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Study on the Effect of Acid Corrosion on Proppant Properties

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Abstract: Pre-acid fracturing is an effective technique to improve productivity of tight reservoirs. While acid injection can clean the formation and improve the fracturing performance by reducing the fracture pressure of the reservoir, the chemical reaction of the acid solution with proppant may reduce the compressive strength of the proppant and therefore negatively affect the fracture conductivity. In this study, we experimentally investigated the solubility of the proppant in acid and the effect of acid corrosion on proppant compressive strength and fracture conductivity. The results show that the concentration of the acid solution has the greatest effect on solubility of the proppant, which is followed by the contact reaction time. Though a proppant of larger particle size indicates a lower solubility, the acid corrosion poses a greater damage to its compressive strength and conductivity. The quartz sand proppant exhibits superior stability to ceramic proppant when they are subjected to acid corrosion. The experimental results could serve as reference for selection of proppant and optimization of acid concentration and duration of acid treatment during pre-acid fracturing.

Keywords: pre-acid fracturing; acid solubility; compressive strength; conductivity

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1. Introduction

The economic development of tight oil and gas reservoirs is highly dependent on the large-scale hydraulic fracturing technology [1,2]. For example, it is difficult to develop Chang 7 reservoir in the Changqing Oilfield and Mahu Block in the Xinjiang Oilfield without hydraulic fracturing due to ultra-low permeability and high heterogeneity of the rock formations. For most of the fracturing treatments for shale resources, due to the influence of the high in-situ stress, it is a common practice to perform a preliminary treatment utilizing hydrochloric acid before the fracturing to reduce the rock fracture pressure [3]. In practice, pre-acid fluids combined with hydraulic fracturing technology were used to improve fracturing performance [4,5].

As early as 1989, A. R. Jennings [6] proposed the application of fracturing and acidizing technology to improve conductivity of sandstone reservoirs utilizing acid liquid fingering phenomenon to etch irregular fracture walls. However, the sandstone formation is not suitable for direct application of acid fracturing. The reason is that part of the sandstone rocks is loosely cemented, and the rock skeleton becomes loose due to high degree of acid dissolution during direct acid fracturing. Insoluble rock minerals or products resulting from the chemical reaction of acid and rocks may lead to blockage of the pores or even sand production [7,8]. In recent years, application of preliminary acidification has shown that it can reduce rock fracture pressure and mitigate pore blockage, which has become an important procedure before hydraulic fracturing. In addition, acidification treatment is shown to be capable of not only improving the performance of new producers by accelerating gel breaking of the gum fracturing fluid and dissolving the residue, but reviving old producers by mitigating pore blockage [9,10].

As an important part of hydraulic fracturing technology, the properties of proppant largely affect the fracture dimension and conductivity, and thereby the ultimate fracturing effect. The acid solution injected into the formation reacts not only with the formation rocks, but with the minerals that make up the proppant. Various mineral components in the proppant show different affinity for the acid, which leads to differences in performance change for different types of proppants [11–13]. The stability of the proppant after contact with the acid is critical to maintain a high level of effective fracture width and ultimate conductivity.

In this work, we investigated the effect of acid solution on proppant solubility, compressive strength, and fracture conductivity. In particular, the factors under consideration included the ratio of hydrochloric acid and hydrofluoric acid, proppant type and particle size, temperature, and contact reaction time. The research results can serve as reference for the optimization of acid solution and proppant in fracturing operation.

2. Experiment Description

2.1. Experimental Samples

Proppant: Two types of proppants (i.e., ceramic proppant and quartz sand proppant) used in Xinjiang Oilfield were selected. The two particle sizes of each type were 20/40 mesh and 30/50 mesh. The mass concentration of proppant in acid solution was 4.2%.

Acid solution: According to the test method for acid solubility of proppant specified in SY/T5108-2014 "Test Method for Proppants for Hydraulic Fracturing and Gravel Filling Operations", which is a standard procedure adopted by Chinese Petroleum Industry, two mud acids were prepared from 38 wt.% hydrochloric acid and 40 wt.% hydrofluoric acid. The volumetric ratios of hydrochloric acid to hydrofluoric acid for the mud acids were 6:1 and 12:3, respectively.

