

Optimization of Fracturing Fluid and Retarded Acid for Stimulating Tight Naturally Fractured Bedrock Reservoirs

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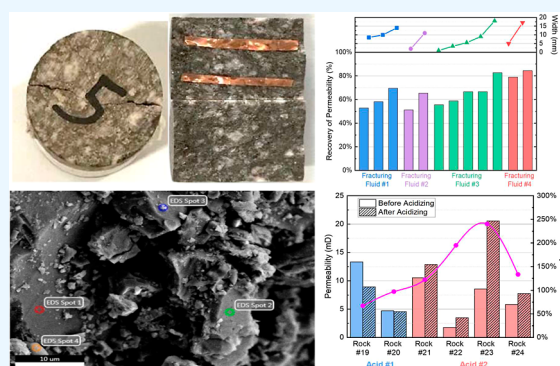
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ABSTRACT: In tight naturally fractured bedrock reservoirs, hydrocarbons are typically stored in fractures, where hydraulic fracturing is needed to connect these fractures to the wellbore. The cross-linked gel is used as the fracturing fluid to reduce the fluid leak-off through natural fractures; however, it can cause formation damage due to its high content of residues after breaking. A synthetic polymer is introduced and evaluated that can maintain a high viscosity to minimize the leak-off, while having a low residue content after breaking. To further enhance the conductivity of the created fracture network, acid is applied to etch and roughen the created fracture faces. Because the target reservoir has a complex mineral composition, a three-step coreflood sequence using reservoir rock samples with controlled fracture widths is established to quantify the enhancement of different retarded acids and to reveal the mechanism behind it. The results indicate the synergy effect of reducing the acid concentration and surfactant adsorption on rock surfaces can lead to an obvious enhancement of the fracture permeability after acidizing, while the mud acid or hydrofluoric acid is not suitable for the target reservoir where concentrations of silicates and clays are relatively high.



1. INTRODUCTION

Bedrock reservoirs are widely distributed worldwide,¹ where hydrocarbons are mainly stored in fractures formed by tectonic movement or dissolution.^{2–7} When developing this type of reservoirs, hydraulic fracturing can be applied to connect these fractures and generate a fracture network for enhancing the hydrocarbon production.^{8–10} During hydraulic fracturing, cross-linked guar is normally used to reduce the leak-off of fracturing fluid through natural fractures.^{11,12} However, the guar has a low hydration rate, which increases the cost of fluid preparation in the field. Meanwhile, as a naturally occurring polymer, the guar has a high content of dissolvable proteins after breaking, which can plug the created fractures and cover the reservoir rock, thus inhibiting the flow of hydrocarbons.^{13–15} To increase the hydration rate, carboxymethyl groups are grafted on saccharides of guar molecules, which makes the carboxymethyl guar.¹⁶ Laboratory evaluation has also shown that the carboxymethyl guar has a higher resistance to temperature and shear rate;^{17–19} however, this modification still cannot reduce the gel residues after breaking. Polyacrylamide is a synthetic polymer that has been widely used in flooding mature reservoirs as a tertiary oil recovery technique.²⁰ Compared with the guar, it has significantly less residues after breaking and does not cause obvious formation damage when flowing in the porous media; moreover, its

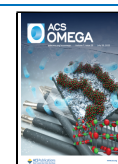
structure can be easily modified to meet different fracturing needs, especially when the reservoir temperature is above 150–180 °C or a friction reduction rate of over 75% is needed.^{21–24} Therefore, formation damage introduced by different types of fracturing fluids needs to be evaluated before studying the stimulation effect of different acid systems for the target reservoir.

Acidizing is first used to mitigate the formation damage of drilling and fracturing fluids in the near-wellbore region, where wormholes are formed that penetrate the damaged region and enhance the rock permeability.^{25,26} In the past decade, when hydraulic fracturing is applied to stimulate low-permeability reservoirs, acid is also applied to roughen the generated fracture faces that enhance the conductivity of the fracture network; this is defined as “acid fracturing”.²⁵ In both acidizing and acid fracturing, the reaction rate between the acid and the reservoir rock needs to be reduced to enhance the penetration depth of the acid and extend the stimulation area, where

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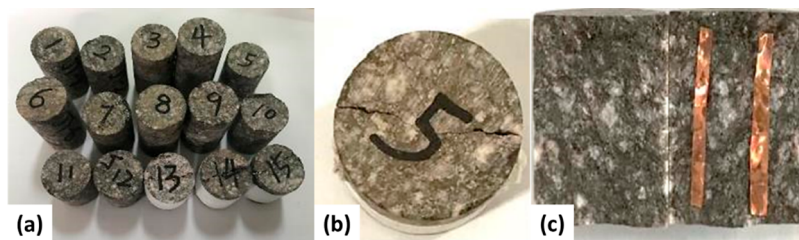


Figure 1. (a) Reservoir rock samples, (b) fractured rock sample, and (c) mimicked naturally fractured rock using copper strips.

different types of retarded acids are developed. Gelled acid and emulsified acid are two major types of retarded acids. In the gelled acid, acid (like hydrochloric acid, HCl) is mixed with polymers (like polyacrylamide), which increases the viscosity of acid, reduces the diffusion rate of hydrogen ions, and thus reduces the reaction rate of acid with the reservoir rock.²⁷ In the emulsified acid, surfactants and solvents are used to generate acid-in-oil emulsions; because the oil phase separates the acid from the reservoir rock and can slowly release the hydrogen ions, the acidizing rate can be significantly reduced that allows the acid to penetrate deep into the reservoir and extends the stimulation area.^{28–30} After carefully designing the surfactant formulation, the emulsified acid can stabilize at 150 °C for 5 h and enhance oil production by 3 times compared to other retarded acid systems.³¹ However, because the oil phase is the main phase that wraps the acid, the emulsified acid requires large amounts of oil and surfactants, which are typically over 40%. Therefore, it is not economical to apply it in the target reservoir.

