenic acid SEG-C + 0.2% clay stabilizer.

Testing process: (1) a 30 L measure of tap water was put into the reservoir, and the ball valve at the lower part of the reservoir was opened; (2) the injected parameters were set to 250 kg/h, 500 kg/h, 1000 kg/h, 1250 kg/h, and 1750 kg/h, and the differential pressure  $\Delta P_0$  for each was recorded, respectively; (3) in the same way, 30 L of scale-inhibiting fracturing fluid was put into the reservoir. The software was run and the differential pressure  $\Delta P_{DR}$  was recorded under different injected rates. The drag-reduction rate was calculated according to Equation (5) [29]:

$$DR\% = \frac{\Delta P_0 - \Delta P_{DR}}{\Delta P_0} \times 100\% \quad (5)$$

where  $DR\%$  is the drag-reduction rate;  $\Delta P_0$  is the pressure difference in Pa when the water passes through the pipe;  $\Delta P_{DR}$  is the pressure difference in Pa when the fracturing fluid passes through the pipe.

The drag-reduction experiment was tested three times at each displacement and the average value was taken. Then, the error was calculated, and error bars were added to the graph.

## 3. Results and Discussion

### 3.1. Experimental Evaluation of Scale Inhibitor

#### 3.1.1. Effect of Temperature on Scale Inhibition

$\text{CaSO}_4$  scale-inhibition rates of six commercial scale inhibitors, when the solution pH is 7 and under different temperatures, are shown in Figure 2. All scale inhibitors had a scale-inhibition rate greater than 60% at room temperature. Among them, the scale-inhibition rate of SC-1, SC-2, and SC-5 was more than 80%, which had a stronger scale-inhibition

ability of  $\text{CaSO}_4$ . With the increase in temperature, the scale-inhibition ability of these scale inhibitors all decreased. SC-1 and SC-5 had the best temperature resistance, and the decrease in scale-inhibition rate was within 20%. The scale-inhibition rate of SC-2 decreased from 87% to about 60% at 70 °C, and the temperature resistance was average. According to an information provided by the manufacturer, SC-1 is an organophosphate scale inhibitor, and it can chelate with metal ions, which can form a quadridentate stereo ring complex. This may be the reason why it is so little-affected by the temperature [30].

