Copolymer MCJS as a Retarder of the Acid–Rock Reaction Speed for the Stimulation of Deep Carbonate Reservoirs

Hongping Quan,[1,2] Huan Li,[2] Zhiyu Huang,[2] Shanshan Dai,[2] Jifeng Jiang[2]

[1]State Key Laboratory of Oil and Gas Reservoir Geology and Exploitation, Southwest Petroleum University, Chengdu, People's Republic of China
[2]School of Chemistry and Chemical Engineering, Southwest Petroleum University, Chengdu, People's Republic of China
Correspondence to: H. Li (E-mail: lihuan13031@126.com)

ABSTRACT: The fast reaction rate between hydrochloric acid and carbonates causes the most acid consumption near the wells, and the acid cannot penetrate the deeper places of the carbonate reservoir; this limits the application of acidizing modifications for the reservoir. In this study, we chose acrylamide, 2-acrylamido-2-methyl-1-propane sulfonic acid (AMPS), allyl alcohol polyoxyethylene ether (APEG), and N-dimethyl-N-vinyl nonadecan-1-aminium chloride (DMAAC-18) to synthesize a quadripolymer (MCJS) that could reduce the reaction rate mentioned previously. The molecular structure of MCJS was characterized by Fourier transform infrared and ^{1}H-NMR spectroscopy. The molecular weight and molecular weight distribution of MCJS was determined by gel permeation chromatography. Carbonate rock was analyzed by X-ray diffraction and energy-dispersive X-ray spectroscopy. The retarding properties of the acid mixed with MCJS (MCJS acid) were investigated, and the resulting reaction rate between the acid and carbonate decreased obviously, even at a low viscosity. Scanning electron microscopy and core flood experiments showed that the MCJS could be adsorbed on the carbonate rock surface and form a hydrated film that delayed the reaction. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 41471.

INTRODUCTION

After years of development, the decrease in oil fields with high permeability has made the modification of low-pressure and low-permeability reservoirs more and more important. Conventional hydrochloric acid (HCl) is the most widely used acid system for the stimulation of carbonate reservoirs. However, the fast reaction rate between the HCl and carbonates causes most of the acid consumption near the well reservoir, and the acid cannot penetrate the deeper places of the carbonate reservoir;[1–4] this limits the application of acidizing modifications.

Recently, gelled acid have effectively improved the permeability of reservoirs as a retarded acid attracts many researchers' interest. Gelled acid is usually composed of HCl as the base acid and a polymer gelling agent as an addictive. Polymer gelling agents are copolymers consisting of various ratios of acrylamide (AM), 2-acrylamido-2-methyl-1-propane sulfonic acid (AMPS), quaternized dimethyl aminoethyl acrylate, and quaternized dimethyl aminoethyl methacrylate. Although a gelled acid with a high viscosity can release hydrogen ions slowly, the accompanying results show that it is difficult for the acid to penetrate the deep places of low-pressure and low-permeability reservoirs because

of its high viscosity. Secondary damage caused by the gelled acid is still apparent after acidization; this includes residual and gelled fluid breakdown problems.[5–9] What is more, the gelling process is often meticulous and time consuming. This is primarily due to the onsite blending and mixing of the base gel and the time that is necessary to produce a consistent base gel. The gelling process is often deliberate to prevent the unhydrated polymer in the reservoir due to the rapid hydration of the polymers.[10,11]

On the basis of the reasons mentioned previously, a quadripolymer with adsorption-retarding admixtures, MCJS, was synthesized by the free-radical polymerization of an environmental quadripolymer of AM, AMPS, allyl alcohol polyoxyethylene ether (APEG), and N-dimethyl-N-vinyl nonadecan-1-aminium chloride (DMAAC-18) in this study. Up to this point, no research has been reported on this copolymer, with its effects of adsorption, to be used in the stimulation of deep carbonate reservoirs as a retarded additive. MCJS acid, with its good flow performance, will make it easily penetrate with the low-pressure and low-permeability acidification treatment, and its back fluids easily discharges back into the ground.
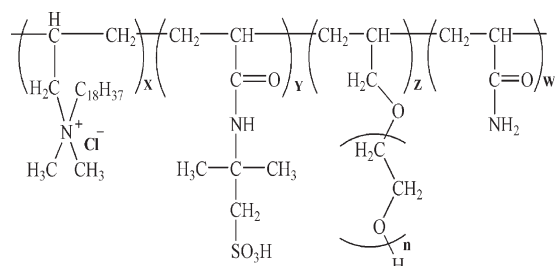
Scheme 1. Chemical structure of MCJS.