To reduce usages of oil and surfactants while keeping the advantage of slow release, the acid can be applied with microemulsions, which is originally designed for the chemical enhanced oil recovery of conventional oil reservoirs.^{32–34} Later, the microemulsion is applied in the fracturing fluid for fracturing shales or other low-permeability reservoirs, which is designed to slowly release surfactants to alter the wettability of the reservoir rock or reduce the interfacial tension between water and oil.^{35–37} Therefore, this type of retarded acid needs to be evaluated and compared with conventional ones for the target reservoir with abundant natural fractures. Besides, there also needs to be an understanding on how different acids perform in the presence of gel residues introduced by different fracturing fluids.

In sandstone or shaly sandstone reservoirs, secondary products from acidizing is another key problem that can significantly limit the acidizing effect. The hydrofluoric acid (HF) can generate insoluble fluorosilicates and fluoroaluminates with aluminosilicates in the reservoir, which can plug fractures and wormholes, thus reducing the well productivity instead.^{38–40} Compared with the conventional mud acid for acidizing sandstones, the gelled acid can improve the uniformity of acidizing by reducing the erosion rate, which can then reduce the sizes of undissolved particles that results in the formation damage.^{41,42} However, it remains unknown how the erosion rate affects the permeability enhancement in rocks with different fracture sizes, and the potential method to improve the formula of the acid system for the target reservoir.

In this study, a three-step coreflood sequence using reservoir rock samples is established to quantify the formation damage due to different types of fracturing fluids, where reservoir rock samples with controlled fracture widths are applied to understand how fracture width affects the degree of formation

damage from gel residues. After optimizing the fracturing fluid for the target reservoir, acidizing effects of different retarded acids are further evaluated and compared using the same coreflood platform. Sizes of the detached fines after acidizing and erosion rates are quantified with the measured permeability enhancement to reveal the mechanism of the new microemulsion acid, which can be a promising candidate for acidizing reservoirs with natural fractures and high concentrations of silicates and clays.

2. MATERIALS AND METHODS

2.1. Target Reservoir and Rock Samples. The target reservoir is located in the northwest of the Qaidam Basin; with an average elevation of 2750 m, it is the highest basin in the world.^{43,44} The reservoir has a depth ranging from 3200 to 4800 m and a reservoir temperature of above 90 °C. The previous core analysis shows the reservoir rock is mainly composed of calcite, feldspar, quartz, and clay. Clay has an average content of 20.4%, in which illite is about 30%, chlorite is about 21%, and smectite is less than 0.2%. The reservoir rock has an average permeability of 0.027 mD and an average porosity of 2.25%. Although the reservoir rock is tight, natural fractures are well developed in the reservoir, whose density is about 2–4 per meter, with fracture widths of 0.01–5 mm. These natural fractures not only store a large amount of natural gas but also act as flow channels in production. Hydraulic fracturing is applied to connect these natural fractures, during which acid is also applied to mitigate the potential formation damage introduced by the cross-linked gel and roughen fracture faces to enhance the conductivity of the created fracture network. This stimulation method combines ideas of conventional acidizing and acid fracturing,^{25,26} and its effectiveness needs to be evaluated for optimizing the fracturing fluid and acid systems.

In this study, 24 core samples are obtained from the reservoir at a depth of 4150 m, as shown in Figure 1a. Natural fractures can be observed in a few core samples, like Rock #5, as shown in Figure 1b. To make their results comparable, the Brazilian splitting method is applied to split each core sample, and two copper strips are placed between two halves of the fractured sample to mimic a reservoir rock with a natural fracture, as shown in Figure 1c. Permeability of the reservoir rock is measured using the pulse decay method with the intact samples without natural fractures, which ranges from 0.001 to 0.009 mD. Table 1 shows the dimensions of these 24 samples, as well as the types of fluids tested in them. Because thicknesses of copper strips between two halves of samples can change when the confining pressure is applied for the coreflood experiment, their thicknesses are measured after each coreflood and averaged as the fracture width, as shown in Table 1.