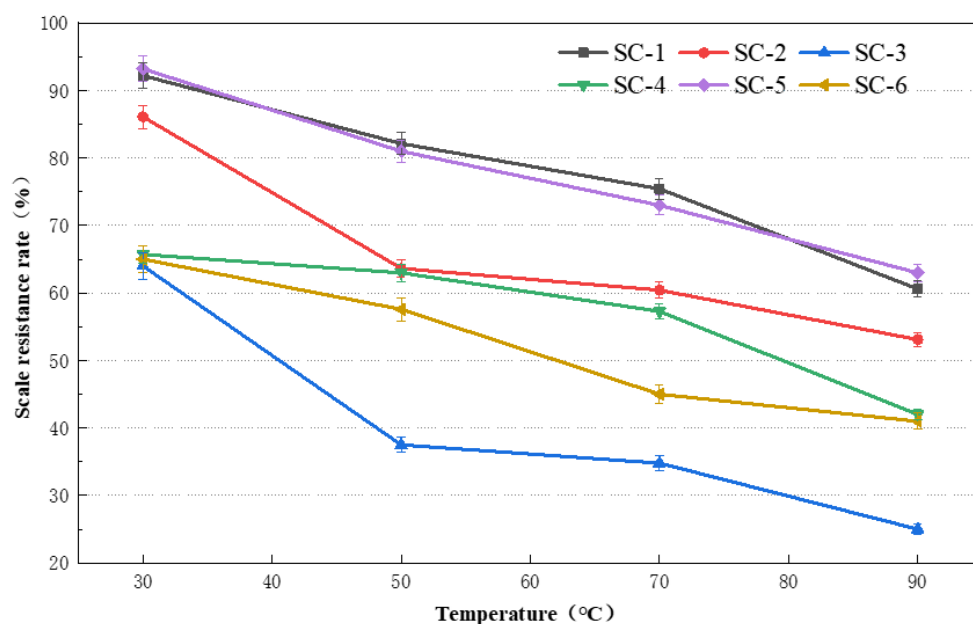


**Figure 2.** Effect of scale inhibitor on calcium sulfate at different temperature at pH of 7.

As shown in Figure 3, when the solution pH is 7, the scale-inhibition effect of  $\text{CaCO}_3$  of six scale inhibitors under different temperature conditions is shown. The scale-inhibition rate of SC-1, SC-2, and SC-5 at room temperature was more than 70%. The scale-inhibition efficiency of SC-5 dropped sharply when the temperature was greater than 50 °C, and SC-5 was the monomer organophosphate scale inhibitor, which also makes it more susceptible to temperature effects. When the temperature rose to 90 °C, the scale-inhibition rate of SC-2 decreased to about 80%, which is lower than 82% of SC-1. Overall, SC-1 has good inhibition ability for both scales is good, and it also has better temperature stability. This is consistent with the strong chelating ability of organic phosphoric acid to calcium at different temperatures.

### 3.1.2. Effect of pH on Scale Inhibition

Figure 4 shows, when the temperature is 25 °C, the  $\text{CaSO}_4$  scale-inhibition effect of six scale inhibitors under different pH levels. Among them, SC-1 and SC-2 have the scale-inhibition rate basically unchanged or even in an increasing trend. According to the manufacturer's information, SC-1 and SC-2 are organophosphate scale inhibitors, the chelating ability of organic phosphate for calcium ions is better under alkaline condition, they have good chemical stability, can be applied to a wide range of pH values, are not easily hydrolyzed, and have an obvious threshold value [13]. SC-5 was most seriously affected by alkalinity, and it decreased from 80% at pH 5 to 20% at pH 11. SC-5 is a polyaspartic acid scale inhibitor. With the increase in alkalinity, the scale-inhibition efficiency of polycarboxylic acid scale inhibitors was limited and weakened, which is similar to the trend reported in some literature [31].