Fracturing fluid: The simulated fracturing fluid was used in the conductivity experiment, which was 4.0 wt.% potassium chloride solution prepared from distilled water and potassium chloride.

2.2. Experimental Methods

2.2.1. Proppant Acid Solubility Test

The proppant solubility in acid was performed with the following procedure. Firstly, a specific amount of proppant was dried for two hours in a drying oven set at 105 °C. A total of 10 g proppant was weighed and poured into a 200 mL plastic measuring cup filled with prepared mud acid. Then, the cup was sealed and placed in a water bath set at a constant temperature. Finally, the sample was vacuum filtered and placed in the drying oven set at 105 °C for 2 h. The calculation formula of acid solubility is:

$$S = \frac{m_s + m_f - m_{fs}}{m_s}$$

where s—the acid solubility of the proppant, %; m_s—the mass of the proppant sample, g; m_f—the mass of the crucible and filter paper, g; and m_{fs}—the mass of the crucible, filter paper, and the proppant after acid dissolution, g.

2.2.2. Proppant Compressive Strength Test

A standard test method for compressive strength of proppant was adopted according to the "QSH1020_1598-2013 Fracturing Proppant Performance Indicators and Test Methods". Firstly, the remaining impurities and debris in the proppant sample after acid dissolution were sieved out. Then, the proppant sample was poured into a standard crushing chamber (Figure 1) (diameter = 50.8 mm) of a cyclic loading hydraulic machine, which was then pressurized to a specified pressure within 1 min at a constant speed and maintained at that pressure for two minutes. Finally, the proppant sample after pressurization was sieved and weighed. The crushing rate was calculated with the formula below:

$$\mu = \frac{w_c}{w_p} \times 100\%$$

where μ—the crushing rate of proppant, %; w_c—the mass of proppant debris, g; and w_p—the mass of proppant sample, g.

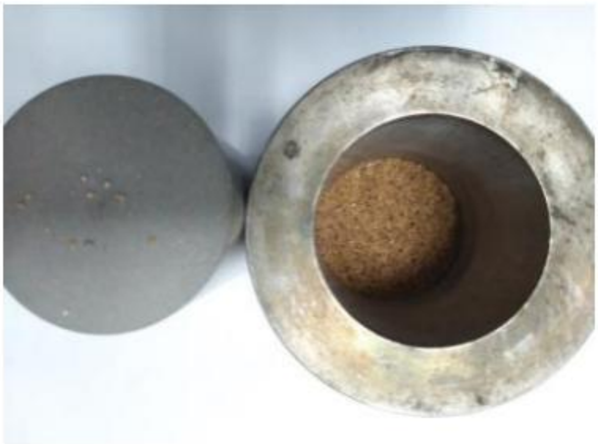


Figure 1. Standard crushing chamber.

2.2.3. Proppant Conductivity Test

A long-term conductivity test system called HXDL-2C developed by Yangtze University (Figure 2) was used to measure the fracture conductivity using a standard procedure from NBT_14023-2017 "Recommended Method for Measuring Long-term Diversion Capability of Shale Proppant Filling Layer". Firstly, the proppant was evenly laid in a standard API diversion chamber inside the system. Then, the system was initiated and continuously acquired various parameters necessary to calculate fracture conductivity, including fracture width, fluid flow rate, and differential pressure. During the whole test procedure, the system was controlled under the simulated field conditions including formation temperature, closure pressure of fracture, and fluid flow state. The fracture conductivity $K_w w_f$ was calculated with the formula below:

$$K_w w_f = \frac{5.555 \times Q_w \mu_L}{\Delta P}$$

where K_w—liquid measured permeability, μm^2; w_f—the thickness of proppant, cm; Q_w—the liquid flow rate, mL/min; μ_w—the liquid viscosity, mPa·s; and ΔP—the differential pressure between two points tested, KPa.

