

Article

Influence of Type and Concentration of Acid on Reaction Kinetics and Reservoir Permeability Enhancement in Tight Limestone Acidizing

Chunsheng Wang ^{1,*}, Chao Xu ¹ , Xiaohu Wang ², Minglei Tian ³ and Enhui Pei ¹ ¹ Key Laboratory of Enhanced Oil and Gas Recovery of Ministry of Education, Northeast Petroleum University, Daqing 163000, China² Offshore Oil Engineering Co., Ltd., LNG Engineering Technology Branch, Tianjin 300461, China³ China Petroleum & Natural Gas Pipeline Engineering Co., Ltd., Langfang 065000, China

* Correspondence: wangchunsheng@nepu.edu.cn

Abstract: This study investigates the acid–rock reaction kinetics and their implications for enhancing tight limestone reservoir stimulation through systematic experiments. Using 14 tight limestone cores, we evaluate the dynamic behavior of single-phase and gelled acids (12%, 15%, and 20% HCl) under controlled reservoir conditions (80 °C; 10–180 min). Three key findings emerge: (1) gelled acids initially exhibit higher reaction rates (0.897%/min) compared to single-phase acids (0.453%/min at 10 min), but their efficiency converges over extended durations; (2) reaction rates for both acid types follow the quadratic decay pattern over time ($R^2 > 0.95$), contrasting with conventional linear assumptions; and (3) reaction time is identified as the primary factor governing permeability enhancement (up to 29,200% improvement), outweighing acid concentration and type. The results demonstrate that concentrations above 15% significantly enhance etching efficiency, while single-phase acids with moderate reaction rates achieve an optimal balance between penetration depth and surface integrity. By integrating gravimetric analysis with permeability–porosity mapping, this work provides a predictive framework for acidizing process design in low-permeability reservoirs. The findings offer practical insights for optimizing acid fracturing operations, emphasizing time-controlled strategies over traditional concentration-focused approaches.

Academic Editors: Shifeng Zhang,
Guoqiang Xing and Mingxian Wang

Received: 26 February 2025

Revised: 7 March 2025

Accepted: 10 March 2025

Published: 14 March 2025

Citation: Wang, C.; Xu, C.; Wang, X.; Tian, M.; Pei, E. Influence of Type and Concentration of Acid on Reaction Kinetics and Reservoir Permeability Enhancement in Tight Limestone Acidizing. *Processes* **2025**, *13*, 851. <https://doi.org/10.3390/pr13030851>

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Keywords: tight limestone; acid–rock reaction kinetics; acid etching degree; permeability enhancement; single-phase acid; gelled acid

1. Introduction

In the ever-changing global energy landscape, the development of petroleum resources remains an important focus. As an unconventional resource, tight oil faces unique challenges due to its low porosity and permeability [1–3]. Acid fracturing is one of the key technologies for stimulation and improvement in carbonate reservoirs [4–10]. However, the acid–rock reactivity of tight limestone remains poorly understood under such extreme conditions [11–14].

Previous studies have explored various aspects of acid–rock reactions in different formations, but the specific mechanism of acid–rock reactions in tight limestone has not been fully elucidated. For example, some works have studied the effects of acid injection with different processes on carbonate rocks [11]; some researchers have investigated the influence of reservoir rock mineral composition on acid etching [15–18]; and some researchers have studied the influence of acid type, flow rate, contact time, and rock type on the non-uniform

morphology of acid-etched rock surfaces [19]. However, their findings may not directly apply to tight limestone, and there is a lack of research on the effect of acid-etching rate on rock acidification.

This study aims to address this issue. Through acid–rock reaction rate experiments on 14 limestone cores with different acid concentrations and reaction times, the kinetic mechanism of the acid–rock reaction was explored. The results of this study will provide necessary theoretical support and practical guidance for the optimization of acid fracturing in tight limestone reservoirs, improvement in tight oil recovery, and development of the energy industry.

2. Experimental Method for Acid–Rock Reaction Rate of Dense Limestone

2.1. Experimental Samples

Experimental cores: all experimental cores were limestone, with a total of 14 pieces. Most of the cores had micro-fractures on the surface. The specific core descriptions are shown in Table 1. X-ray diffraction (XRD) was used to analyze the mineral composition of the cores. The results showed that the main minerals were calcite (approximately 74%), quartz (approximately 21%), clay, and other impurities, as shown in Figure 1.