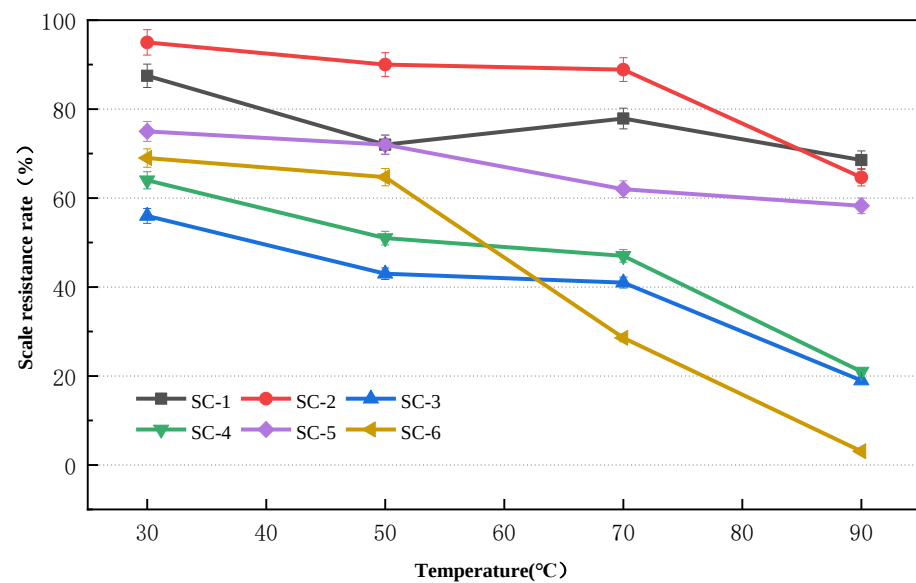


**Figure 3.** Effect of scale inhibitor on calcium carbonate at different temperatures at pH of 7.

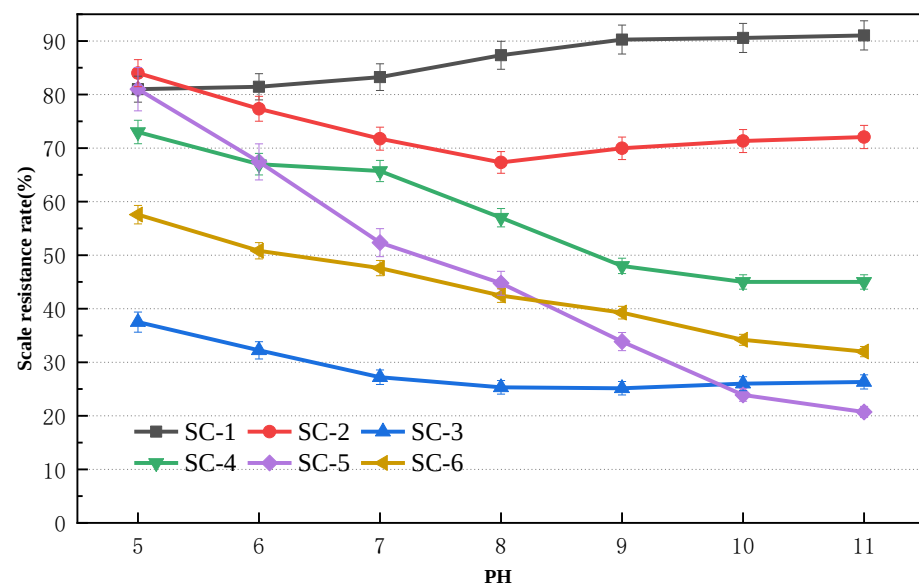


**Figure 4.** Effect of scale inhibitor on calcium sulfate at different pH levels and room temperature.

The  $\text{CaCO}_3$  scale-inhibition effect of six scale inhibitors under different pH conditions is shown in Figure 5. In an alkaline environment,  $\text{CO}_3^{2-}$  does not hydrolyze to  $\text{HCO}_3^-$ , and its concentration in liquid phase is higher. Due to its low solubility product, it is easier to precipitate into scale when  $\text{CO}_3^{2-}$  and  $\text{Ca}^{2+}$  concentration is high. Therefore, the scale-inhibition effect of  $\text{CaCO}_3$  is poor under alkaline environment. When the solution is weakly acidic with  $\text{pH} = 5$ , the scale-inhibition rate of SC-1 and SC-2 is larger than 75%. Although the scale-inhibition rate of SC-1 is slightly lower than that of SC-2 at lower pH, it can still maintain above 60% under strong alkaline environment. SC-1 is the most stable and strongest scale-inhibition effect compared with other five scale inhibitors. The results indicate that organic phosphoric acid has good chelating ability to calcium in both acidic and basic conditions.