Table 1. Information of Core Samples

core number	diameter (cm)	length (cm)	fracture width (μm)	treating fluids
#1	2.505	2.698	8.5	fracturing fluid #1
#2	2.500	4.020	10.0	fracturing fluid #1
#3	2.514	2.727	14.0	fracturing fluid #1
#4	2.510	3.229	2.0	fracturing fluid #2
#5	2.510	2.847	11.0	fracturing fluid #2
#6	2.500	2.629	1.0	fracturing fluid #3
#7	2.516	4.251	3.5	fracturing fluid #3
#8	2.501	4.110	5.5	fracturing fluid #3
#9	2.510	3.980	9.0	fracturing fluid #3
#10	2.516	4.040	18.0	fracturing fluid #3
#11	2.509	3.470	5.0	fracturing fluid #4
#12	2.508	3.502	17.0	fracturing fluid #4
#13	2.510	4.650	26.0	chosen fracturing fluid + acid #1
#14	2.510	3.530	30.0	chosen fracturing fluid + acid #1
#15	2.530	3.560	11.5	chosen fracturing fluid + acid #2
#16	2.520	3.540	17.0	chosen fracturing fluid + acid #2
#17	2.530	4.220	15.0	chosen fracturing fluid + acid #2
#18	2.510	4.190	19.0	chosen fracturing fluid + acid #2
#19	2.510	3.200	22.5	optimization of acid #1
#20	2.520	4.090	16.5	optimization of acid #1
#21	2.530	3.720	21.0	optimization of acid #2
#22	2.510	3.890	13.0	optimization of acid #2
#23	2.470	4.650	20.5	optimization of acid #2
#24	2.520	3.040	17.0	optimization of acid #2

2.2. Fluids. During on-site acid fracturing, in order to make the liquid adapt to the reservoir conditions, reduce damage, and improve fracture conductivity, relevant components are added to achieve the objectives of temperature and salt resistance, antismearing, drainage, and production increase, which are verified by on-site experiments. After on-site use effect and economic comparison, the four cross-linked gels and two retired acids are selected for research.

In this study, four different types of cross-linked gels are first evaluated and compared for the target reservoir, from which a baseline is also established for evaluating different acids. Once the optimal fracturing fluid is chosen, the three-step coreflood experiment is conducted to evaluate two different retarded acids, from which the effect of the new microemulsion acid can be understood, and the mechanism behind it can be revealed.

2.2.1. Mimicked Formation Brine. The mimicked formation brine used in this study has the same compositions as the formation brine in the target reservoir, which consists of 2% KCl, 5% NaCl, 0.36% MgCl_2 , and 0.48% CaCl_2 .

2.2.2. Mimicked Fracturing Fluids. Because the matrix of reservoir rock has permeability as low as a few microDarcies, hydraulic fracturing is used to link the microfractures and form a fracture network to promote the flow of hydrocarbons. For high-temperature reservoirs with natural fractures, the cross-linked gel is typically used during the fracturing to reduce the leak-off of the fracturing fluid. In this study, formation damage caused by four different types of cross-linked gels are evaluated and compared, from which the gel with the minimum damage can be chosen for the field operation.

Fracturing fluid #1 is the typically used cross-linked gel in the target reservoir, which has a guar concentration of 0.45, 0.5% organic borate cross-linker, and 0.1% gel breaker.

Fracturing fluid #2 is a modified version of fracturing fluid #1. To reduce the potential damage of gel residuals, the guar concentration is reduced from 0.45 to 0.35%.

In fracturing fluid #3, the conventional guar is substituted by the carboxymethyl guar, which has a better performance at a high temperature and a higher hydration rate. It has 0.55% carboxymethyl guar, 1% organic borate cross-linker, and 0.35% gel breaker.

In fracturing fluid #4, the conventional guar is substituted by a type of modified polyacrylamide with high-temperature resistance and low residues after breaking. It contains 0.5% polyacrylamide, 0.4% organic borate delayed cross-linker, and 0.6% gel breaker.

Besides, the above four types of mimicked fracturing fluids all contain 0.5% temperature-stabilizing agent (i.e., antioxidant), 1% clay stabilizer (e.g., KCl and/or quaternary ammonium salts), and 0.5% flowback surfactant that reduces the surface tension from 72 mN/m to around 25 mN/m. Table 2 shows the information of these four fracturing fluids including their maximum application temperatures and their viscosities at the maximum temperature.

Table 2. Viscosities of Four Types of Mimicked Fracturing Fluids

fluid name	maximum application temperature ($^{\circ}\text{C}$)	viscosity at the maximum temperature (mPa·s)
fracturing fluid #1	150	186
fracturing fluid #2	150	155
fracturing fluid #3	180	248
fracturing fluid #4	200	260

2.2.3. Acids. During the field operation, acid is used to enhance the conductivity of natural fractures by etching the fracture faces and reducing the gel residues. For naturally fractured reservoirs as the target one in this study, acid is retarded where chemicals are mixed with the acid to reduce the reaction rate of acid with the reservoir rock, thus increasing the depth of acidizing. In this study, two types of retarded acids are evaluated, compared, and further optimized.

Acid #1 is conventionally used gelled acid, where 0.6% acid-soluble polymer (a modified polyacrylamide) is mixed with 15% hydrochloric acid (HCl) to increase the viscosity of the acid solution. In addition, a 2% corrosion inhibitor (Mannich base) is used to reduce the wellbore corrosion at a high temperature, and 2% chelating agent is used to eliminate the effects of iron ions on polymers; meanwhile, 1% clay stabilizer and 0.5% flowback surfactant are also used as the fracturing fluid. Acid #1 has a viscosity of 39 mPa·s at 25 $^{\circ}\text{C}$.

Acid #2 is a new type of retarded acid, where HCl is mixed with oil-in-water microemulsions to achieve the delay-releasing effect. To synthesize this microemulsion, 20% nonionic surfactant, 10% cationic surfactant, 10% cyclohexane, and 20% isopropanol are mixed, agitated, and placed for equilibrium. Then, 7% of this microemulsion is further mixed with 12% HCl and 5% organic phosphonic acid; besides, 2% corrosion inhibitor, 2% chelating agent, 1% clay stabilizer, and

0.5% flowback surfactant are also used as acid #1. Acid #2 has a viscosity of 6 mPa·s at 25 °C.