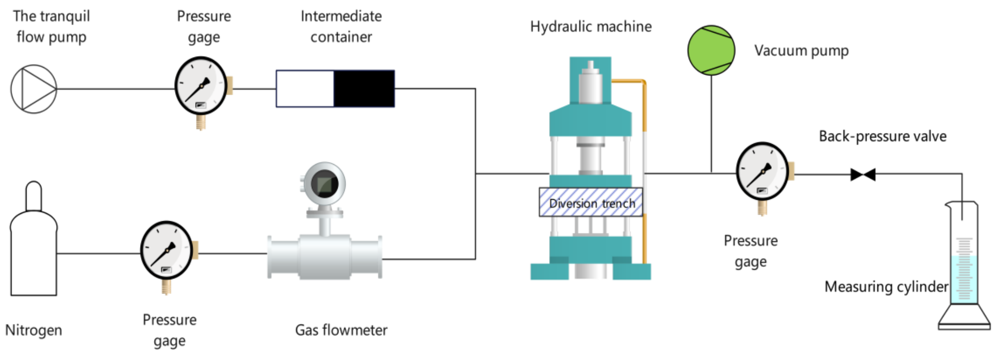


Figure 2. The schematic diagram of the long-term conductivity test system.

3. Discussion of Experimental Results

3.1. Proppant Acid Solubility Test

The dissolution of the proppant by the acid solution leads to the formation of debris, which blocks the pores and reduces conductivity. The solubility is closely related to the temperature, types and particle size of proppants, concentration of acid solution, and contact reaction time. Therefore, we investigated the effects of these factors on the acid solubility of two types of proppants (i.e., ceramic proppant and quartz sand proppant).

3.1.1. Effect of Temperature on Acid Solubility

The ceramic and quartz sand proppant of 20/40 mesh were soaked in the mud acids at 65 °C and 85 °C for half an hour. The test results (Table 1) show that the proppant's solubility in acid increases significantly with temperature, and the degree of the increase in solubility is also greater for the proppant in the mud acid with higher concentration of hydrofluoric acid (i.e., mud acid with ratio of 12:3) than that in the lower one. This suggests that proppants in the formation may undergo a process like diagenesis at higher temperatures [14,15] and the products may block the seepage channels among the proppants. The chemical reaction may result in a reduction of porosity of the proppant pack under high temperature and high stress, thereby reducing the fracture conductivity. Therefore, for formations with a relatively high temperature, it is advisable to inject a certain amount of liquid before acid injection to reduce the formation temperature and thereby decrease the corrosion effect of the acid liquid on the proppant.

Table 1. Acid solubility of proppant under different temperature conditions.

Type	Particle Size (Mesh)	Soaking Time (h)	Temperature (°C)	Dissolved Proppant (%)	
				Mud Acid (6:1)	Mud Acid (12:3)
Ceramic	20/40	0.5	65	1.09	4.02
Quartz Sand				0.85	1.97
Ceramic			85	1.37	5.58
Quartz Sand				1.16	2.79

3.1.2. Acid Solubility of Different Types of Proppants

Table 1 also shows that the solubility of ceramic proppant of the same particle size is significantly higher than that of quartz sand proppant under the same conditions. It is believed that this is attributable to the difference in composition of these two types of proppants. In other words, the main component of ceramic proppant is bauxite, which is composed of alumina and other clay minerals, whereas quartz sand proppant is mainly composed of silicate minerals with silica as the major component. HCl in mud acid does not react with silica, while HF reacts quickly with clay minerals and slowly with silica. Therefore, ceramic proppant is more soluble than quartz sand proppant due to the existence of a large amount of clay minerals on its surface.

3.1.3. Effect of Proppant Particle Size on Acid Solubility

The experimental result in Table 2 shows that the acid solubility of the same type of proppant with a smaller particle size is greater than that with a larger particle size. Under the same mass, the number of proppant particles with a smaller size will be greater than that with a larger size. Thus, the contact area with the acid solution is larger for the proppant with smaller size. In addition, the penetration depth of acid in proppant with a smaller size accounts for a larger portion of the particle diameter, i.e., larger reaction volume. Therefore, the larger contact area and reaction volume contribute to the higher acid solubility of proppant with a smaller particle size.