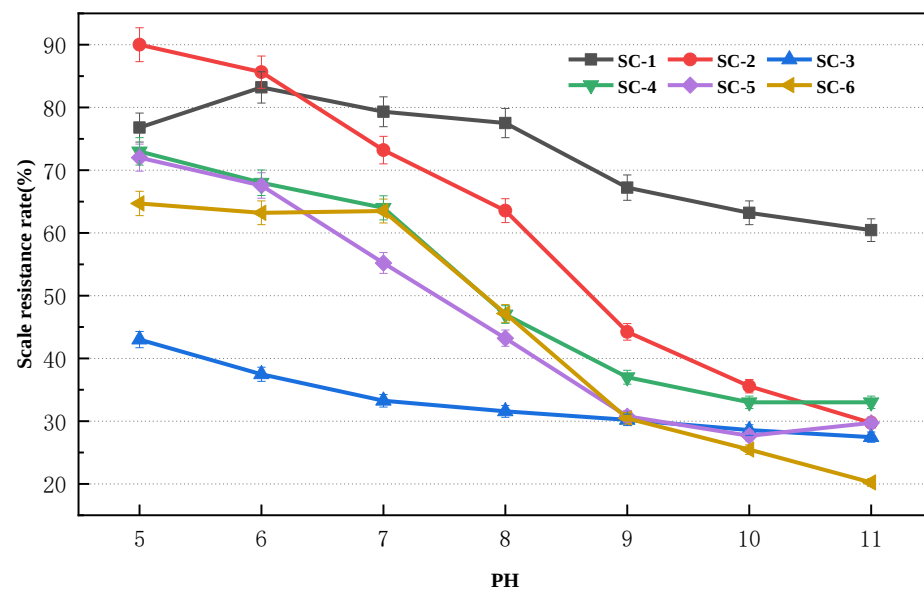


**Figure 5.** Effect of scale inhibitor on calcium carbonate at different pH levels and room temperature.

### 3.1.3. Influence of Scale-Inhibitor Concentration and Anti-Mixing Scale Evaluation Experiment

After a single scale-inhibition test, the scale inhibitors SC-1, SC-2, and SC-5 were selected, and their mixed scale-inhibition ability was further studied. The results are shown in Figure 6. Scale inhibitor SC-5 has the weakest scale-inhibition ability, and the scale-inhibition rate is only 42.8%. The scale-inhibition rate of SC-1 is 78.57% higher than that of SC-2. This is consistent with the results of a single scale-inhibition experiment. This suggests that SC-1 is preferred as the scale inhibitor for scale-inhibition fracturing fluid. Compatibility experiments are needed to verify its applicability.

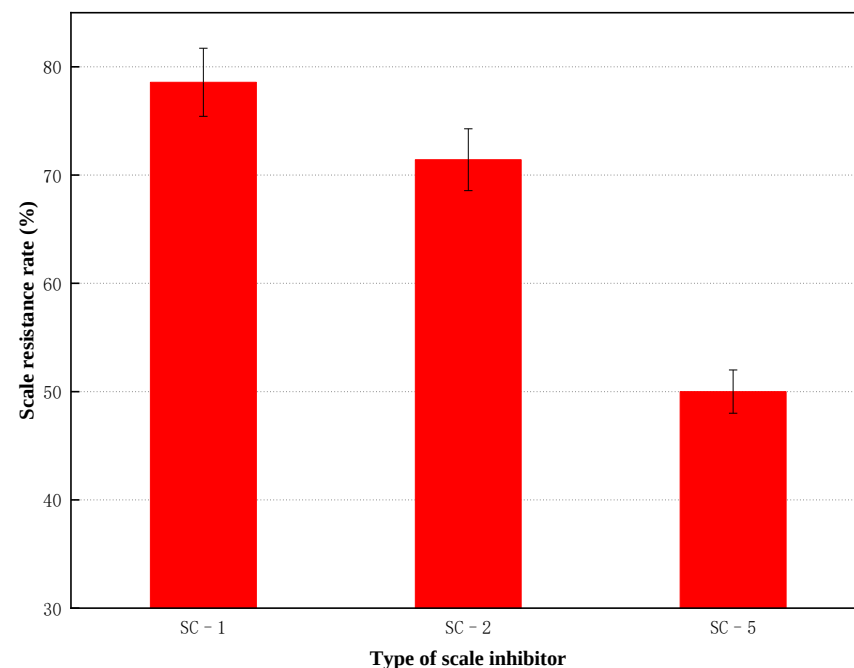


**Figure 6.** The mixed scale-inhibition ability of three optimal scale inhibitors at pH = 7 and room temperature.

As shown in Tables 3 and 4, the concentration of scale inhibitor SC-1 affected the scale-inhibition rate. The scale-inhibition abilities increase gradually with the scale-inhibitor

concentration. However, the scale inhibitor has a threshold effect [32]. There is an economic dose achieving good scale-inhibition effect. It is generally believed that this dose can just complete chelation reaction. For  $\text{CaCO}_3$ , the optimal concentration of scale inhibitor is 0.07%, and the scale-inhibition rate can reach 77%. For  $\text{CaSO}_4$ , the optimal concentration of scale inhibitor is 0.3%, and the scale-inhibition rate is 87%. Therefore, if there is more  $\text{CaCO}_3$  scale in the reservoir, the dose should be low, and if the  $\text{CaSO}_4$  scale is more, the dose needs to be increased.