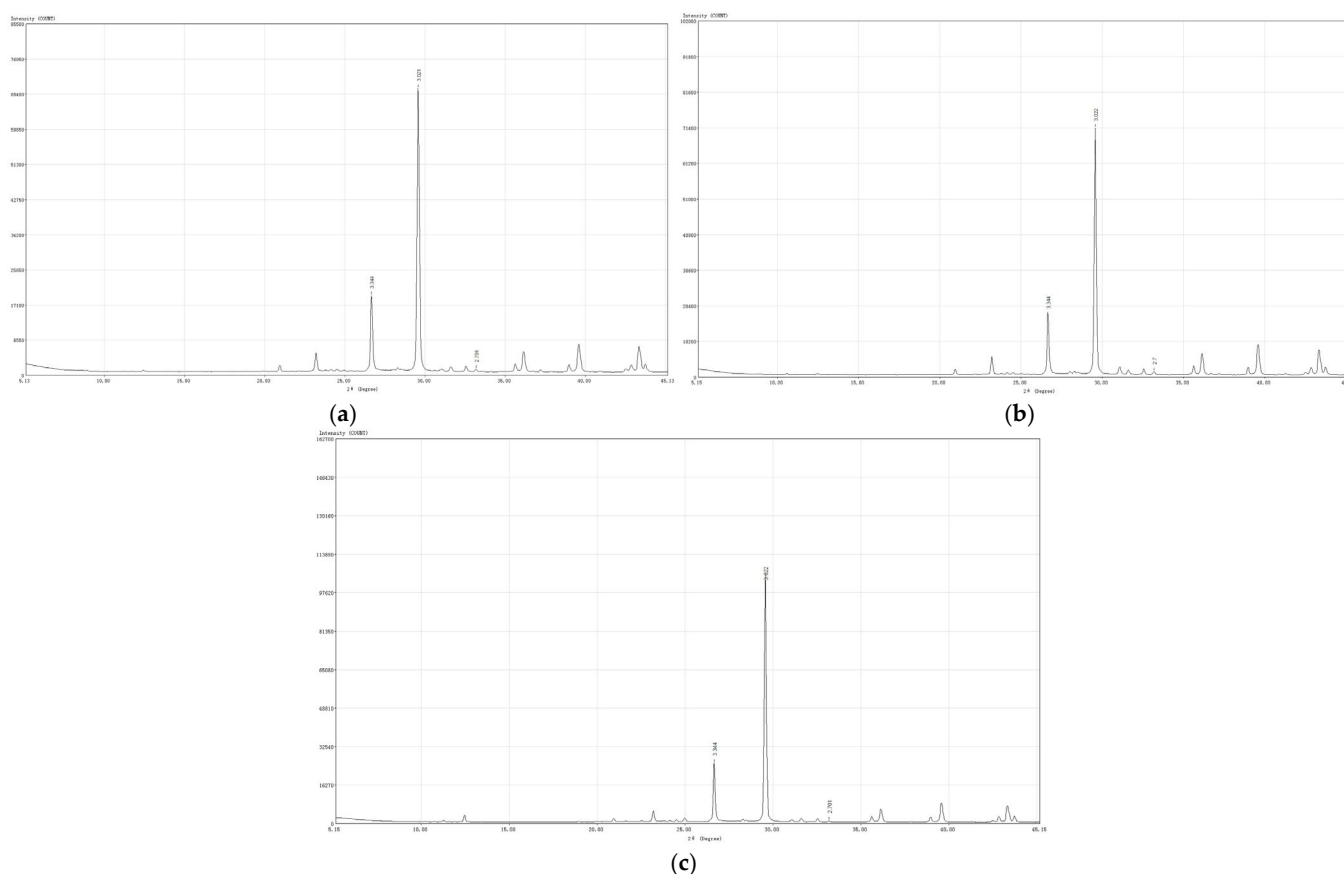


Figure 1. Mineralogical composition of tight limestone cores via XRD analysis. (a) A-1,A-2; A-3,D-1,D-2; (b) A-4,A-5,C-1,C-2,C-3,C-4,C-5; and (c) B-1,B-2.

The basic data of the 14 experimental cores are shown in Table 2. The size specifications were standard samples of 2.5×5 cm. The density of the 16 cores was relatively uniform, approximately 2.6 to 2.8 g/cm³. The permeability of the cores varied greatly, ranging from 0.0013 to 1.083 mD.

Table 1. Core description of acid–rock reaction experiment.

Core Number	Number of Fractures	Development Degree	Characteristics of Dissolved Pores and Caves
A-1	4	Fewer fractures, irregular in shape, and mostly transversely distributed on the side of the core.	There were tiny, dissolved pores on the surface of the core.
A-2	3	Fewer fractures on the surface of the core, and all were closed.	There were tiny, dissolved pores on the surface of the core.
A-3	1	There was only one regular fracture, which was a closed fracture.	There were dissolved pores, but they were not obvious.
A-4	1	There was only one regular fracture, which was a closed fracture.	None.
A-5	7	Higher amount of fractures, irregular in shape, and a few were crossed.	There were dissolved pores on the surface of the core.
B-1	3	Fewer fractures, irregular in shape, and all were closed.	No obvious dissolved pores were seen.
B-2	2	Fewer fractures, irregular in shape and large in spacing, and all were closed.	There were tiny, dissolved pores on the surface of the core.
C-1	2	Fewer fractures on the surface of the core, and all were closed.	None.
C-2	17	Higher amount of fractures, irregular in shape, and most were crossed and closed.	There were dissolved pores, but they were not obvious.
C-3	4	Fewer fractures, irregular in shape, and crossed.	No obvious dissolved pores were seen.
C-4	3	Fewer fractures, concentrated in distribution, and slightly opened.	None.
C-5	15	Higher amount of fractures accompanied by dissolution phenomena, small gaps, and mainly open.	The dissolution was relatively severe.
D-1	3	Fewer fractures, regular in shape, evenly distributed, and closed.	None.
D-2	2	One through fracture and one closed fracture; the dissolution phenomenon was not obvious.	There were dissolved pores, but they were not obvious.

Table 2. Basic core data of acid–rock reaction rate.

Core Number	Permeability (mD)	Porosity (%)	Dry Weight (g)
A-1	0.0013	1.7982	67.441
A-2	0.0016	1.3446	67.24
A-3	0.0029	1.1799	67.184
A-4	0.014	2.3082	70.19
A-5	0.003	2.2558	65.986
B-1	0.0028	1.2998	67.702
B-2	0.0088	1.7544	66.062
C-1	0.006	2.1087	67.697
C-2	0.094	2.2113	67.159
C-3	0.0041	1.9413	67.139
C-4	1.083	3.9126	69.776
C-5	0.008	1.9257	66.125
D-1	0.002	1.215	66.812
D-2	0.0027	1.6613	67.685

2.2. Experimental Reagents and Equipment

When studying the acid–rock reaction in tight limestone, the selection of acid concentrations in the 12–20% range was based on previous research and field application experience. This concentration range can ensure a certain dissolution effect on limestone and control the reaction rate to a certain extent, facilitating the observation of the dynamic process of the acid–rock reaction.

The experimental acid solutions were gelled acid and single-phase acid. The base acid solution was hydrochloric acid with concentrations of 12%, 15%, and 20%. The concentration of distilled water was changed accordingly, and other additives remained unchanged, as shown in Table 3.

Table 3. Basic data of single-phase acid and gelled acid.

Single-Phase Acid System		Gelled Acid Solution System	
Additives	Concentration	Additives	Concentration
HCl hydrochloric acid	20%	HCl hydrochloric acid	20%
Acid retarding agent	3%	Thickening agent 1	0.20%
Acid drag-reducing agent	0.20%	Thickening agent 2	2%
Distilled water	76.80%	Distilled water	77.80%

Experimental equipment: constant temperature box RHP-1000 (Guangdong Huanrui Testing Equipment Co., Ltd., Dongguan, China; temperature control accuracy of ± 0.5 °C), one-thousandth electronic precision balance (Shanghai Zanwei Weighing Apparatus Co., Ltd., Shanghai, China; measurement accuracy of 0.001 g), and beaker.