EXPERIMENTAL

Materials

The main products, AMPS, AM, and azo two isobutyl acetamiprid hydrochloride, were obtained from Chengdu Kelong Chemical Reagent Factory (China). APEG-1000 was industrial grade from Jiangsu Haian Petrochemical Factory (China). DMAAC-18 was industrial grade from Jiangsu Fumiao Chemical Reagent Factory (China).
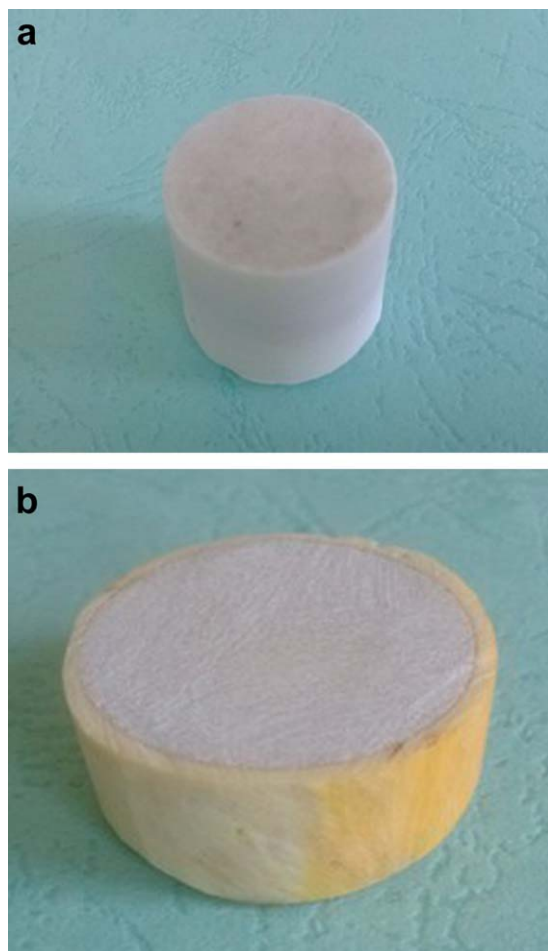
Synthesis

APEG (0.5 g) was dissolved in 21.5 mL of distilled water, and then, DMAAC-18 (0.16 g), AMPS (1.035 g), and AM (2.13 g) were added to the previous monomer solution, and the mixed solution was stirred for 10 min. Then, the initiator, azo two isobutyl acetamiprid hydrochloride (0.0113 g), was introduced into the solution when the water bath was heated to 50°C. After 6 h of the reaction, the resulting product was purified by several rounds of precipitation with ethanol and dried at 50°C to a constant weight. The chemical structure of the MCJS copolymer is shown in Scheme 1.

Characterization

The pellet samples were prepared by the pressing of the mixture of the copolymer and KBr powder and then measured with Fourier transform infrared (FTIR) spectroscopy (WQF-520, China) in the range between 4000 and 500 cm^{-1}. ^{1}H-NMR was recorded on a Bruker spectrometer (Ascend 400 MHz, Switzerland) on samples in deuterium oxide (D$_2$O) at room temperature. The molecular weight data of the copolymer was determined by gel permeation chromatography (GPC; Waters e2695). The polymer was dissolved in distilled water to form a solution with a concentration of 2 mg/mL. The measurement was performed at the room temperature (23°C) for 90 min.

The carbonate rock mainly included dolomite marble [CaMg(CO$_3$)$_2$] and calcite marble (CaCO$_3$). The two carbonate rocks exhibited different reaction mechanisms when it was treated with HCl. Therefore, the composition of the carbonate sample could be analyzed to accurately determine the reaction rate. The purity of carbonate was determined by X-ray diffraction (XRD; X′ Pert PRO MRD, Holland) and energy-dispersive X-ray spectroscopy (EDS; England). The XRD diffractogram was recorded in the angle range between 5° and 55° with Cu Kα X-rays at 85 W. To explore the admixture acid-retarding mechanism of the reaction and carbonate, rocks of the reaction between the acid and carbonate rock were used for scanning electron microscopy (SEM; JSM7500F, Japan) analysis of the surface morphology and the volume changes.
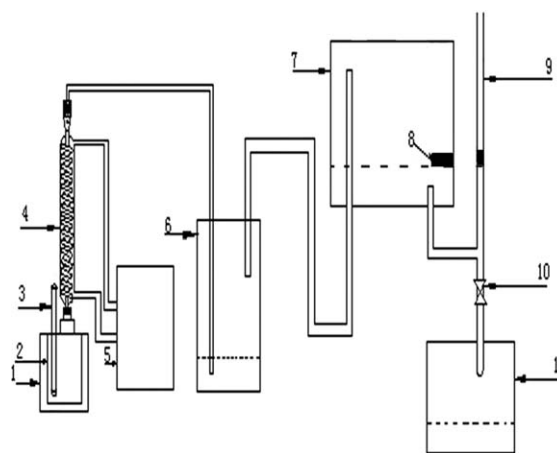