**Table 3.** Scale-inhibition rate for  $\text{CaCO}_3$  of SC-1 at different concentrations.

| Scale-Inhibitor Concentration (%) | 0.01% | 0.03% | 0.05% | 0.07% | 0.09% |
|-----------------------------------|-------|-------|-------|-------|-------|
| Scale-Inhibiting Rate (%)         | 70%   | 71%   | 73%   | 77%   | 78%   |

**Table 4.** Scale-inhibition rate for  $\text{CaSO}_4$  of SC-1 at different concentrations.

| Scale-Inhibitor Concentration (%) | 0.1% | 0.2% | 0.3% | 0.5% | 0.7% |
|-----------------------------------|------|------|------|------|------|
| Scale-Inhibiting Rate (%)         | 65%  | 70%  | 87%  | 90%  | 91%  |

For  $\text{CaCO}_3$ , at room temperature, when the scale inhibitor is SC-1, the samples with the scale-inhibition rate under different pH conditions are counted, and the sample variance  $S_1^2$  is calculated, and when the pH is 7, and the scale inhibitor is SC-1, the samples with the scale-inhibition rate at different temperatures are counted, and the sample variance  $S_2^2$  is calculated. At room temperature, when pH = 7, the scale-inhibition rate samples of different scale inhibitors are counted, and the sample variance  $S_3^2$  is calculated.  $S_1^2$  ( $\text{CaCO}_3$ ) = 0.0062,  $S_2^2$  ( $\text{CaCO}_3$ ) = 0.0043, and  $S_3^2$  ( $\text{CaCO}_3$ ) = 0.0219. It can be seen from the variance data that the type of scale inhibitor has the greatest impact on the scale-inhibition rate. Similarly, For  $\text{CaSO}_4$ ,  $S_1^2$  ( $\text{CaSO}_3$ ) = 0.0016,  $S_2^2$  ( $\text{CaSO}_3$ ) = 0.0149, and  $S_3^2$  ( $\text{CaSO}_3$ ) = 0.0313, which indicates that the biggest impact on the scale-inhibitor rate is still the type of scale inhibitor.

### 3.2. Compatibility Study

As shown in Figure 7, the fracturing fluid after addition of SC-1 scale inhibitor at 90 °C has good compatibility, and no white flocculent or precipitation appeared in the sample bottle after 48 h of heating. Therefore, the scale inhibitor SC-1 can be added to the fracturing fluid system as an additive, and the autogenous acid SEG-C did not affect the compatibility of the system. However, a small number of fine bubbles appeared in the sample bottle after heating for 15 min. It is presumed that the autogenous acid generated acid which reacted with  $\text{CO}_3^{2-}$  in the fracturing fluid to produce  $\text{CO}_2$ . The autogenous acid can reduce the concentration of  $\text{CO}_3^{2-}$  in the solution, which would play an auxiliary scale-inhibition effect.

### 3.3. Scale-Inhibiting Effect of Fracturing Fluid

Figures 8 and 9 show the NMR T2 spectra of cores before and after scaling. Core b-1 applied conventional slickwater displacement, and b-2 applied scale-inhibiting effect of fracturing fluid. Scaling ions dominantly flow through the large pores, and the incompatible ions preferentially scale in the large pores of the propping zone. Although  $\text{CaCO}_3$  does not completely block the pores after scaling, the scale crystals deposited and grew perpendicularly to the pore surface, resulting in a gradual decrease in the pore size of 10,000 nm large pores and an increase in the pore size of 10 nm small pores.

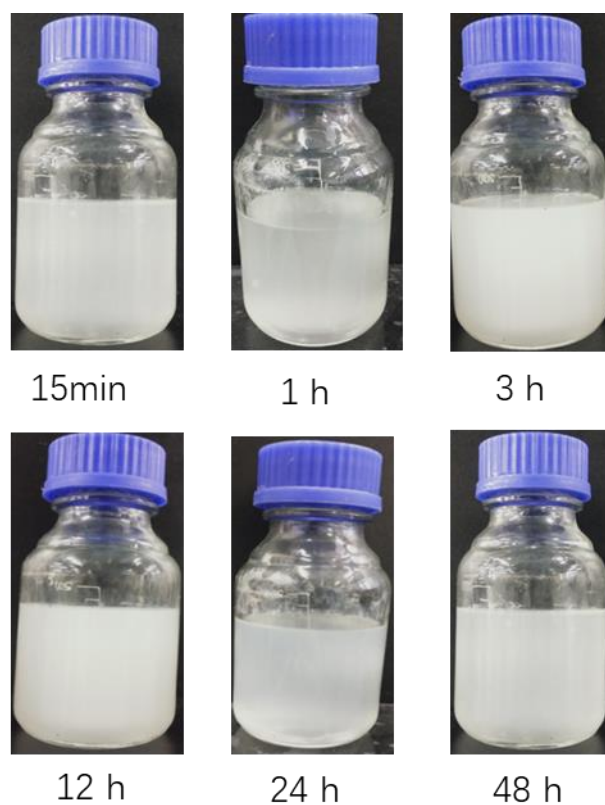


Figure 7. The compatibility of scale-inhibiting fracturing fluid system.