2.3. Experimental Methods

Conventional acid–rock reaction rate experiments usually involve saturating the core column with water after vacuuming and placing it in a core holder to displace a certain amount of acid solution at a fixed flow rate. The mass change before and after the experiment and the changes in porosity and permeability are measured to calculate the acid–rock reaction rate and acid etching degree. However, the permeability of the Taiyuan Formation limestone cores used in this experiment was extremely low, ranging from 0.0013 to 1.083 mD, belonging to ultra-low permeability cores. The water permeability could not be measured, and it was difficult to saturate the cores with water. Therefore, the conventional experimental method could not be used for the acid–rock reaction rate experiment. Instead, the gravimetric method was adopted. The gravimetric method has the advantages of simple operation and no need for complex equipment. The acid–rock reaction rate and acid etching degree were calculated by measuring the mass change before and after the acid etching reaction for a certain time.

Acid etching degree (%) = (mass before acid immersion mass after acid immersion)/mass before acid immersion

Acid–rock reaction rate (%/min) = acid etching degree/acid immersion time

The experimental schemes for the reaction rates of single-phase acid and gelled acid with limestone are shown in Tables 4 and 5. Fourteen cores were used in the experiment. The experimental temperature was 80 °C. The acid solution types were single-phase acid and gelled acid, and the acid concentrations were 20%, 15%, and 12%. The acid immersion times were 10 min, 20 min, 30 min, 60 min, and 180 min.

Table 4. Experimental scheme design of single-phase acid–rock reaction rate.

Core Number	Acid Solution Type	Acid Concentration (%)	Acid Immersion Time (min)
A-1	Single-phase acid	20	10
A-2	Single-phase acid	20	20
A-3	Single-phase acid	20	30
A-4	Single-phase acid	20	60
A-5	Single-phase acid	20	180
B-1	Single-phase acid	12	30
B-2	Single-phase acid	15	30

Table 5. Experimental scheme design of gelled acid–rock reaction rate.

Core Number	Acid Solution Type	Acid Concentration (%)	Acid Immersion Time (min)
C-1	Gelled acid	20	10
C-2	Gelled acid	20	20
C-3	Gelled acid	20	30
C-4	Gelled acid	20	60
C-5	Gelled acid	20	180
D-1	Gelled acid	12	30
D-2	Gelled acid	15	30

2.4. Experimental Procedure

1. Core sample preparation: Use a wire cutting machine and water saw to prepare the full-diameter core into core samples. Place the cores in a constant temperature box and dry them at 60 °C for 24 h, and then measure their initial weights;
2. Prepare single-phase acid and gelled acid with concentrations of 12%, 15%, and 20%. Weigh each reagent accurately according to the proportion and mix them slowly under stirring conditions to ensure the uniformity of the solutions;
3. Place the cores and the prepared acid solutions in a constant temperature box and preheat them at 80 °C for 2 h. After preheating, place the cores in the acid solutions for reaction. After the reaction time, take out the cores;
4. Rinse the cores with running water for 15 min. Then, place the cores in a constant temperature box, dry them at 60 °C for 24 h, and measure their weights after the reaction;
5. Calculate the acid etching reaction rate and acid etching degree using the data.

3. Experimental Results and Analysis of the Reaction Rate of Acid Rock

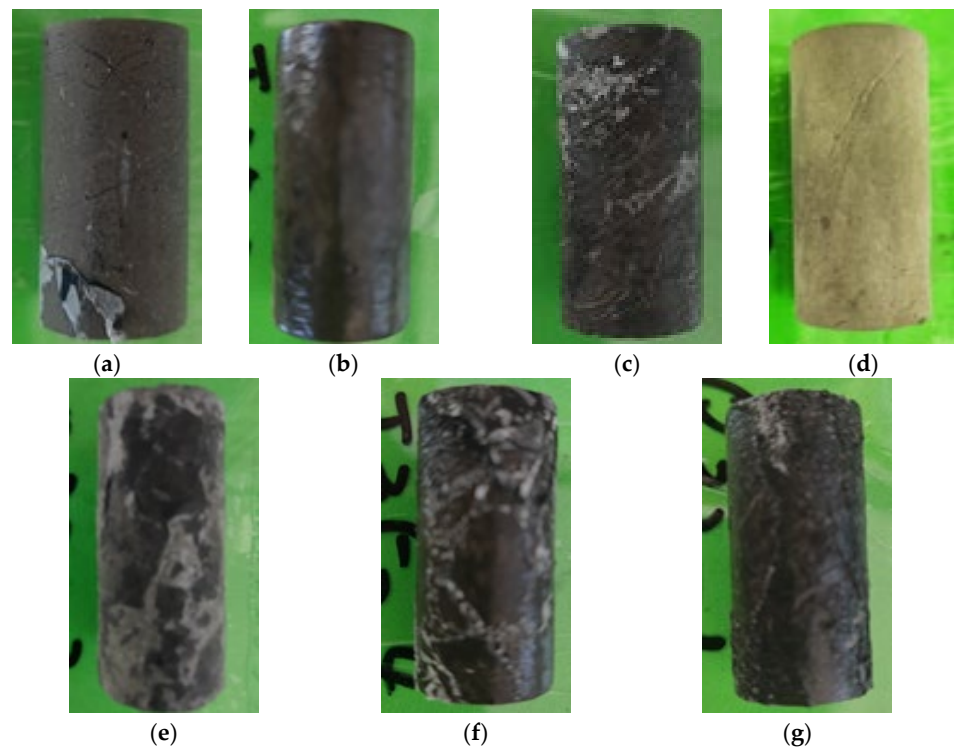
3.1. Experimental Results

3.1.1. Experimental Results of Single-Phase Acid–Rock Reaction Rate

After the experiment, all the cores showed different degrees of acid etching. The core descriptions are shown in Table 6, and the core pictures are shown in Figure 2. The lithology of core A-4 was significantly different from that of other cores, and the acid etching degree was the lowest. White minerals adhered to the surfaces of cores A-2, A-5, B-1, and B-2 after acid etching.

