

Research Article

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Development of a novel heat- and shear-resistant nano-silica gelling agent

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Abstract: The efficient and sustainable development of deep marine carbonate rock reservoirs in the Sichuan Basin has higher technical requirements for reservoir acidizing alteration technology. However, the acidification effect of deep marine carbonate rock reservoirs was hampered by the drawbacks such as uncontrollable acidification rate of the reservoir, the large friction resistance, and the great acid filtration. A novel heat- and shear-resistant nano-silica gelling agent CTG-1 is prepared based on nano-silica and combined with amide compounds. The influence of different factors on the acid filtration performance and heat- and shear-resistant capacity of carbonate rock reservoirs were analyzed, and then the mechanism of nano-silica gelling agent for acid filtration reduction in carbonate rock reservoirs is revealed. The research results showed that the filtration resistance of acid solution decreases slightly with the increase in the content of nano-silica gelling agent and reservoir pressure. The viscosity, fluid loss coefficient, and friction-reducing rate are as high as 25 mPa s, $2.4 \times 10^{-2} \text{ m}^3 \text{ min}^{1/2}$, and 71%, respectively, showing significantly better result than that of commonly used commercial gelling agents. The development of nano-silica gelling agent provides a reliable reference for effectively improving the acidification

and stimulation effect of deep marine carbonate rock reservoirs.

Keywords: nano silica, fluid loss control, temperature resistance

1 Introduction

The non-renewable resources such as oil and gas are being enormously consumed due to the rapid development of the global economy. Improving oil and gas recovery in reservoirs has become an important means and approach to solve the shortage of oil and natural gas [1,2]. At present, the commonly-used tertiary oil recovery methods and reservoir stimulation measures are mainly acidizing and plugging removal, wax removal, profile control and water plugging, and fracturing techniques [3]. It is possible to maximize oil and gas recovery by taking different reservoir stimulation measures for reservoir with specific characteristics. As a type of high-efficiency reservoir stimulation measure, acidizing stimulation technology for carbonate rock reservoir has become the key to improve oil and gas recovery [4,5].

However, the acid solution is difficult to enter, which attributed a fault to the low porosity of the reservoir causing great frictional resistance in the acidification process of ordinary carbonate rock reservoirs. The acidification reaction after the acid solution enters the carbonate rock reservoir is rapid, the extension capacity of acidified fractures is low, showing low sweeping coefficient and large filter loss coefficient [6–9]. Based on this, experts and scholars proposed the use of synthetic gelling agents to reduce the acid filtration capacity and friction-reducing performance of carbonate rock reservoirs [10–12]. Although it can alleviate the acid filtration loss of carbonate rock reservoirs to a certain extent and increase the fracture extension capacity of the reservoir, there have been still many defects such as low acid viscosity and poor stability under high temperature and high shear conditions. However, a measure that can alleviate the acid fluid friction and filtration capacity of carbonate

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rock reservoirs has not been found so far [13]. The searching for a high-efficiency acidifying gelling agent that is temperature- and shear-resistant has become an important direction for the stimulation of carbonate rock reservoir.

In this study, a nano-silica temperature- and shear-resistant gelling agent was synthesized according to the current research on acidifying gelling agent. The influence of factors such as reservoir pressure and shear rate on the rheology and filtration performance of acid solution was performed, and the mechanism of filtration resistance, temperature resistance, and shear resistance of nano-acidified gelling agent on carbonate rock reservoirs were revealed from microscopic perspective.

2 Methods and materials

2.1 Experimental drugs and materials

Nano-silica (99.5%, radius 15–30 nm), acrylamide, 2-acrylamide-2-methylpropanesulfonic acid, *N*-allyl-*p*-toluenesulfonamide,

octane base phenol polyoxyethylene ether (99.8%, analytical reagent), ethanol, benzene, and chloroform provided by Sinopharm Chemical Reagent Co., Ltd, and all are of analytical grade. The ultrapure water is prepared by the laboratory, and the core is artificial carbonate rock. In addition, we also selected polyacrylamide (PAM) (Figure 2b) as the commercially available gelling agent to investigate the effect of the synthetic gelling agent on the properties of acid solution. The molecular weight of PAM is 5,822, and the degree of polymerization is 82. The molecular structure is a linear straight-chain polymer.