Figure 1. Carbonate rock samples of the acid and rock reaction: (a) before and (b) after the carbonate rock was encapsulated in epoxy resin. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 2. CO$_2$ gas-collecting device: (1) hot-type magnetic heating stirrer, (2) reactor, (3) thermometer, (4) condenser pipe, (5) low-temperature constant-temperature bath, (6) buffer bottle, (7) CO$_2$ gas-collecting bottle, (8) liquid level balance sensor, (9) liquid column, (10) drain valve, and (11) liquid volume measurement.
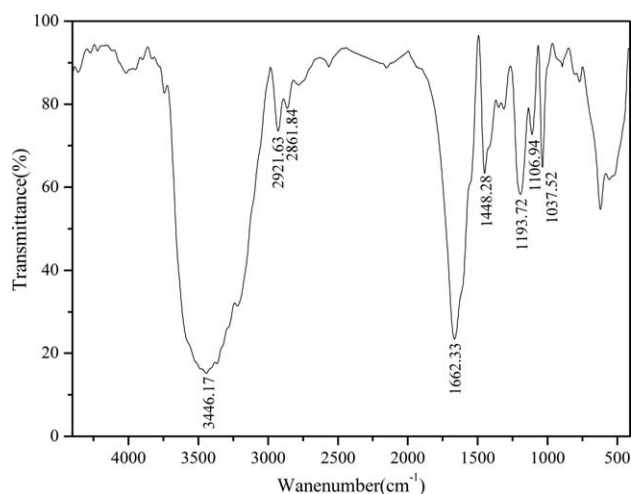
Figure 3. FTIR spectrum of MCJS.

Carbonate Sample Preparation

The process of the acid and carbonate reaction led to changes in the contact area of the acid and carbonate (S); this impacted the acid and carbonate rock reaction rate. Therefore, S was fixed to accurately determine the reaction rate.

In this study, the carbonate rock was made so that S was 5 cm^2 after encapsulation by the epoxy resin. The carbonate samples are shown in Figure 1(a,b).

CO$_2$ Gas Collection

The CO$_2$ gas-collection device is shown in Figure 2.

As shown in Figure 2, the gas-collecting device was made up of 11 parts. The hot-type magnetic heating stirrer was used to heat and mix the acid. The reaction of the acid and carbonate rock generated gases, and this was accompanied by a lot of heat. This resulted in an expansion of the gas volume. To accurately quantify the volume of generated CO$_2$, a low-temperature constant temperature reaction bath was used to reduce the temperature of the system. In this course, ethyl alcohol was used as the cooling solvent, and the condensation temperature was set to -5°C. The CO$_2$ gas was produced by the reaction of HCl and carbonate rock stored in the gas-collecting bottle; this was filled with a saturated carbonate solution. Another set of liquid-level balance sensors was added and placed parallel to the collecting bottle to balance the atmospheric pressure. When the generated gas was injected into the collecting bottle, the saturated carbonate solution was discharged, and the speed of the discharged volume of liquid was measured to calculate the gas production rate.

Determination of the Reaction Rates

The acid–rock reaction rate was an important parameter for investigating the reaction of the acid and carbonate rock. The acid–rock reaction rate efficiently reflected the retardation properties of the MCJS acid. Therefore, the CO$_2$ gas produced by the reaction of the acid and carbonate rock was collected by a gas-collecting device. The collected CO$_2$ was used to calculate the acid–rock reaction rate. The calculation steps were as follows.

According to the ideal gas state equation

$$PV = nRT \qquad (1)$$

The CO$_2$ gas was refrigerated to room temperature (25°C). According to the ideal state equation, we calculated the molar volume of the gas at 25°C:
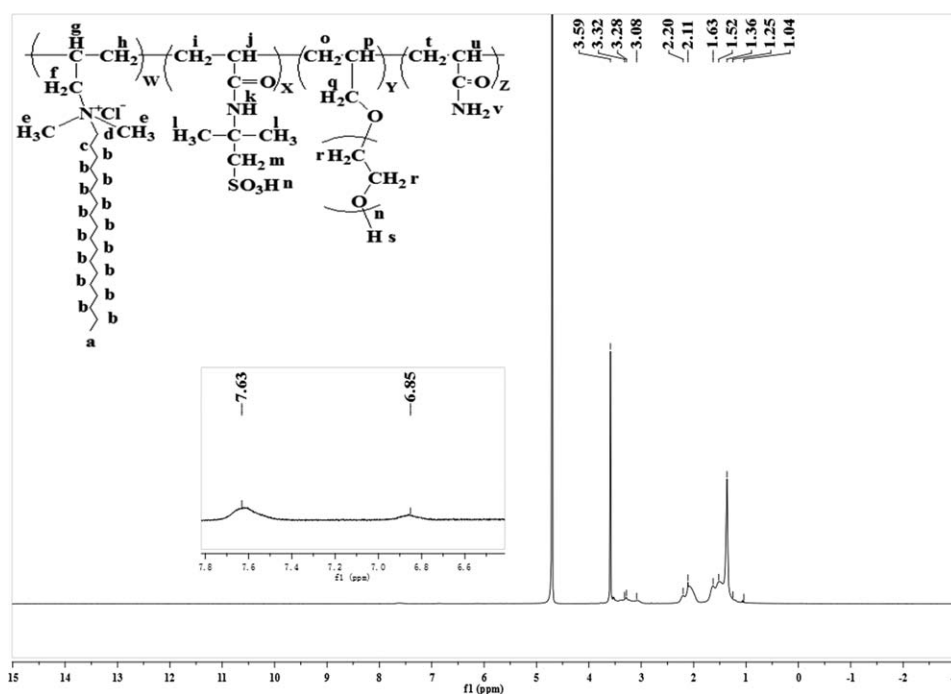

Figure 4. ^{1}H-NMR spectrum of MCJS.