The rotating-disc test is conducted to quantify the reaction rates of different acids with the reservoir rock. In the test, the reservoir rock is cut into a disk with a diameter of 3.81 cm and a thickness of 2 cm; then, the disk is submerged in a certain volume of acid and placed in the rotating-disc apparatus at the mimicked reservoir temperature; the disc is continuously rotated at a constant rate of 800 rev/min, during which ion concentrations in the acid is measured with time. A more detailed procedure of this measurement can refer to the published work by Rabie et al. (2011).⁴⁵ Figure 2 shows the

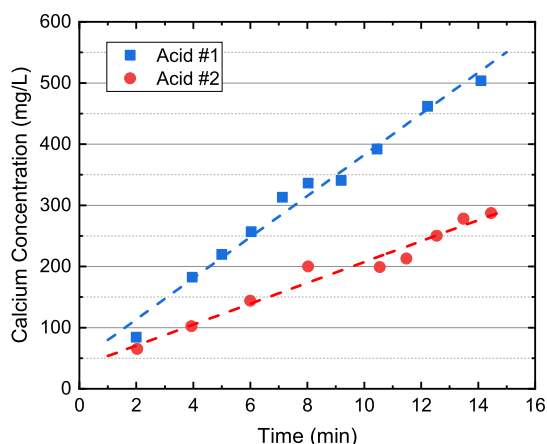


Figure 2. Change of calcium concentration in different acids from the rotating-disc test.

change of calcium concentration in different acids with time. Compared to the regular HCl, the erosion rates of both acid #1 and acid #2 are less vigorous with the reservoir rock. By increasing the acid viscosity, acid #1 reduces the erosion rate to less than one-fifth of the regular HCl; when the acid is mixed with microemulsions and forms acid #2, the erosion rate is further reduced to only one-tenth of the regular HCl.

2.4. Methods. **2.4.1. Measurement of Gel Residues.** Residues of the cross-linked gel can plug the fractures and adhere to the reservoir rock, both of which can result in the formation damage that reduces the well productivity. In the lab, the gel breaking test is conducted to quantify the gel content after breaking. First, the mimicked fracturing fluid is placed in the 90 °C water bath for 2 h. Then, the fluid is filtered by vacuum through a filter paper with hole sizes of 15–20 μm , and residues left on the filter paper are weighted after dried. The whole measurement is repeated at least three times, and the measured residue weights are averaged as the residue content of this type of fracturing fluid.

2.4.2. Evaluation of Rock-Permeability Change due to Different Working Fluids. There are different methods to characterize the formation damage caused by fracturing fluid, such as pressure conduction, conductivity, and coreflood experiment, and so forth, but the pressure conduction is mainly tested for cores with low porosity and permeability that are difficult to displace, and the conductivity experiment is mainly tested for simulated high permeability cores such as sand filling pipes. This paper mainly studies the influence of fracturing fluid and acid on the conductivity of core fractures, the use of core displacement device is more in line with the actual situation on site.

Coreflood setup is used to evaluate the formation damage of the reservoir rock due to different fracturing fluids, and the permeability enhancement of the reservoir rock after being treated by different acids. Before each experiment, the mimicked fracturing fluid and the acid are loaded in piston-accumulators in the left oven shown in Figure 3, and a



Figure 3. Coreflood setup for evaluating the permeability damage due to different working fluids.

reservoir rock sample is loaded in a core-holder with a confining pressure of 10 MPa in the right oven shown in Figure 3. Both ovens are set at the reservoir temperature, which is 90 °C in this study. The whole system, including accumulators, core-holders, and tubings, are made of the acid-resistant Hastelloy alloy.

Then, a three-step coreflood sequence is conducted as detailed below.

Step 1: saturation of the mimicked formation brine. The reservoir rock sample is first dried and then split into two halves through the Brazilian splitting method. After a pair of thin copper strips are placed between the fractured rock sample to mimic a naturally fractured rock, the sample is loaded into the core holder, as shown in Figure 3. After both ovens reach 90 °C, the confining pressure is applied and the core is vacuumed in the core holder. After the whole system stabilizes for 24 h, the formation brine is injected into the core holder at a constant flow rate by an ISCO pump. The indoor experimental flow rate calculation ignores the size of the cylinder diameter and directly converts the field and indoor through the linear speed cm/min. Assuming the reservoir thickness is 500 m, the wellbore radius is 0.2 m, and the production rate is 100 m³/d, the flow rate is found to be 0.2 mL/min in the lab for the chosen core sample by keeping the interstitial velocity the same. Once the pressure drop across the core sample plateaus, the permeability is calculated through the Darcy's law (K_1).

Step 2: invasion of the mimicked fracturing fluid gel breaking solution. The gel breaking solution is injected from the opposite direction at a constant flow rate of 4 mL/min, which simulates the process that the injection direction of fracturing fluid during on-site fracturing is opposite to that during flowback production. The injection stops after 30 min of fluid breakthrough through the sample. The core is isolated in the core holder and lets the gel breaking solution stay for another 2 h. Then, the mimicked formation brine is injected at a constant flow rate of 0.2 mL/min as in Step 1. The permeability of the rock sample is measured again and named

K_2 . The ratio of K_2 to K_1 gives the permeability recovery after the invasion of the gel breaking solution, from which the best fracturing fluid can be chosen that has the highest recovery rate and the minimum formation damage.