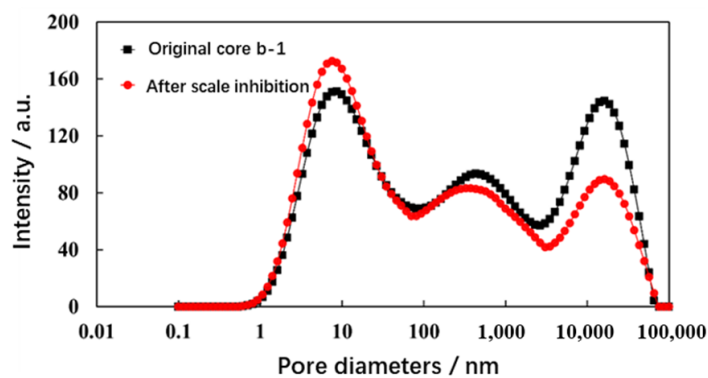


Figure 8. NMR curve of propped core b-1 before and after scaling without scale inhibitor.

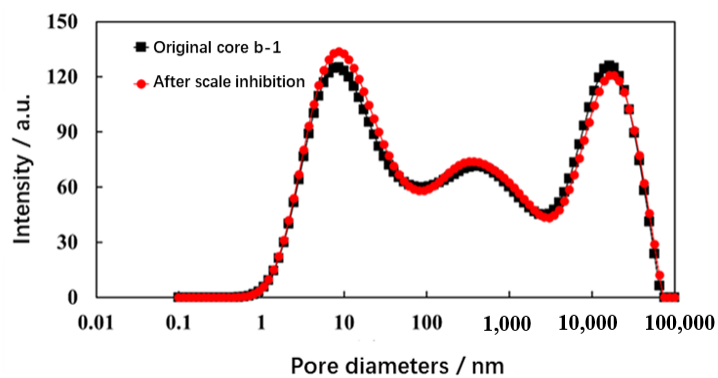


Figure 9. NMR curve of propped core b-2 before and after scaling with scale-inhibitor fracturing fluid.

After the scale-inhibiting fracturing fluid was injected into the core, the amount of  $\text{Ca}^{2+}$  and  $\text{CO}_3^{2-}$  scaling was reduced by the chelating effect of the scale inhibitor SC-1.

In addition, a small amount of scaling in the pore space was destroyed by the lattice distortion effect [33]. Both the signal strength of 10 nm small pores and 1000 nm large pores were basically unchanged. This indicated that the scale-inhibiting fracturing fluid system effectively prevented the scaling of large pore spaces in the propping zone.

Table 5 gives the numerical results of damage rate and scale-inhibition rate. For conventional slick water, the damage rate is 31.16% after scaling. After adding the scale inhibition, the scaling damage is almost negligible. The amount of relaxation signal changes to 5864.28 from 5983.31, and the calculated scale-inhibition rate reaches 96.29%, which can effectively reduce scaling damage.

**Table 5.** Calculation of damage rate and scaling-inhibition rate by NMR.

|                         | Integral Area of Core Relaxation Signal |                     | Damage Rate/% | Scale-Inhibition Rate/% |
|-------------------------|-----------------------------------------|---------------------|---------------|-------------------------|
|                         | Original Core                           | Cores after Scaling |               |                         |
| Without scale inhibitor | 10,299.63                               | 7089.97             | 31.16         | 0                       |
| With scale inhibitor    | 5983.31                                 | 5864.28             | 1.99          | 96.29                   |

### 3.4. Drag-Reduction Evaluation of Scale-Inhibiting Fracturing Fluid

Figure 10 shows the variation of drag reduction rate with displacement. The drag-reduction rate of conventional slickwater after adding scale inhibitor SC-1 can exceed 75%. This indicates that organic phosphate chelators do not affect the drag-reduction rate of slickwater fracturing fluid.