Table I. GPC Results of MCJS

| M_n	M_w	peak molecular weight (MP)	z-average molecular (M_z)	$M_z + 1$	Polydispersity
2.3×10^5	4.6×10^5	5.3×10^5	6.6×10^5	7.9×10^5	1.98

$$\frac{nR}{P} = \frac{V}{T} = \frac{V_1}{T_1} \Rightarrow V_1 = \frac{V}{T} \times T_1 \qquad (2)$$

where V is the molar volume of the ideal gas (22.4 L/mol), T is the absolute temperature of the ideal gas (273.15 K), V_1 is the molar volume at 25°C, and T_1 is the absolute temperature, P is the pressure; n is the amount of substance, and R is the perfect gas constant, 25°C.

With eq. (2) and the 25°C molar volume of gas, we obtained

$$V_1 = \frac{22.4 \times 298.15}{273.15} = 24.45 \text{ L/mol}$$

The reaction of the acid and carbonate was as follows:[12]

$$2HCl + CaCo_3 \rightarrow CaCl_2 + CO_2 + H_2O \qquad (3)$$
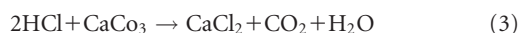
The reaction rate calculation method was as follows:[13–15]

$$u = \frac{n_{(CaCO_3)} M_{(CaCO_3)}}{st} = \frac{n_{(CO_2)} M_{(CaCO_3)}}{st}$$

$$= \frac{[V_{(CO_2)}/1000] V_1 M_{(CaCO_3)}}{st} \qquad (4)$$

$$= \frac{0.00409 V_{(CO_2)}}{st} (gcm^{-2}min^{-2})$$

where u is the reaction rate of the acid and carbonate rock (g cm^{-2}·min^{-1}), $V_{(CO_2)}$ is the gas volume per unit of reaction time (mL), S is the contact area of the acid and carbonate (cm^2), and t is the unit of the reaction time (min), $n_{(CaCO_3)}$ is the amount of substance of $CaCO_3$, mol. $n_{(CO_2)}$ is the amount of substance of CO_2, mol. $M_{(CaCO_3)}$ is the molar mass of $CaCO_3$, g/mol. $V_{(CO_2)}$ is the CO_2 volume per unit reaction time, mL.

MCJS Retarding Capability Test
A retarding acid solution can obviously delay the reaction rate, and it makes the acid solution be injected deeply into the reser-
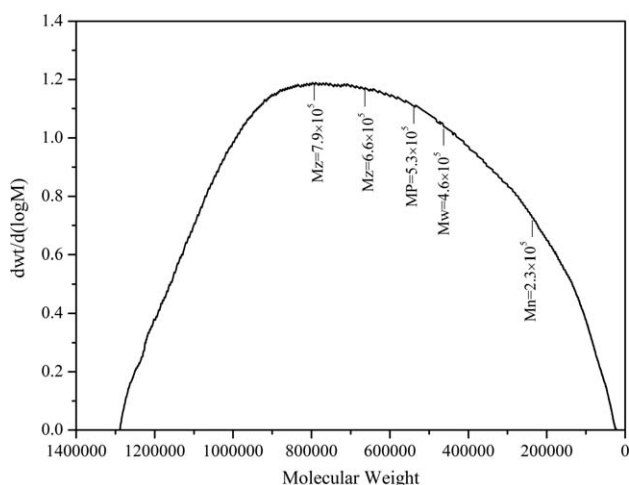
voir for enhanced oil and gas recovery. Hence, the retarding capability of the MCJS acid was measured. MCJS was added to the HCl solution at a mass concentration of 20%. The reaction of the HCl solution with the MCJS addition and carbonate rock was carried out at 75°C, and S was 5 cm^2. The MCJS acid solution could be boiled at high temperatures because of its low viscosity, and this could cause an inaccurate determination of the reaction rate. Therefore, the temperature of the acid–rock reaction was fixed at 75°C on the basis of the reservoir temperature of Xinjiang Oil Field; this made the properties of the MCJS acid more convenient for application. The viscosity variation in the process of the carbonate reaction with the retarding acid of MCJS was measured. The viscosity was measured by a rotational viscometer (ZNN─D6, China) at 170 s^{-1}.

Core Flood Experiments
The core flood experiments with the MCJS acid were run by a core gas permeability tester (H19915, China) and a core acidification flow meter (SL32-180, China). The experimental temperature was 75°C, and the liquid flow rate was 0.01 mL/min. The effects of the MCJS copolymer as a retarder and the acidic treatment on the permeability of the carbonate were measured by the core gas permeability tester (H19915, China) and the core acidification flow meter (SL32-180, China). The experimental temperature was 75°C, and the liquid flow rate was 0.01 mL/min.