Step-3: Treatment of acid. After a series of corefloods with Step 1 and Step 2 shown above is conducted on core samples (rocks #1–#12 as shown in Table 1), the best fracturing fluid can be chosen by comparing recovery rates of their permeabilities. Then, a new core sample is loaded into the core holder, saturated with the mimicked formation brine (Step 1), and invaded by the chosen fracturing fluid (Step 2). An acid is injected into the core sample at a constant flow rate of 2 mL/min for 1 pore volume (PV) or 3 PVs. Because there is insufficient acid in the acidizing process, in order to ensure the acidizing effect and fully etch the fracture wall, continue to inject acid to 3 PVs under an injection amount of 1 PV. After acidizing for 1 h, the mimicked formation brine is injected again at a constant flow rate of 0.2 mL/min as in Step 1. The permeability of the rock sample is measured again and named K_3 , from which the permeability enhancement by this acid can be quantified using the ratio of K_3 to K_1 . The whole three-step sequence is repeated for different acids and different injected PVs for comparison. After each sequence is finished, the rock sample is taken out of the core holder and opened for observing the tomography of fracture faces using a scanning electron microscope; meanwhile, detached fines on the rock surface are detected using the energy-dispersive spectroscopy (EDS), and this can help optimize the acid formula.

2.4.3. Measurement of Erosion Rate of Acid. Erosion rate of an acid with the reservoir rock is a key parameter to the acid optimization. To measure the erosion rate, the reservoir rock is first ground into powders of 40/70 mesh. Second, 1.5 g of rock powders (m_1) are added in 30 mL acid, which is then heated up to 90 °C and stirred at 150 rev/min for a certain amount of time. Third, after the acid cools down to the room temperature, remaining rock powders are screened, and rinsed by the distilled water for three times. Finally, rock powders are dried in an oven of 100 °C and their remaining mass is measured (m_2). The erosion rate of this acid at this time is defined as the ratio of ($m_1 - m_2$) to m_1 . The whole measurement procedure is repeated for different acidizing times from 15 min up to 4 h and different acids.

3. RESULTS AND DISCUSSION

3.1. Fracture Permeability. When the fractured reservoir rock samples are tested through the three-step coreflood sequence, their initial permeabilities are measured in Step 1 as baselines for a later comparison. The permeabilities of all 24 rock samples evaluated in this study have been plotted against their fracture widths, as shown in Figure 4. Because thicknesses of copper strips between the two halves of reservoir rocks can change after the confining pressure is applied during the coreflood experiment, their thicknesses are measured after each three-step coreflood sequence, as shown in Table 1. Data points show that measured permeabilities increase with the third power of fracture widths in the tested range of 2–30 μm , which agrees well with the classic formula of the laminar flow in a narrow slit.^{46,47}

3.2. Gel Residues of Different Fracturing Fluids. Although four types of fracturing fluids have viscosities of over 150 mPa·s after cross-linking, viscosities of their breaking solutions are all less than 5 mPa·s, which meets the requirement of field applications. Gel residues in their breaking

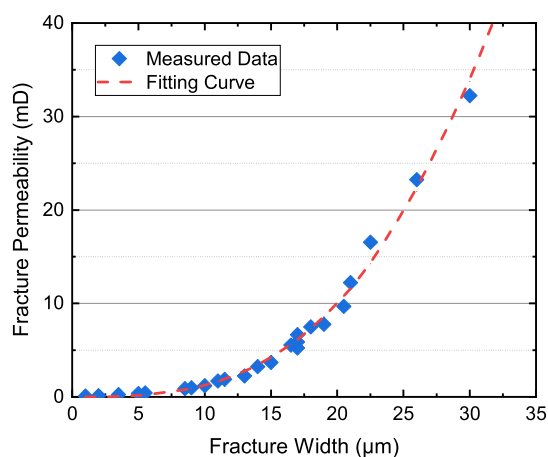


Figure 4. Change of permeability of the fractured rock sample with fracture width.

solution are filtered, dried, and quantified as introduced in Section 2.4.1. As shown in Figure 5, fracturing fluids made of

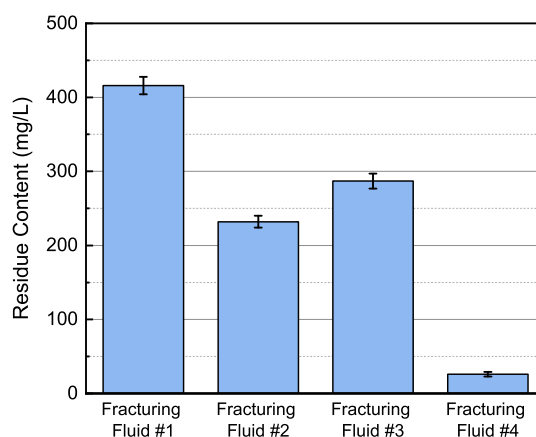


Figure 5. Residue contents of four types of fracturing fluids.

guars or modified guars (i.e., fracturing fluid #1–#3), all have residue contents of above 200 mg/L, which is 10 times more than the one made of modified polyacrylamides (i.e., fracturing fluid #4). Results of gel residue measurement suggest that fracturing fluid #4 likely has the minimum formation damage to natural fractures in the reservoir, which is further examined through the coreflood experiment as shown below.