Table 2. Acid solubility of proppants under different acid solutions and soaking times.

Proppant	Mesh	T, (°C)	Soaking Time (h)	Weight Before (g)	Mud Acid (6:1)		Mud Acid (12:3)	
					Weight After (g)	Proppant Solubility (%)	Weight After (g)	Proppant Solubility (%)
Ceramic	20/40	65	0.5	10	9.89	1.09	9.60	4.02
			1	10	9.75	2.54	9.18	8.17
			2	10	9.70	2.96	9.06	9.38
	30/50	65	0.5	10	9.87	1.35	9.51	4.94
			1	10	9.65	3.52	9.04	9.63
			2	10	9.58	4.23	8.85	11.46
Quartz Sand	20/40	65	0.5	10	9.92	0.85	9.80	1.97
			1	10	9.84	1.64	9.66	3.41
			2	10	9.80	1.97	9.60	4.05
	30/50	65	0.5	10	9.90	1.04	9.76	2.43
			1	10	9.81	1.92	9.55	4.47
			2	10	9.79	2.10	9.48	5.17

Note: Each set of data is measured by multiple sets of repeated experiments.

3.1.4. Effect of Acid Concentration on Acid Solubility

Table 2 also shows that the factor that has the greatest influence on the acid solubility of the proppant is the acid concentration. In general, the solubility in the 12:3 acid solution is significantly higher than that in the 6:1 acid solution. For the ceramic proppant, the acid solubility in the high-concentration acid solution (i.e., mud acid with ratio of 12:3) is about four times as high as that in the low-concentration acid solution at the initial stage (0.5 h), and it eventually reaches around three times at 2 h. In addition, the acid solubility of ceramic proppant is higher than that of quartz sand.

The shape of the proppant changes greatly after dissolution (Figure 3). The appearance of quartz sand proppant of 20/40 mesh in low acid concentration (6:1) changes from yellow (before acid soaking) to transparent crystal (after acid soaking), whereas that of the quartz sand proppant being soaked in high acid concentration (12:3) becomes turbid and white. The turbid and white appearance may result from the dissolution of minerals on the surface. This will lead to a loose surface and reduced performance. Therefore, in a field acidization practice, it is advisable to control the acid concentration. In particular, when there is a pore blockage in the formation, it is suggested to use an acid solution of low concentration and increased volume. Meanwhile, the flowback of acid after reaction may be conducted as soon as possible to reduce contact time. Alternatively, after injection of acid for a period of time, a slug of water can be injected to dilute the acid and therefore reduce the degree of corrosion of the proppant.

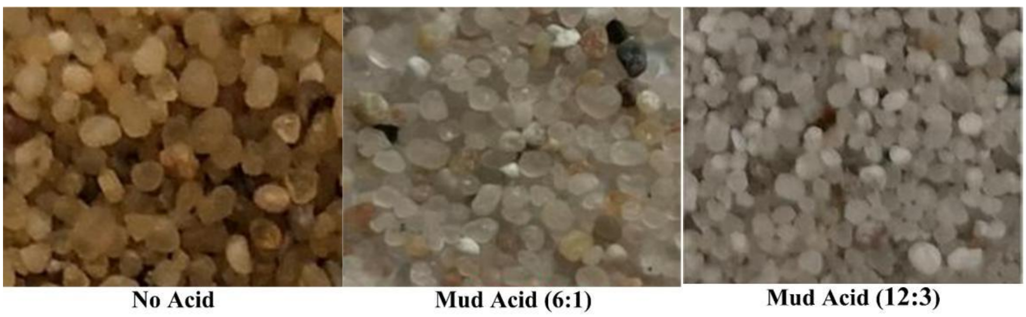


Figure 3. Photomicrograph of proppant after mud acid soaking experiment.