Table 6. Core condition after single-phase acid–rock reaction.

Core Number	Acid Etching State
A-1	The surface of the core was partially peeled off and did not have self-supporting high conductivity.
A-2	Acid etching worms appeared but were relatively small and did not have high self-supporting conductivity.
A-3	Acid etching worms appeared but were relatively small and did not have high self-supporting conductivity.
A-4	The acid etching degree of the core was the lowest; slight acid etching signs could be seen at the fractures, and it did not have self-supporting high conductivity.
A-5	The depth of the worm fractures on the core was relatively shallow, but the number of worm fractures was relatively large and had self-supporting high conductivity.
B-1	There were many worm fractures on the core, and they had a certain depth and self-supporting high conductivity.
B-2	There were many worm fractures on the core, and they had a certain depth and self-supporting high conductivity.

**Figure 2.** Core samples after the acid–rock reaction rate experiment with single-phase acid. (a) A-1; (b) A-2; (c) A-3; (d) A-4; (e) A-5; (f) B-1; and (g) B-2.

Single-Phase Acid–Rock Reaction Rate

When the concentration was 20%, the acid etching reaction rate of limestone could reach 0.453%/min when the acid etching time was 10 min; when the acid etching time was 20 min, the acid etching reaction rate of limestone was 0.341%/min; when the acid etching time reached 180 min, the acid etching reaction rate of limestone was approximately 0.096%/min. The average acid etching reaction rate at 10 min was about 5 times that at 180 min. Results of the acid–rock reaction rate of single-phase acid are shown in Table 7.

Table 7. Results of the acid–rock reaction rate of single-phase acid.

Core Number	Acid Concentration (%)	Acid Immersion Time (min)	Mass Before Acid Immersion (g)	Mass After Acid Immersion (g)	Acid Etching Degree (%)	Acid Etching Rate (%/min)
A-1	20	10	67.441	64.388	4.527	0.453
A-2	20	20	67.24	62.659	6.813	0.341
A-3	20	30	67.184	57.325	14.675	0.489
A-4	20	60	70.19	62.346	11.175	0.186
A-5	20	180	65.986	54.634	17.204	0.096
B-1	12	30	67.702	61.179	9.635	0.321
B-2	15	30	66.062	58.625	11.258	0.375

3.1.2. Experimental Results of Gelled Acid–Rock Reaction Rate

After the experiment, all the cores showed different degrees of acid etching. The core descriptions are shown in Table 8, and the core pictures are shown in Figure 3. The lithology of core C-4 was significantly different from that of other cores, and the acid etching degree was the lowest. White minerals adhered to the surfaces of cores C-3 and D-4 after acid etching.

Table 8. The condition of the core after the gelled acid–rock reaction.

Core Number	Acid Etching State
C-1	There were slightly visible acid etching worm fractures on the core, but they were relatively small and did not have self-supporting high conductivity.
C-2	There were slightly visible acid etching worm fractures on the core, but they were relatively small and did not have self-supporting high conductivity.
C-3	There were slightly visible acid etching worm fractures on the core, but they were relatively small and did not have self-supporting high conductivity.
C-4	The acid etching degree of the core was low, and no acid etching worms were seen, and it did not have self-supporting high conductivity.
C-5	The surface of the core was covered with worm fractures, and the worm fractures had a certain depth and had self-supporting high conductivity.
D-1	The acid etching degree of the core was low, and no acid etching worms were seen, and it did not have self-supporting high conductivity.
D-2	There were slightly visible acid etching worm fractures on the core, but they were relatively small and did not have self-supporting high conductivity.

Gelled Acid–Rock Reaction Rate

When the acid etching time was 10 min, the acid etching reaction rate of limestone could reach 0.897%/min; when the acid etching time reached 180 min, the acid etching reaction rate of limestone was 0.172%/min. With the increase in acid etching time, the acid etching reaction rate of the core approximately decreased in a logarithmic trend. The acid etching reaction rate at 10 min was about 5.2 times that at 180 min. Results of the acid–rock reaction rate of gelled acid are shown in Table 9.

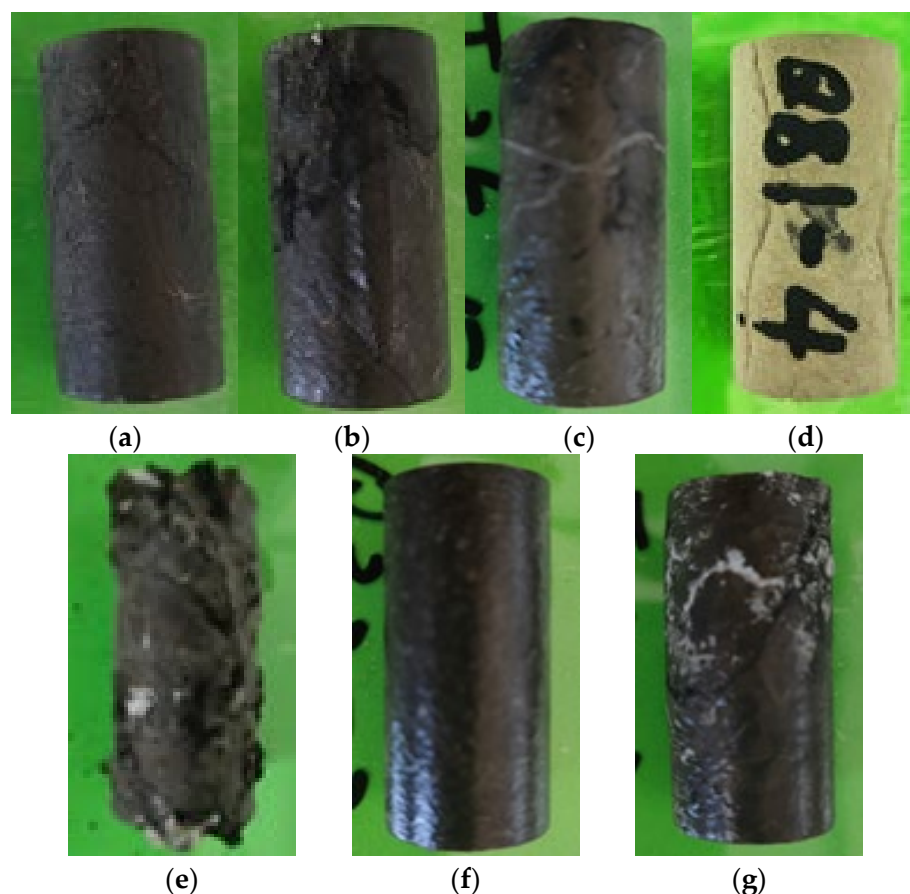


Figure 3. The cores after the experiment on the acid–rock reaction rate of gelled acid. (a) C-1; (b) C-2; (c) C-3; (d) C-4; (e) C-5; (f) D-1; and (g) D-2.