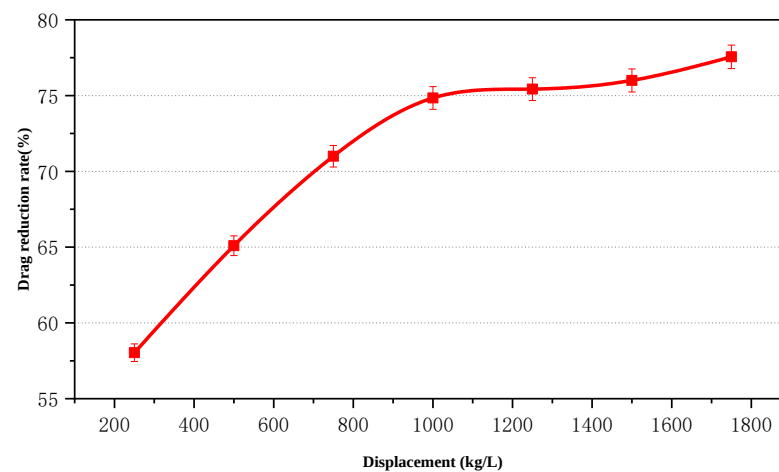


**Figure 10.** Drag-reduction test of scale-inhibiting fracturing fluid.

## 4. Conclusions

In this paper, six commercial scale inhibitors were systematically evaluated and optimized under different conditions of temperature, pH, and concentration. Then, the optimal scale inhibitor was combined with conventional slickwater fracturing fluid to produce a scale-inhibiting fracturing fluid. Finally, the compatibility, scale-inhibiting effect, and drag reduction of this new fracturing fluid were tested. The following conclusions were obtained:

(1) The scale-inhibition ability of six commercially available scale inhibitors was evaluated. Among them, organo-phosphonic acid scale inhibitor SC-1 performed well, and its scale-inhibition rate was 69% and 61% for  $\text{CaCO}_3$  and  $\text{CaSO}_4$  even at 90 °C. When the pH of the system is between 5 and 11, the scale-inhibition rate of SC-1 is stable around 80% for  $\text{CaSO}_4$  and above 60% for  $\text{CaCO}_3$ .

(2) We tested the concentration of scale inhibitor for preventing  $\text{CaCO}_3$  scales, and the results showed that the most optimal concentration of the scale inhibitor was 0.07%. For inhibiting  $\text{CaSO}_4$  scales, the optimal concentration of the scale inhibitor was 0.3%. Furthermore, for mixed scales, 0.3% of the scale inhibitor was also recommended. SC-1 has

optimal scale-inhibition ability for mixed scales, and the scale-inhibition rate for mixed scales can reach 78% at room temperature. Among them, the type of scale inhibitor is the most important factor affecting the scale-inhibition rate.

(3) After SC-1 was combined with the conventional fracturing fluid (0.08% drag-reducing agent DR800+0.3% SC-1+4% autogenous acid SEG-C+0.2% clay stabilizer), no white flocculent or precipitation appeared within 48 h. This indicates that the scale-inhibitor fracturing system is stable.

(4) The scale-inhibiting fracturing fluid system can effectively prevent scaling in the large pores of the core and the propping zone. Its scale-inhibition rate can reach 96.29% and the scale damage is negligible. In contrast, conventional slickwater has a 31.16% decrease in porosity.

(5) The scale-inhibiting fracturing fluid system maintains a good drag reduction, with a drag-reduction rate of 75.18% at a 1750 kg/h flow. There is no bad effect on properties of slickwater after adding the preferred scale inhibitor.

In summary, the scale-inhibiting fracturing fluid system described in the paper has good stability and scale-inhibition ability, both in different temperatures and pH environments. In addition, the new fluid maintains good compatibility and drag-reduction performance. At present, the technology can effectively solve the scaling problems of the propping zone in the fracturing process in reservoirs below 90 °C during the fracturing process, which has a positive effect on oil and gas production increase.

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**Conflicts of Interest:** The authors declare no conflict of interest.

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