RESULTS AND DISCUSSION

Characterization
Figure 3 presents the FTIR spectrum of MCJS. There was a strong absorption peak at 3446.17 cm^{-1} assigned to the stretching vibrations of N─H. The peaks observed at 2921.63 and 2861.84 cm^{-1} were due to the stretching vibrations of ─CH$_3$ and ─CH$_2$, respectively. The peak at 1662.33 cm^{-1} was attributed to the stretching vibrations of C═O. The bands at 1448.28

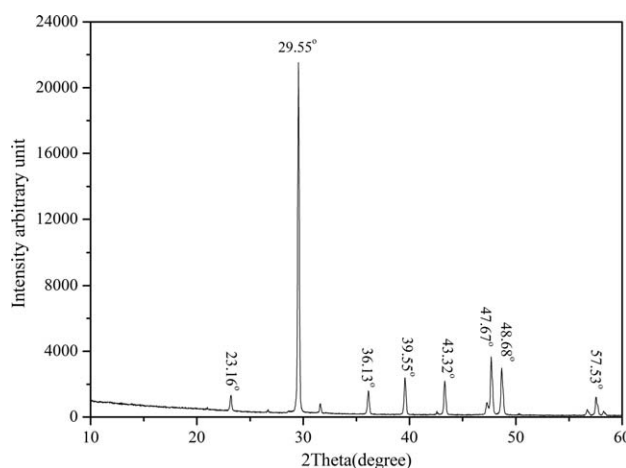**Figure 5.** Molecular weight distribution of MCJS. wt: weight. M: molecular weight.

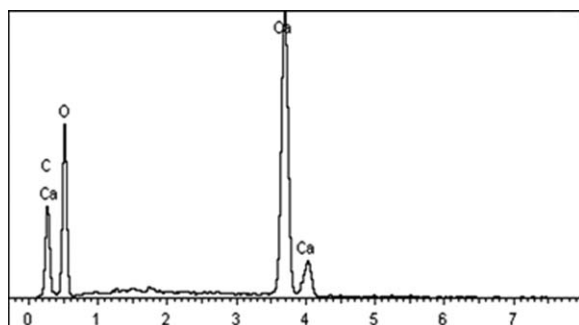**Figure 6.** XRD patterns of the carbonate rock.

Figure 7. Energy dispersion X-ray analysis of the carbonate rock.

and 1193.72 cm^{-1} were due to the stretching vibrations of C—H and —SO$_3^-$, respectively. The absorptions at 1106.94 and 1037.52 cm^{-1} were associated with the C—O—C stretching vibrations. The obtained product was basically consistent with the designed composition. Further characterization, including ^{1}H-NMR, was performed to confirm this structure.

^{1}H-NMR spectrum of MCJS is shown in Figure 4.

^{1}H-NMR (400 MHz, D$_2$O): 1.04 (a, —CH$_3$), 1.25–1.36 [b, l, h, —(CH$_2$)$_{15}$—, CH$_3$—C—CH$_3$, C—CH$_2$—C], 1.52 [i, o, t, —CH$_2$—CH—(C═O)—, —CH$_2$—CH—CH$_2$—, —CH$_2$—CH—(C═O)—NH$_2$], 1.63 (c, —N$^+$—CH$_2$—CH$_2$—), 2.11 (p, g, —CH—CH$_2$—O—, —CH—CH$_2$—N$^+$), 2.20 [j, u, CH—(C═O)—NH—, —CH—(C═O)—NH$_2$], 3.08 (m, —CH$_2$—S), 3.28 (d, f, —N$^+$—CH$_2$—, CH$_2$—N$^+$—), 3.32 (e, —N$^+$—CH$_3$), 3.59 (q, r, —CH$_2$—O—, —CH$_2$—CH$_2$—O—), 6.85 (v, —NH$_2$), 7.63 [k, (C═O)—NH—].

When we combined these results with the FTIR spectra shown in Figure 3, we concluded that the MCJS was successfully synthesized.

The GPC data of MCJS are shown in Table I and Figure 5.

The molecular weight result shows that the average weight of MCJS was low and confirmed that the viscosity of the MCJS acid solution was maintained at a low value, as discussed previously.

Carbonate Rock Sample Analysis
The XRD and EDS patterns are shown in Figures 6 and 7 and Table II.