3.3. Formation Damage due to Different Fracturing Fluids. Coreflood experiments are conducted to evaluate the reduction of rock permeability after the invasion of different types of fracturing fluids. In each coreflood, one type of fracturing fluid gel breaking solution is injected into a core sample saturated with the mimicked formation brine and breaks down within the core, which is followed by another round of formation brine injection. Permeabilities of the rock sample measured from both brine injections are used to calculate the permeability reduction due to gel residues. Figure 6 shows fracture widths and permeability recovery rates of rock samples after being invaded by different gel breaking solutions. For each type of fracturing fluid, a similar trend can be observed where the permeability recovery increases with the fracture width. For the conventional cross-linked guar, the permeability reduction rate is around 40% (fracturing fluid #1). Reducing the guar concentration can decrease the

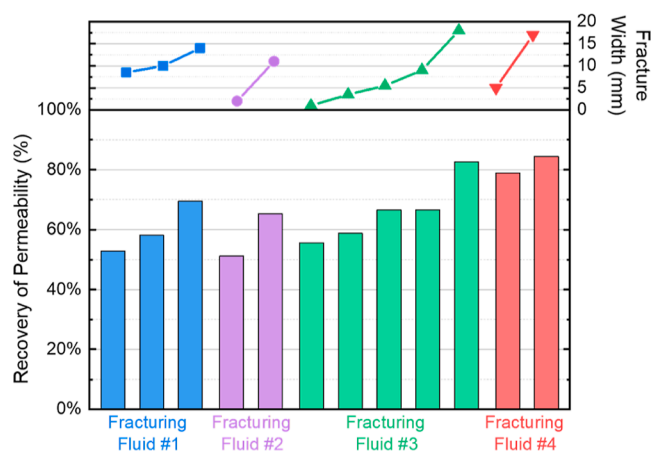


Figure 6. Fracture width and permeability recovery of fractured rocks after being invaded by different fracturing fluids (blue, purple, green, and red bars represent fracturing fluids #1–#4).

concentration of guar residues, but it has a limited effect on preventing the permeability reduction due to guar residues (fracturing fluid #2). In fracturing fluid #3, carboxymethyl guar is a type of guar derivatives, where carboxymethyl groups are grafted on saccharides of guar molecules to enhance the hydration rate.⁴⁵ However, this does not reduce the insoluble protein molecules in the naturally occurring guar, and thus both the residue content and permeability reduction have not decreased compared to conventional guar. As shown as green bars in Figure 6, only rock #10 has a permeability reduction smaller than 20% (a permeability recovery rate of 83%), but this is attributed to a larger fracturing width that is less susceptible to guar residues after breaking. For fracturing fluid #4, when the synthetic polymer is used, recovery rates of rock samples can increase up to 80% for fracture widths ranging from 5 to 18 μm , and this agrees with the result from the residue content measurement, as shown in Figure 5.

3.4. Permeability Enhancement after Acidizing.

Because fracturing fluid #4 has the minimum formation damage to the fractured rock sample among the four types of fracturing fluids, it is used in Step 2 of the three-step coreflood sequence to further evaluate the permeability enhancement by different acids. After fracturing fluid #4 invades the formation brine-saturated rock sample, an acid (acid #1 or acid #2) is injected into the sample at a constant flow rate of 2 mL/min for 1 PV or 3 PVs. After the coreflood setup is shut in for 1 h to allow the rock–acid interaction, the formation brine is injected again into the core sample to quantify the permeability enhancement from acidizing.

As shown in Figure 7, rock permeability is enhanced by 39–89% after 1 PV of acid #1 treatment, which is further increased to about 110% after 3 PV of acid treatment. When the microemulsion acid (acid #2) is used, larger permeability enhancements after acidizing are observed for rock samples with narrower fractures; the enhancement increases to 148% for a fracture width of 12 μm (rock #15) and further to 550% for a fracture width of 17 μm (rock #16). Narrow fractures are more susceptible to secondary products or precipitations from acidizing, and this is further studied with microscopic characterization methods to make the acid effective to reservoirs with wider distributions of natural fractures as shown below.

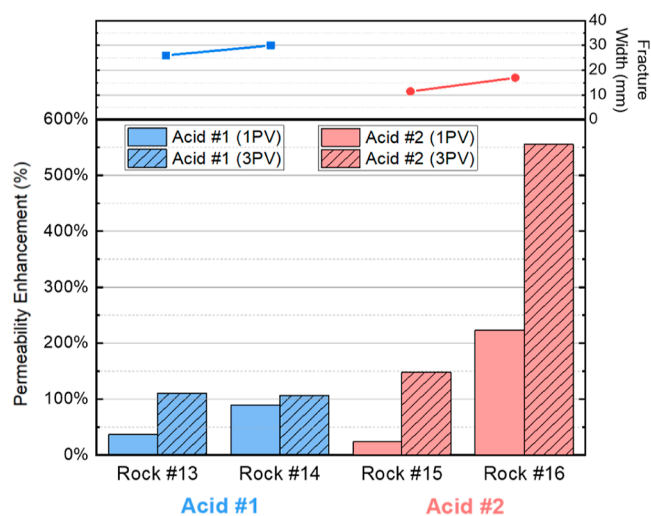


Figure 7. Permeability enhancement after acidizing by different acids and PVs.