Table 9. Results of the acid–rock reaction rate of gelled acid.

Core Number	Acid Concentration (%)	Acid Immersion Time (min)	Mass Before Acid Immersion (g)	Mass After Acid Immersion (g)	Acid Etching Degree (%)	Acid Etching Rate (%/min)
C-1	20	10	67.697	61.626	8.968	0.897
C-2	20	20	67.159	57.637	14.178	0.709
C-3	20	30	67.139	57.265	14.707	0.49
C-4	20	60	69.776	63.285	9.303	0.155
C-5	20	180	66.125	45.703	30.884	0.172
D-1	12	30	66.812	60.077	10.081	0.336
D-2	15	30	67.685	59.812	11.632	0.388

3.2. Result Analysis

3.2.1. The Same Concentration, Different Times

With the increased acid reaction time, the difference in acid etching rates between the two acid solutions gradually decreased. Comparing the acid etching degrees of single-phase acid and gelled acid, the acid etching degree of gelled acid was higher than that of single-phase acid. The etching results of 20% single-phase acid under different reaction times are shown in Table 10. The etching results of 20% gelled acid under different reaction times are shown in Table 11.

Table 10. Comparison of the acid etching results of single-phase acid at different times.

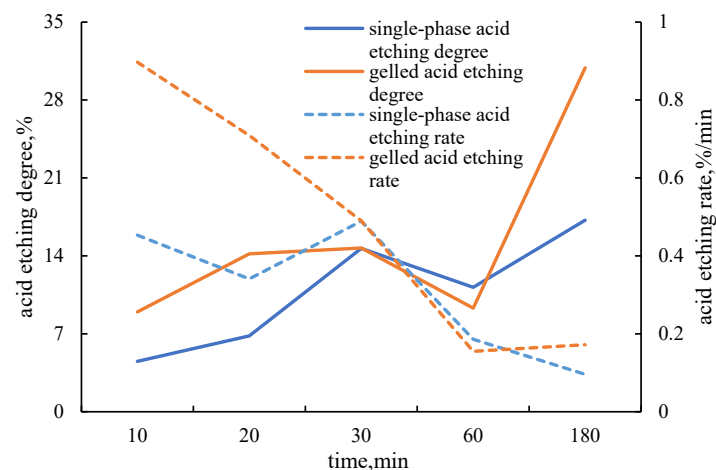
Core Number	Acid Concentration (%)	Acid Immersion Time (min)	Acid Etching Degree (%)	Acid Etching Rate (%/min)
A-1	20	10	4.527	0.453
A-2	20	20	6.813	0.341
A-3	20	30	14.675	0.489
A-4	20	60	11.175	0.186
A-5	20	180	17.204	0.096

Table 11. Comparison of the acid etching results of gelled acid at different times.

Core Number	Acid Concentration (%)	Acid Immersion Time (min)	Acid Etching Degree (%)	Acid Etching Rate (%/min)
C-1	20	10	8.968	0.897
C-2	20	20	14.178	0.709
C-3	20	30	14.707	0.49
C-4	20	60	9.303	0.155
C-5	20	180	30.884	0.172

Comparative Analysis

The experimental results show that when the acid immersion time is less than 30 min, there is a significant difference between the acid etching reaction rate and acid etching degree of gelled acid and those of single-phase acid. The former was about twice the latter. However, with the increase in acid–rock reaction time, the difference gradually decreased. When the acid immersion time was greater than 30 min, although the difference was not significant, the acid etching rates of both single-phase acid and gelled acid decreased significantly. From the perspective of chemical reaction kinetics, in the initial reaction stage, the acid concentration was relatively high, and the chemical reaction rate was mainly affected by the contact area between the acid solution and the rock surface and the number of active sites. Due to its viscosity characteristics, gelled acid stayed on the core surface for longer, increasing the effective contact area, so the reaction rate and degree were higher. As the reaction proceeded, the acid concentration decreased, and the reaction was gradually controlled by diffusion. At this time, the diffusion rates of the two acid solutions gradually approached, resulting in the reaction rate and degree also tending to be similar. A comparison of the acid etching results of single-phase acid and gelled acid at different times is shown in Figure 4.

**Figure 4.** Comparison of the acid etching results of single-phase acid and gelled acid at different times.

Quadratic Decay Model of Reaction Rates

Regression analyses were performed using OriginLab 2023, with significance thresholds set at $p < 0.01$. Residual normality was verified via Shapiro–Wilk tests ($p > 0.05$), ensuring model validity. To quantify the temporal evolution of acid–rock reaction rates, a quadratic regression model was applied to experimental data from both single-phase and gelled acids (20% HCl concentration). The reaction rate (R , %/min) was modeled as a function of time (t , min) using Equation (1):

$$R = a \cdot t^2 + b \cdot t + c \quad (1)$$

where a , b , and c are fitting coefficients. The regression analysis was performed using the least squares method in OriginLab 2023, with the coefficient of determination (R^2) calculated by Equation (2):

$$R^2 = 1 - \frac{\sum (R_{\text{observed}} - R_{\text{predicted}})^2}{\sum (R_{\text{observed}} - \bar{R}_{\text{observed}})^2} \quad (2)$$

The fitting equation for single-phase acid (20% HCl) is shown in Equation (3); the result is $R^2 = 0.963$, $p < 0.001$:

$$R = -0.0008t^2 - 0.012t + 0.594 \quad (3)$$

The fitting equation for gelled acid (20% HCl) is shown in Equation (4); the result is $R^2 = 0.958$, $p < 0.001$:

$$R = -0.0012t^2 - 0.008t + 0.921 \quad (4)$$

The quadratic attenuation model prediction of the reaction rate of single-phase acid (20% HCl) is compared with the actual observed values, as shown in Table 12. The quadratic model demonstrates superior accuracy compared to linear or exponential fits. This decay pattern aligns with the transition from surface-controlled dissolution (early stage) to diffusion-limited kinetics (later stage), driven by declining acid concentration gradients and pore-clogging by the reaction by-products.