As shown in Figure 6, the peaks at 23.16°, 29.55°, 23.16°, 39.55°, 43.32°, 47.67° 48.68°, and 57.53° were due to the crystalline nature of the carbonate sample; this showed that the interplanar spacing and the intensity of the diffraction peak were consistent with the CaCO$_3$ standard drawing.[16–18] Moreover, carbonate sample contained C, O, and Ca elements and

Table II. Elemental Contents of the Carbonate Rock

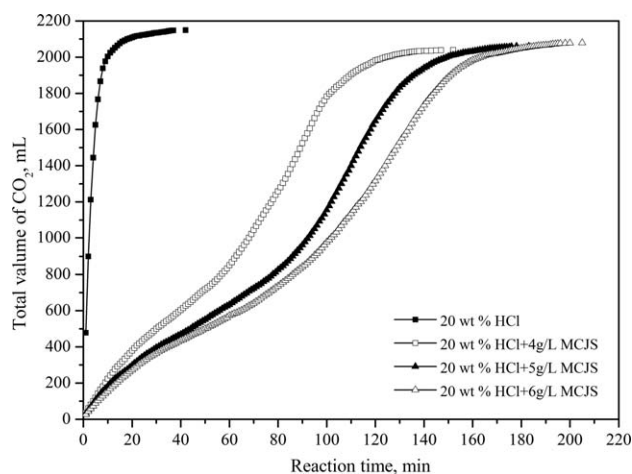| Element	wt %	atom %
C (K)	20.63	28.00
O (K)	59.27	62.54
Ca (K)	20.10	8.46

Figure 8. Effect of the MCJS concentration on the total volume of CO$_2$.

no other impurities; the results of this high purity on the carbonate specimens are shown in Figure 7 and Table II.

MCJS Retarding Capability Test
The results of the test of the MCJS retarding capability are shown in Figures 8 and 9.

Figure 8 shows that the total volume of CO$_2$ increased gradually during the acid and carbonate rock reaction. The reaction between 20 wt % HCl and carbonate rock was very fast and was almost completes in 40 min; however, the reaction time increased gradually as the concentration of MCJS increased. Moreover, with increasing concentration of MCJS in the acid solution, the growth speed of the total volume of CO$_2$ decreased in an obvious manner. Figure 9 shows that reaction rate of the acid and carbonate rock decreased with increasing concentration of MCJS. When the concentration of MCJS reached 5 g/L, the reaction time lasted at least 150 min; namely, with increasing MCJS, the rate of the reaction decreased. The MCJS molecules were absorbed on the surface of the carbonate rock and formed a hydrated film that covered the carbonate rock surface; this could hinder the contact between H$^+$ with the surface of the carbonate rock and, thus, reduce the reaction rate of the acid
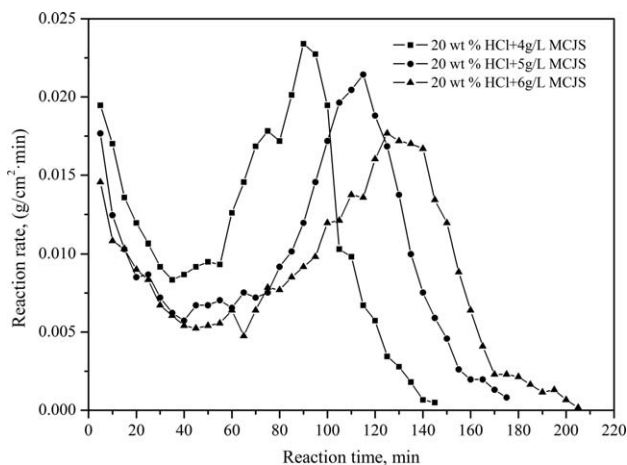

Figure 9. Effect of the MCJS concentration on the reaction rate of HCl and the carbonate rock.
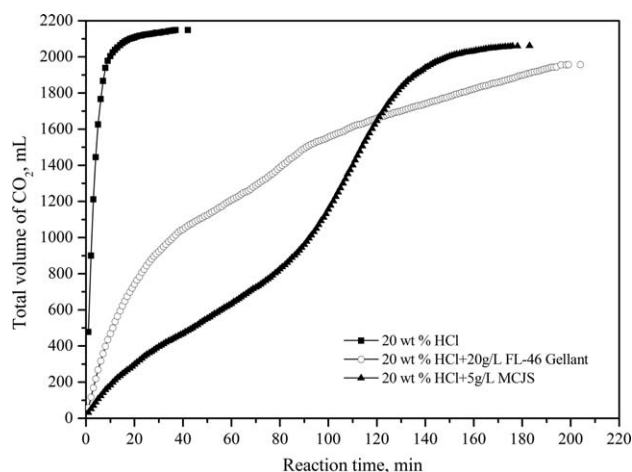
Figure 10. Total volume of CO_2 versus the reaction time of the MCJS acid compared with that of the gelled acid.