3.5. Acid Damage and Optimization. After each three-step coreflood sequence, the core sample is taken out of the core holder and open for observing the acidizing products with SEM and EDS. As shown in Figure 7, the permeability enhancement of rock #15 is only 148% after 3 PVs of acid #2 treatment, which is only one third of Rock #16 with a slightly larger fracture width. When the rock sample is open and one fracture face is placed in the SEM, one can find that a large number of particles fall off from the rock, which could potentially migrate and plug narrow fractures during the production, as shown in Figure 8. Besides large particles that

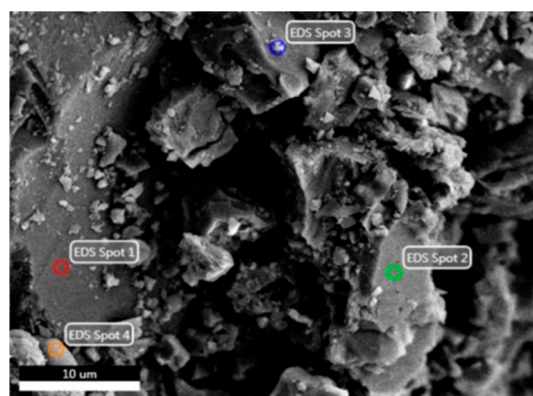


Figure 8. SEM image of fracture face after acidizing by acid #2 (core #15).

have similar crystal structures, fine particles are also observed and further selected in the SEM for the EDS analysis as pointed in Figure 8. As shown in Figure 9, their composition is mainly silicate that is undissolved in HCl.

To reduce the erosion rate that reduces the uneven interaction between the reservoir rock and the acid, the polymer concentration is changed for acid #1 and the HCl concentration is changed for acid #2 to explore the effect of erosion rate on acidizing fracture faces and thus the permeability enhancement of the fractured rock. Besides, since the reservoir rock has silicate minerals like quartz and feldspar, HF is mixed with HCl in the microemulsion acid

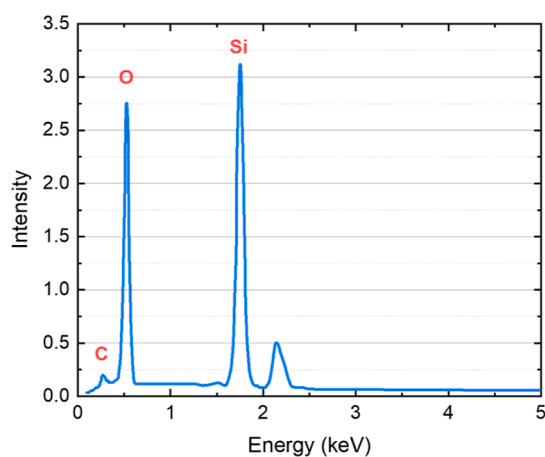


Figure 9. EDS spectrum of acidizing products observed in the SEM image shown in Figure 8.

(acid #2) and compared with formulas with different HCl concentrations.

Columns in Figure 10 show permeabilities of different rock samples before (blank columns) and after (shaded columns)

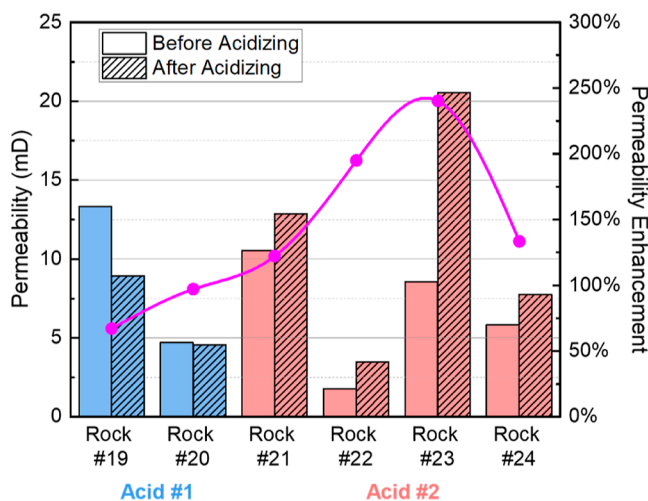


Figure 10. Permeabilities and permeability enhancements of fractured rocks after being treated by acids with different formulas.

being treated by acids with different acid formulas, while data points in Figure 10 show their permeability enhancements from acidizing. Table 3 lists the information of core samples

Table 3. Information of Core Samples in Acidizing Tests

rock number	fracture width (μm)	initial permeability (mD)	treating fluids	permeability before acidizing (mD)	permeability after 1 PV acidizing (mD)	permeability recovery rate (%)
#13	26.0	23.24	acid #1 (baseline, 0.6% polymer)	20.55	7.58	36.9
#15	11.5	1.88	acid #2 (baseline, 12% HCl)	1.52	0.36	23.9
#19	22.5	16.55	acid #1 (0.4% polymer)	13.33	8.94	67.1
#20	16.5	5.55	acid #1 (0.8% polymer)	4.69	4.55	97.0
#21	21.0	12.23	acid #2 (12% HCl, repeat)	10.54	12.87	122.1
#22	13.0	2.24	acid #2 (4% HCl)	1.79	3.49	195.0
#23	20.5	9.69	acid #2 (8% HCl)	8.55	20.55	240.4
#24	17.0	6.66	acid #2 (12% HCl + 1.5% HF)	5.82	7.76	133.3

evaluated in these acidizing tests, as well as their permeabilities and permeability enhancements, as shown in Figure 10. For acid #1, increasing the viscosity of the acid by increasing the polymer concentration allows a relatively uniform erosion of fracture faces, which can reduce the possibility of generating large-size particles that plug the fracture during acidizing. For the tested rock samples with fracture widths of 11.5 to 26 cm, permeability enhancements after acidizing are all below 100%, and no clear trend is observed with the increase of gel concentration; this indicates formation damage remains when moderately increasing the acid viscosity. Therefore, increasing the polymer concentration under the economic constraint cannot reduce the erosion rate of the gelled acid that makes this type of acid effective to the target reservoir.