Table 12. Single-phase acid, 20% HCl.

Core Number	Acid Concentration (%)	Acid Immersion Time (min)	Observed Rate (%/min)	Predicted Rate (%/min)
A-1	20	10	0.453	0.462
A-2	20	20	0.341	0.325
A-3	20	30	0.489	0.491
A-4	20	60	0.186	0.195
A-5	20	180	0.096	0.103

3.2.2. The Same Time, Different Concentrations Comparative Analysis

The etch results of different concentrations of single-phase acid under a 30 min reaction time are shown in Table 13. The etch results of different concentrations of gelled acid under a 30 min reaction time are shown in Table 14. The experimental results showed that with the increase in acid concentration, the differences in acid etching degree and acid etching rate between the two acid solutions gradually decreased. However, at each concentration, the acid etching degree and the acid etching rate of gelled acid were still slightly higher than those of single-phase acid. When the concentration was greater than 15%, the difference

between the two narrowed more significantly. When the concentration exceeded 15%, although there was still a difference, it had less impact on the acidizing effect. According to the chemical reaction rate equation, the acid–rock reaction rate positively correlates with the acid concentration. The increase in concentration increases the number of hydrogen ions per unit volume and enhances the reaction activity, resulting in an increase in the reaction rate and degree. At the same time, due to the action of additives in the acid solution, the performance difference between the two acid solutions is relatively weakened at higher concentrations. A comparison of the acid etching results of single-phase acid and gelled acid at different concentrations is shown in Figure 5.

Table 13. Comparison of the acid etching results of single-phase acid with different concentrations.

Core Number	Acid Concentration (%)	Acid Immersion Time (min)	Acid Etching Degree (%)	Acid Etching Rate (%/min)
B-1	12	30	9.635	0.321
B-2	15	30	11.258	0.375
A-3	20	30	14.675	0.489

Table 14. Comparison of the acid etching results of gelled acid with different concentrations.

Core Number	Acid Concentration (%)	Acid Immersion Time (min)	Acid Etching Degree (%)	Acid Etching Rate (%/min)
D-1	12	30	10.081	0.336
D-2	15	30	11.632	0.388
C-3	20	30	14.707	0.49

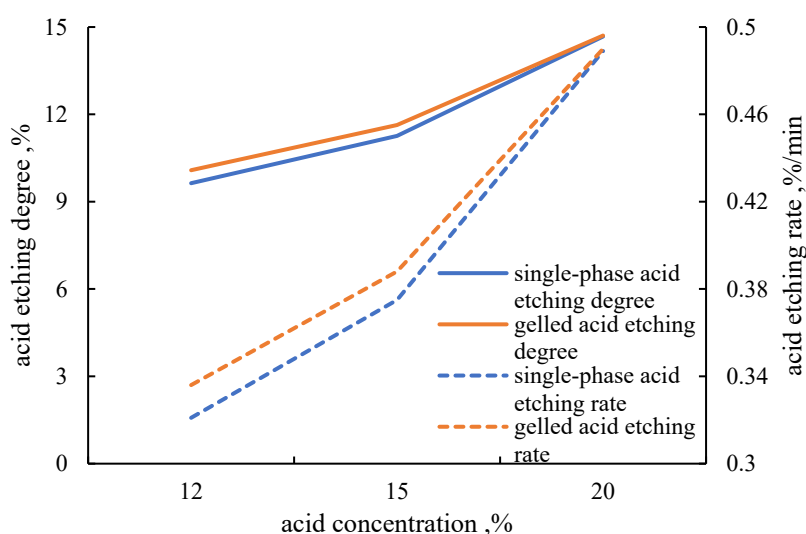


Figure 5. Comparison of the acid etching results of single-phase acid and gelled acid at different concentrations.

3.2.3. Changes in Permeability and Porosity

The general trend in acid etching degree was increasing. However, due to the absence of dissolved pores and caves on the surface of core A-4, its acid etching degree was lower than that under the same conditions. From the perspective of microscopic permeability and porosity, different core time groups showed that the permeability change degree ranged from 7130.80% to 29,200%, and the porosity change degree ranged from 75.29% to 160.53%. When the time factor was not sufficient, the number of fractures and the presence of dissolved pores and caves on the core surface had less influence on the high conductivity of

the core. The time factor accounted for a larger proportion. Time > the number of dissolved pores, caves, and fractures. Permeability had a greater influence on the formation of acid etching worms. The low permeability of tight limestone acid–rock reservoirs affected the flow of the acid solution, resulting in the acid solution being unable to penetrate deep into the core and only forming dissolution on the core surface, with no obvious acid etching worms appearing. Moreover, a reduction in fractures, small porosity, and even obvious dissolved pores hindered the formation of acid etching worms at higher concentrations. The number and depth of worm fractures were related to the original number and type of fractures. During the acidizing process, the acidizing time and concentration should be reduced for cores with more fractures. Porosity and permeability properties before and after acid etching are shown in Table 15.

Table 15. Porosity and permeability properties before and after acid etching.