Figure 11. Reaction rate of the MCJS acid compared with that of the gelled acid.

and carbonate rock. When the adsorption reached saturation, the rate of the reaction dropped to the minimum value. In addition, the rate of the reaction first increased and later sharply decreased. The change in the reaction rate implied that in the earlier stage, the MCJS was absorbed on the surface of the carbonate rock and decreased the contact between H^+ and the carbonate rock; this led to a low reaction rate. With the continuous progress of the reaction, the degradation of MCJS occurred, and the existence of a large amount of Ca^{2+} decreased the absorption of MCJS on the surface of the carbonate rock because of electrostatic interaction. This made the contact area between the carbonate rock and the acid increase and also increased the reaction rate. Finally, the reaction rate gradually decreased because of the decline in the concentration of H^+. As shown in Table III, with increasing reaction time, the MCJS molecules degraded in the acid solution, and the viscosity of the acid solution decreased. In the process of the acid–rock

Table III. Effects of the Concentration of MCJS and the Reaction Time on the Viscosity of the Acid

MCJS concentration (g/L)	Reaction time (min)	Viscosity (mPa·s)
4	0	3.0
	30	3.0
	60	2.5
	120	1.8
5	0	4.5
	30	3.0
	60	2.6
	120	1.5
6	0	6.0
	30	4.5
	60	3.0
	120	1.8

The viscosity of the MCJS acid was measured by a rotational viscometer (ZNN-D6, China) at 170 s^{-1}.

reaction, the viscosity always remained under 10 mPa·s. The MCJS acid still retarded the acid well with the reaction speed under the conditions of low viscosity.

Retarding Capability of the MCJS Compared with that of Gelled Acid

Because of its high viscosity, it is difficult for gelled acid to flow back into the ground; this may damage the reservoir.[8,9] To overcome the previous disadvantages, the viscosity of the MCJS was investigated, and the retarding capabilities of the MCJS and a commercial gelling agent (FL-46) were compared, as shown in Figures 10 and 11.

As shown in Figure 10, compared with the gelled acid solution (2% FL-46 + 20 wt % HCl), the MCJS acid solution (0.5% MCJS + 20 wt % HCl) exhibited an almost identical reaction time. The reaction time of the MCJS acid solution was much longer than that of the acid solution without any additive. Figure 11 shows that the reaction rate of the gelled acid solution dropped obviously in the beginning (<40 min), and the reaction rate maintained at a comparatively low value over the next 160 min (40–200 min). However, the reaction rate of the MCJS acid solution dropped slowly in the first 40 min (<40 min), and it was maintained at a value close to that of the gelled acid solution (40–80 min). In the following 30 min (80–110 min), it increased again, and the highest reaction rate appeared at 110 min. Then, it decreased slowly until the end of the reaction was reached. In this reaction progress, the reaction rate of the gelled acid solution dropped from a high value to a low value, whereas the reaction rate of the MCJS acid solution maintained a stable low value in the same process. The MCJS acid solution was

Table IV. Viscosity of the Retarded Acid

Type	Viscosity (mPa·s)
0.5% MCJS + 20 wt % HCl	6.0
2% FL-46 + 20 wt % HCl	33.0

The viscosity of the MCJS acid was measured by a rotational viscometer (ZNN-D6, China) at 170 s^{-1}.

effective in reducing the reaction rate between the acid and carbonate. As shown in Table IV, the viscosity of the gelled acid solution was much higher than that of the MCJS acid solution.
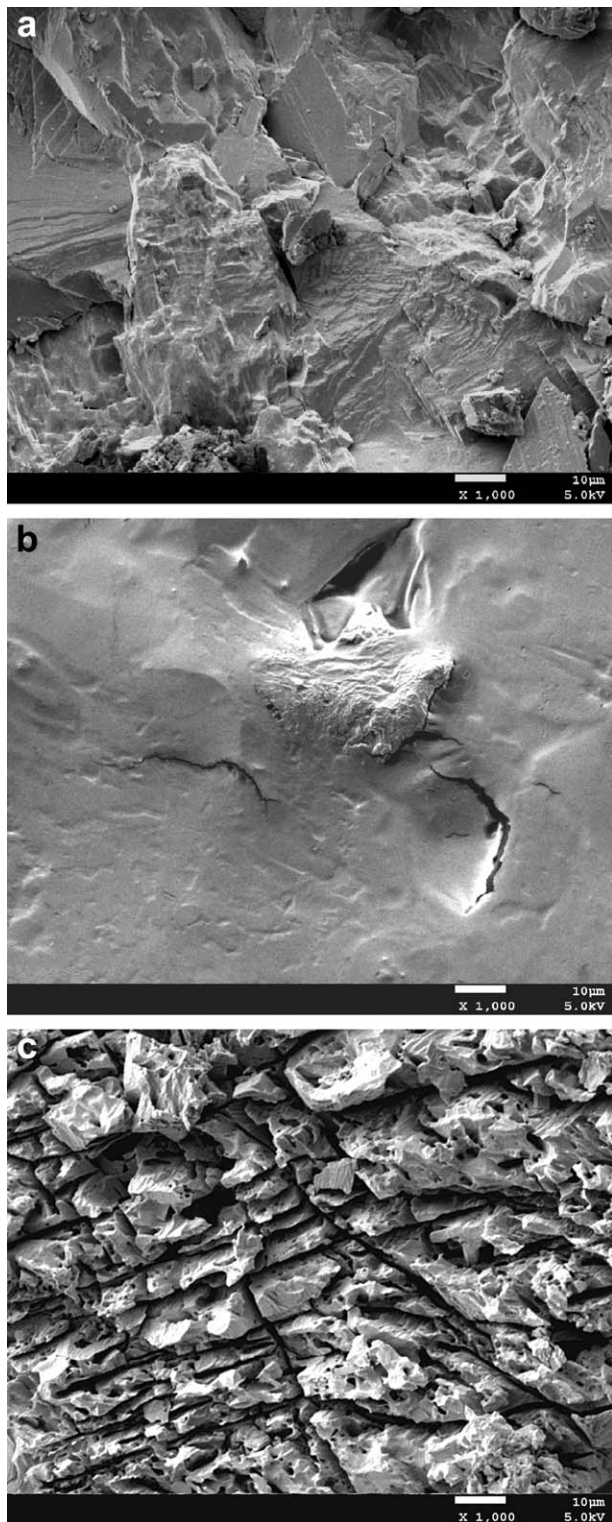
Table V. Date of the Core Permeability Damage