3.1.5. Effect of Contact Reaction Time on Acid Solubility

Table 2 shows that the solubility of proppant in acid increases with reaction time. The acid solubility for 1 h is around two times as great as that for 0.5 h. The trend of increased solubility also keeps from 1 h to 2 h though the increase rate gets smaller. The great solubility at the initial stage of reaction is a result of a higher concentration of acid solution and content of reactive minerals. With the reduced concentration and reactive minerals, the acid solubility will approach maximum and maintain stability. The result shows that the importance of factors affecting acid solubility of proppant can be ranked in the following decreasing order: acid concentration > contact time > particle size.

3.2. Damage to Proppant Compressive Strength

Following the procedure of the acid solubility experiment, a sufficient amount of proppant was prepared for proppant crushing rate test. The test pressures for ceramic proppant and quartz sand proppant were 52 MPa and 35 MPa, respectively, considering the relatively weaker compressive strength of quartz sand. Test results (Table 3) show that the compressive strength of the ceramic proppant is generally superior to that of quartz sand proppant. Since the debris resulting from crushed proppants may block the seepage channel and cause secondary pollution, it is advisable to use ceramic proppant for deep formations, which tend to exert great closure pressure. By contrast, the quartz sand proppant may be selected for shallow formations.

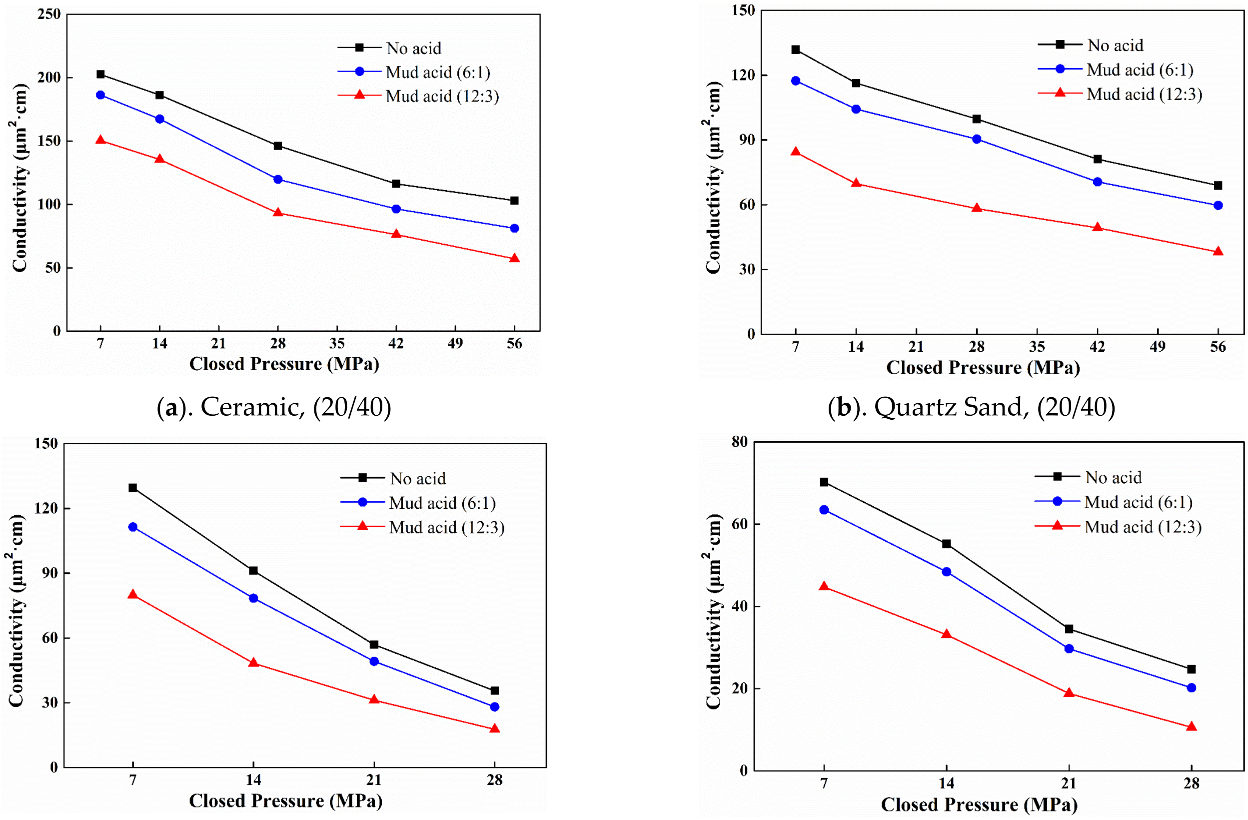
Table 3. Changes in compressive strength after acid soaking.