Core Number	Acid Solution Type	Acid Concentration (%)	Acid Solution Time (min)	Permeability mD		Porosity %	
				Before	After	Before	After
A-1	Single-phase acid	20	10	0.0013	0.094	1.7982	3.152
A-2	Single-phase acid	20	20	0.0016	0.145	1.3446	2.975
A-3	Single-phase acid	20	30	0.0029	0.386	1.1799	2.956
A-4	Single-phase acid	20	60	0.014	3.112	2.3082	4.858
A-5	Single-phase acid	20	180	0.003	0.879	2.2558	5.877
B-1	Single-phase acid	12	30	0.0028	0.205	1.2998	2.479
B-2	Single-phase acid	15	30	0.0088	0.782	1.7544	3.034
C-1	Gelled acid	20	10	0.006	0.313	2.1087	3.298
C-2	Gelled acid	20	20	0.094	6.447	2.2113	3.495
C-3	Gelled acid	20	30	0.0041	0.473	1.9413	3.531
C-4	Gelled acid	20	60	1.083	6.576	3.9126	6.072
C-5	Gelled acid	20	180	0.008	2.177	1.9257	5.367
D-1	Gelled acid	12	30	0.002	0.133	1.215	2.256
D-2	Gelled acid	15	30	0.0027	0.217	1.6613	2.833

3.2.4. Analysis of the Acid–Rock Damage Mechanism of the Microscopic Structure of Tight Limestone

In the experiment of this study, it was found that the acid solution used showed unique etching characteristics on the tight limestone samples. For single-phase acid it mainly exhibited a selective etching mode during the reaction with limestone. Some easily soluble mineral components were preferentially dissolved on the limestone surface, while some relatively insoluble minerals remained, resulting in a microscopically uneven structure on the rock surface or the peeling of the rock epidermis. It could be seen that calcite crystals were preferentially dissolved, and the remaining relatively insoluble minerals, such as quartz, formed protrusions. In the initial reaction stage, the acid etching reaction near the tiny, dissolved pores on the core surface was relatively intense. Over time, the acid solution gradually penetrated the core. However, due to the limitations of the ultra-low permeability and porosity of the tight limestone, the distribution of the overall etching degree showed an obvious gradient change. The etching in the acid immersion area was relatively severe, while the etching degree in the deep area away from the surface was relatively weak. The morphology of the core fracture surface after single-phase acid etching is shown in Figure 6.

When gelled acid was used, the situation was different. Due to the viscosity characteristics of gelled acid, its flow on the core surface was relatively slow. The initial etching rate was slightly higher than that of single-phase acid. However, as the reaction continued, it could maintain a relatively stable reaction environment on the core surface, making the etching process more uniform. However, in the parts where the core had fractures or

micro-fractures, the acid solution could more easily enter these channels, and the local etching rate would still increase, resulting in an increase in the width and depth of the fractures to a certain extent. The morphology of the core fracture surface after gelled acid etching is shown in Figure 7.

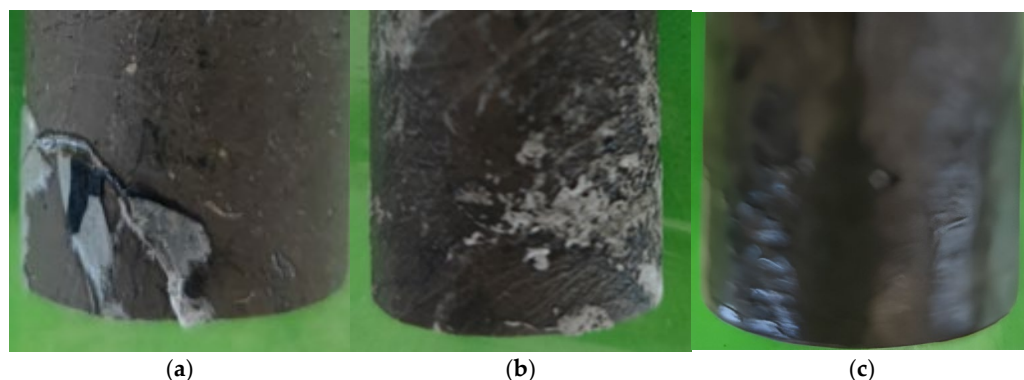


Figure 6. The morphology of the core fracture surface after single-phase acid etching. (a) A-1; (b) A-2; (c) A-3.

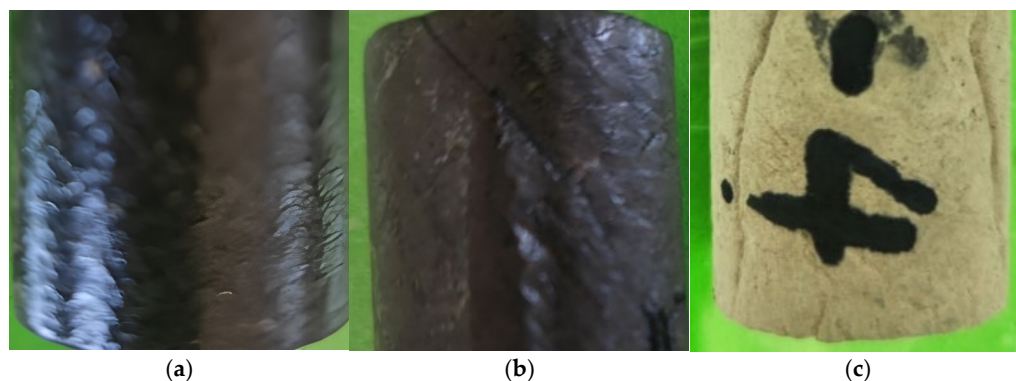


Figure 7. The morphology of the core fracture surface after gelled acid etching. (a) D-1; (b) C-2; and (c) C-4.

With the extension of the reaction time, the fracture morphology on the surface of the limestone became more significant under the action of both single-phase acid and gelled acid. This was mainly due to the differences in mineral composition and structure between the fracture area and the surrounding matrix, as well as the relatively high porosity in the fracture area providing a more favorable channel for the flow of acid solution. Through careful observation and analysis of the experimental phenomena, it was determined that when the acid solution reacted with the tight limestone, it preferentially eroded along the natural fractures and high porosity areas and continuously extended to the deeper areas, thus changing the microscopic structure and permeability distribution of the core and forming high conductivity channels. From a mineralogical perspective, calcite has a relatively high solubility in hydrochloric acid. Its dissolution process would change the pore structure and mechanical properties of the rock, and the presence and dissolution characteristics of minerals such as quartz affected the selectivity and overall effect of acid etching.