Type	Core size (mm)	Initial core permeability (mD)	Permeability of the 1 pore volume (PV) injecting acid (mD)
0.5% MCJS + 20% HCl	24.8 × 63.9	9.5	12.4
0.5% MCJS + 20% HCl	24.5 × 62.8	8.9	11.6
0.5% MCJS + 20% HCl	25.1 × 62.1	10.9	13.0

Figure 12. SEM results of the carbonate under different conditions: (a) the untreated carbonate sample, (b) the carbonate sample after 30 min dissolution by HCl, and (c) the carbonate sample after 180 min of dissolution by HCl.

Both the gelled acid and MCJS acid exhibited good depth acidizing effects; however, the MCJS acid showed more advantages for applications because of its low viscosity, which made the acid solution easy to pump into the reservoir and flow back on the ground. In addition, as shown in Figures 10 and 11 and Table IV, the low-viscosity MCJS acid solution showed good retarding function because of the MCJS additive. Meanwhile, the high-viscosity gelled acid solution also exhibited an obvious retarding function without other retarding additive. This suggested that viscosity change in the acid solution influenced the H^+ release and further influenced the reaction rate.

SEM Analysis of the Carbonate

As shown in Figure 12(a), the untreated carbonate sample contained a large amount of cement and appeared to have an uneven and rough surface. As shown in Figure 12(b), the carbonate sample that was treated by HCl with MCJS for 30 min formed a thin-layer adsorption film, and the carbonate rock surface looked relatively smooth. The adsorption film prevented the hydrogen ions from contacting the surface of the carbonate rock; this resulted in a decrease in the reaction rate of the acid and carbonate rock. As shown in Figure 12(c), the carbonate sample that was treated by HCl with MCJS for 180 min formed a uniform void and grooves, and the thin film broke away from carbonate surface. This showed that the added MCJS could be absorbed on the carbonate rock surface, and it exhibited excellent breaking ability and low damage to the reservoir during the process of acidification.

Core Flood Experiments

As shown in Table V, the core permeability increased after treatment by the MCJS acid. In addition, the carbonate surface formed a uniform void and grooves after dissolution, and combined with the results from Figure 12(c), this suggested that the MCJS acid solution performed well in the acidic treatment.

CONCLUSIONS

AM, AMPS, APEG, and DMAAC-18 were chosen in this study to prepare the quadripolymer MCJS, which was then applied in an acid solution to reduce the reaction rate between the acid and carbonate rock. The properties of the carbonate rock were analyzed by EDS and XRD, and its main composition was $CaCO_3$. The molecular structure of MCJS was characterized by FTIR and ^{1}H-NMR spectroscopy. The weight-average molecular

weight (M_w) was 4.6 $\times$ 10^5, the number-average molecular weight (M_n) was 2.3 $\times$ 10^5, and its polydispersity was equal to 1.98. As the concentration of MCJS was 5 g/L, the reaction time between the MCJS acid solution and carbonate rock was more than 150 min, and the viscosity of the acid remained under 10 mPa s; these were helpful for the MCJS acid in penetrating deeper into the reservoir and discharging back into the ground. With the continuous progress of the reaction, the degradation of MCJS occurred, and the electrostatic interaction enhanced. This made the contact area between the carbonate rock and the acid increase and further influence the reaction rate. Compared with the gelling acid FL-46, the MCJS acid exhibited an almost identical reaction time. The viscosity of the MCJS acid was lower than that of the gelled acid; this made it easier for the MCJS acid to penetrate the low-pressure and low-permeability reservoir and reduce damage to the reservoir again. The high-viscosity gelled acid solution also exhibited an obvious retarding function without any other retarding additive. This suggests that the viscosity change of the acid solution affected the H$^+$ release and further influenced the reaction rate. The SEM and core flood analysis implied that the absorption of MCJS on the surface of the carbonate rock hindered the contact between H$^+$ and the surface. After the acid and carbonate rock reacted, the absorption film broke away from the surface of the carbonate, and the carbonate surface formed uniform void and grooves. The core permeability increased after treatment with the MCJS retarded acid. The addition of MCJS in the process of acidification exhibited good function as an acidic treatment.

ACKNOWLEDGMENTS

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