Type	Mesh	Pressure (MPa)	Crushing Rate (%)		
			No Acid	Mud Acid (6:1)	Mud Acid (12:3)
Ceramic	20/40	52	1.4	2.5	5.9
	30/50	52	1.1	1.9	5.2
Quartz Sand	20/40	35	3.6	5.2	8.3
	30/50	35	3.2	4.7	7.8

The results also show that the crushing rate increases significantly after acid dissolution for both proppants. For example, the crushing rate of ceramic proppant of 30/50 mesh after dissolution in acid solution (12:3) is around five times as high as that without acid dissolution (i.e., from 1.1% to 5.2%). Another observation is that the crushing rate of proppant with a smaller particle size is lower than that of a larger size although the former is subjected to greater solubility. This is because the contact area is small between proppants of larger particle size and the particles are subjected to greater stress. Therefore, they are prone to fragmentation. In addition, the increased rate of crushing after acid dissolution for quartz sand proppant is smaller compared to that for ceramic proppant since the smaller solubility of quartz sand brings about smaller damage to compressive strength. However, the overall crushing rate after acid dissolution of quartz sand proppant is higher than that of ceramic proppant and thereby is not suitable for a reservoir with high closure stress.

3.3. Damage to Conductivity

The conductivity test was performed with proppant being evenly placed in a diversion chamber with a sand concentration of 10 kg/m^2, which was acidified, dried, and sieved in advance. Experimental results (Figure 4) show that the conductivity of the proppant after dissolution in acid of low concentration (6:1) reduces by a relatively smaller extent, whereas that in a high concentration (12:3) decreases by over 50%. In addition, the conductivity damage of ceramic proppant is higher than that of quartz sand proppant. For example, the conductivity of ceramic proppant of 20/40 mesh and 30/50 mesh is reduced by 58% and 50%, respectively. For proppant of both types, the proppant of larger particle size shows greater damage. The proppant of larger particle size can maintain a high level of conductivity due to the large pore volume between particles. However, it is subject to fragmentation due to combined effects from acidization and high closure stress. The resulting fragments may lead to blockage of the pores and thereby reduced conductivity. Therefore, it is advisable to select the quartz sand proppant for acidization treatment in formations with low formation pressure to achieve high efficiency in both cost and performance.



(**a**). Ceramic, (20/40)

(**b**). Quartz Sand, (20/40)

(**c**). Ceramic, (30/50)

(**d**). Quartz Sand, (30/50)

Figure 4. (**a**–**d**) The conductivity of ceramic and quartz sand of different sizes under different closure pressures after mud acid soaking.

4. Conclusions

(1) Acid concentration and contact reaction time are the most dominant factors affecting the solubility of proppant in acid. When conducting pre-acid operation, it is not advisable to use a high concentration of acid. Alternatively, it is desirable to inject a certain amount of fracturing fluid to dilute the acid concentration before injecting proppant. Another measure is to conduct the flowback as soon as possible to reduce the damage to the proppant performance.

(2) The larger contact area of the small particle proppant with the acid solution leads to larger solubility compared to that for proppant of a larger particle size. However, the compressive strength of smaller size proppant is superior to that of larger size and the degree of damage to conductivity is also small. Therefore, a small particle proppant is preferred under the requirement of a certain conductivity.

(3) The quartz sand proppant presents high stability under acidic conditions although its compressive strength is weak. In shallow formations with a closure pressure less than 28 MPa, the pre-acidification combined with fracturing using quartz sand proppant may produce superior performance.

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