3.2.5. Influence of Reaction Rate Decay on Wormhole Propagation Dynamics

The quadratic decay model of reaction rates (Equations (3) and (4)) provides critical insights into the spatiotemporal evolution of wormhole networks in tight limestone acidizing. Wormhole propagation is governed by the interplay between acid penetration

depth and dissolution efficiency, both of which are profoundly influenced by the observed kinetic behavior.

1. Early-Stage Surface-Controlled Dissolution

- Gelled acid exhibits a $2\times$ higher initial reaction rate (0.897%/min) compared to those of single-phase acid (0.453%/min at 10 min), leading to preferential etching at microfracture intersections (e.g., Core C-5 developed 30.88% etching with interconnected wormholes after 180 min; Table 9).
- Single-phase acid, despite lower initial rates, achieves deeper penetration due to slower decay (0.096%/min at 180 min), forming elongated wormholes in low-permeability cores (e.g., Core A-5 showed 17.20% etching with distributed worm channels; Table 7).

2. Late-Stage Diffusion-Limited Kinetics

- After 30 min, reaction rates of both acids converge (0.489%/min for single-phase vs. 0.49%/min for gelled acid), resulting in similar wormhole densities but distinct morphologies.
- Single-phase acid forms tortuous wormholes with higher connectivity (Core A-4 achieved 29,200% permeability improvement at 60 min; Table 15), whereas gelled acid produces broader but shorter worm channels (Core C-5 showed 21,700% improvement at 180 min).

3. Mechanistic Analysis

- Selective etching pathways: In the diffusion-limited phase, acid preferentially flows through existing wormholes rather than creating new ones, leading to increased channel tortuosity (Figure 6a–c).
- Acid concentration gradients: The declining H^+ ion concentration gradient reduces dissolution efficiency, restricting wormhole branching and depth (Figure 7a–c).

4. Discussion

Although this study has achieved certain results, there are still some deficiencies. Future research can further optimize the experimental design. For example, adding factors of temperature and pressure changes under the condition of simulating the actual reservoir should be considered, and the influence of formation water on the acid–rock reaction so that the experimental results are more in line with the actual working conditions should be introduced. At the same time, new acid solution systems or additive combinations should be explored, and retarders, drag-reducing agents, and thickening agents with better performance should be developed through molecular design and other means to improve the acid fracturing effect. In addition, multi-scale acid–rock reaction research and combining microscopic molecular simulation and macroscopic reservoir numerical simulation technology should be carried out to comprehensively and deeply reveal the acid–rock reaction mechanism and provide more accurate theoretical support and technical guidance for the acid fracturing stimulation of tight limestone reservoirs.

5. Conclusions

This study systematically investigates the acidizing performance of single-phase and gelled acids in tight limestone cores through gravimetric analysis and permeability testing. By quantifying reaction kinetics and microstructural evolution, we address the critical challenge of optimizing acidizing strategies for low-permeability reservoirs. The findings provide a theoretical foundation for improving stimulation efficiency in tight oil development. Three key conclusions emerge:

1. The acid–rock reaction rates of single-phase acid and gelled acid in limestone both show a decreasing trend with time. When the acid–rock reaction time was greater than 30 min, the decreasing amplitude of the acid–rock reaction rate decreased, and the increase in the cumulative acid etching degree decreased. When the acid–rock reaction time was 30 min, the acid–rock reaction rate of single-phase acid was between 0.321 and 0.489%/min, and the acid etching degree was between 9.635 and 14.675%. The acid–rock reaction rate of gelled acid was between 0.336 and 0.49%/min, and the acid etching degree was between 10.081 and 14.707%. The acid–rock reaction rate of gelled acid in limestone reservoirs was higher than that of single-phase acid. In order to achieve better near-wellbore plug removal and deep reservoir stimulation, single-phase acid with a moderate reaction rate is preferred.
2. Under the same experimental conditions, the acid–rock reaction rates and acid etching degrees of gelled acid and single-phase acid both increased with the increase in concentration. When the concentration was greater than 15%, the increase in the acid–rock reaction rate and acid etching degree accelerated. The acid–rock reaction rate and acid etching degree at a concentration of 20% were 1.3 times greater than those at 15%. With the increase in concentration, the gap between the acid–rock reaction rates of single-phase acid and gelled acid decreased. Both acid types exhibited quadratic reaction rate decay ($R^2 > 0.95$).
3. From the perspective of microscopic permeability and porosity, the influence comparison was time > number of dissolved pores, caves, and fractures. The number and depth of worm fractures were related to the original number and type of fractures. During the acidizing process, the acidizing time and concentration should be reduced for cores with more fractures.

These findings provide a predictive framework for acidizing design in tight carbonate reservoirs, advocating time-controlled strategies over traditional concentration-focused approaches. Further research should address dynamic reservoir conditions and multi-scale fluid–rock interactions to advance the technology.

Author Contributions: Conceptualization: C.W. and C.X.; methodology: C.W.; validation: C.W., C.X. and X.W.; formal analysis: C.W. and C.X.; investigation: C.W. and C.X.; resources: C.W.; data curation: C.W. and C.X.; writing—original draft preparation: C.W. and C.X.; writing—review and editing: C.X., X.W., M.T. and E.P.; visualization: C.W.; supervision: C.X.; project administration: X.W. and M.T.; funding acquisition: C.W., X.W. and M.T. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the National Natural Science Foundation of China, grant number 52074090; the Natural Science Foundation of Heilongjiang Province, grant number LH2019E017; and the Key Research and Development Program of Heilongjiang Province, grant number JD22A004.

Data Availability Statement: The original contributions presented in the study are included in this article. Further inquiries can be directed at the corresponding author.

Acknowledgments: This research was supported by the Key Laboratory of Enhanced Oil and Gas Recovery of the Ministry of Education at Northeast Petroleum University, which provided administrative and technical support and was instrumental in advancing this study.

Conflicts of Interest: Xiaohu Wang was employed by the Offshore Oil Engineering Corp of Liquefied Natural Gas Engineering Technology Branch. The remaining authors declare that this research was conducted without any commercial or financial relationships that could be construed as a potential conflict of interest. Minglei Tian was employed by Oil and Gas Pipeline Engineering Co., Ltd., Langfang. The remaining authors declare that this research was conducted without any commercial or financial relationships that could be construed as a potential conflict of interest.

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