When HCl is mixed with water-in-oil microemulsions, slowly released surfactants from microemulsions can adsorb the rock surface, decrease its erosion rate, and prevent the generation of large particles. Because the fracture width can affect the permeability enhancement after acidizing, another baseline measurement with 12% HCl is conducted in a fractured rock with a fracture width of 21 μm (rock #21). Figure 11 shows the

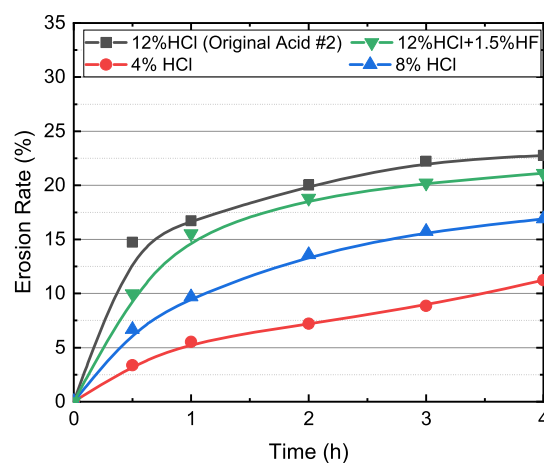


Figure 11. Change of erosion rate of acid #2 with the HCl concentration.

change of erosion rate of reservoir rock powders when the HCl concentration decreases in acid #2. The erosion rate decreases by 26% when the HCl concentration decreases from 12 to 8%, which increases the permeability recovery rate by about 100% (rock #23); the erosion rate decreases by 51% when the HCl concentration decreases from 12 to 4%, which can increase the

permeability recovery rate by over 700% (rock #22). In general, permeability enhancements are both observed in rock samples with fracture widths of 11–13 or 16–21 μm , while the rock sample with a narrow fracture tends to have a larger enhancement after acidizing because it is more susceptible to the migrant of fines generated from acidizing. Moreover, for a low-permeability rock whose leak-off coefficient is low, leak-off of acid into the rock matrix can be minimized, and thus the etching area of fracture faces can be extended. However, when HF is used, no obvious enhancement is observed (rock #21 vs rock #24), and this is attributed to secondary precipitations from acidizing such as fluorosilicates and fluoroaluminates.^{39,40} Therefore, the synergy effect of reducing the acid concentration and surfactant adsorption on the rock surface can lead to an obvious enhancement of the fracture permeability after acidizing, but HF is not suitable for the target reservoir where concentrations of silicates and clays are relatively high.

4. CONCLUSIONS

In tight naturally fractured bedrock reservoirs, hydrocarbon is mainly stored in natural fractures. Hydraulic fracturing is needed to connect these fractures and generate pathways for the hydrocarbon to flow into the wellbore. In the target reservoir, acidizing is also applied to roughen the created fracture faces to enhance the permeabilities/conductivities of these fractures. For reservoirs with high temperatures, the cross-linked gel is required to maintain sufficient viscosity to minimize the leak-off through natural fractures; however, the cross-linked gel can generate insoluble residues after breaking, which potentially plug fractures and reduce their permeabilities.

In this study, a three-step coreflood sequence is developed to evaluate and optimize the fracturing fluid and acid for stimulating the target reservoir. In each coreflood sequence, the reservoir rock sample is split, between which a pair of copper strips are placed to control the fracture width. The main findings of this experimental study are as follows.

- (1) Although the carboxymethyl guar can increase the viscosity and hydration rate of the cross-linked fluid compared with the conventional guar, it still has a residue content of over 280 mg/L and is thus not recommended for field operations.
- (2) When the synthetic polymer is used to viscosity the fracturing fluid, insoluble residues can be minimized, and the permeability recovery of the reservoir rock can be increased up to 80%.
- (3) Large detached particles due to nonuniform etching and the migrant of undissolved fines are the two main causes of the permeability reduction of naturally fractured rock samples.
- (4) For the conventional gel acid, increasing the polymer concentration can reduce the erosion rate of the reservoir rock and reduce the generation of large-sized particles that plug fractures; however, the enhancement is limited under the economic constraint and thus unsuitable for the target reservoir.
- (5) A new type of microemulsion acid is introduced, in which slowly released surfactants from the microemulsion can adsorb the reservoir rock and significantly reduce the erosion rate during acidizing. The synergy effect of reducing the acid concentration and surfactant

adsorption on rock surfaces can lead to an obvious enhancement of the fracture permeability after acidizing.

- (6) Although the mud acid or HF can be used for acidizing sandstone reservoirs, it is not suitable for the target reservoir where concentrations of silicates and clays are relatively high and acidizing residues can lead to a significant permeability reduction.

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Notes

The authors declare no competing financial interest.

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