2.2 Experimental instruments

The measuring device used in this investigation was designed by the laboratory (Figure 1) and it can realize the evaluation of rheology and filtration performance of acid solution used in carbonate rock reservoirs. The deionized water in the storage tank can be drawn by the hydraulic pump and introduced into the mixed storage tank for temporary storage. Then, the deionized water with a certain pressure was pushed into the dissolving

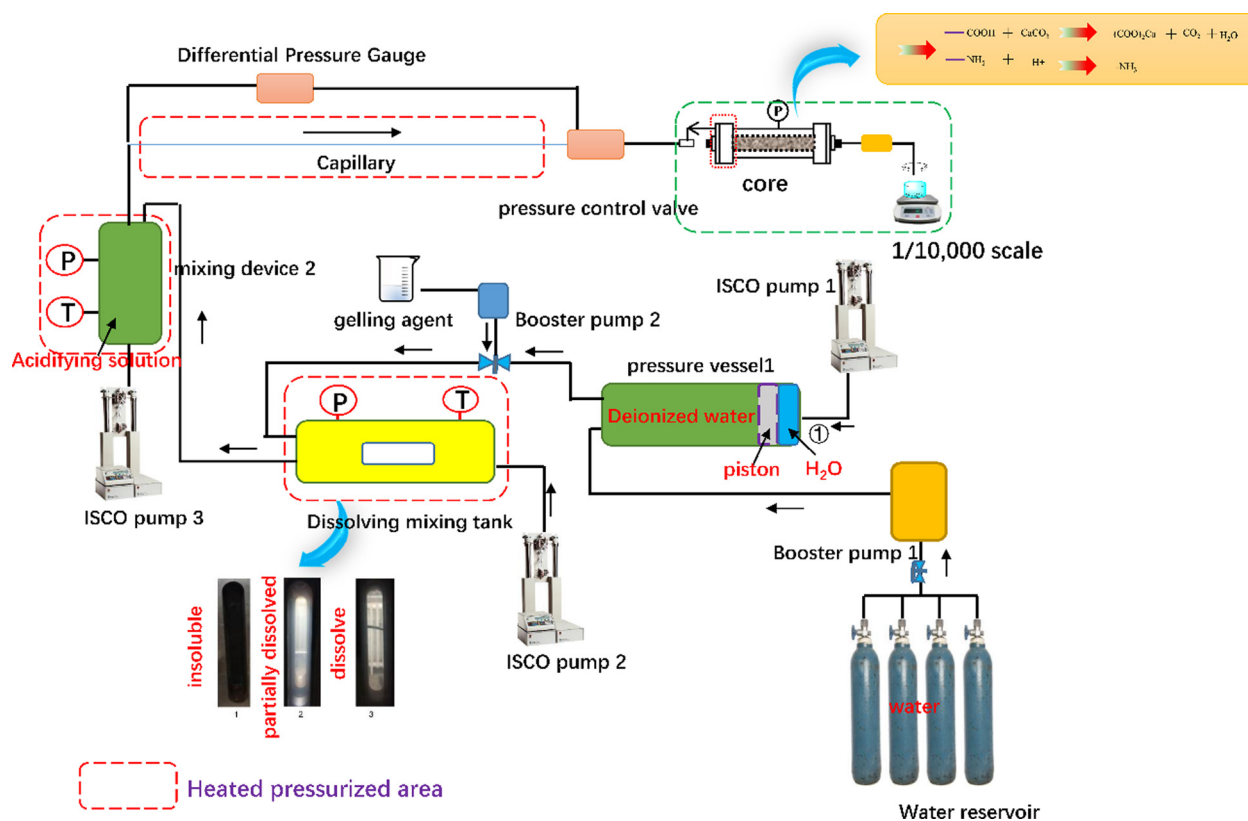


Figure 1: Experimental evaluation device and schematic diagram of acid rheology and filtration performance.

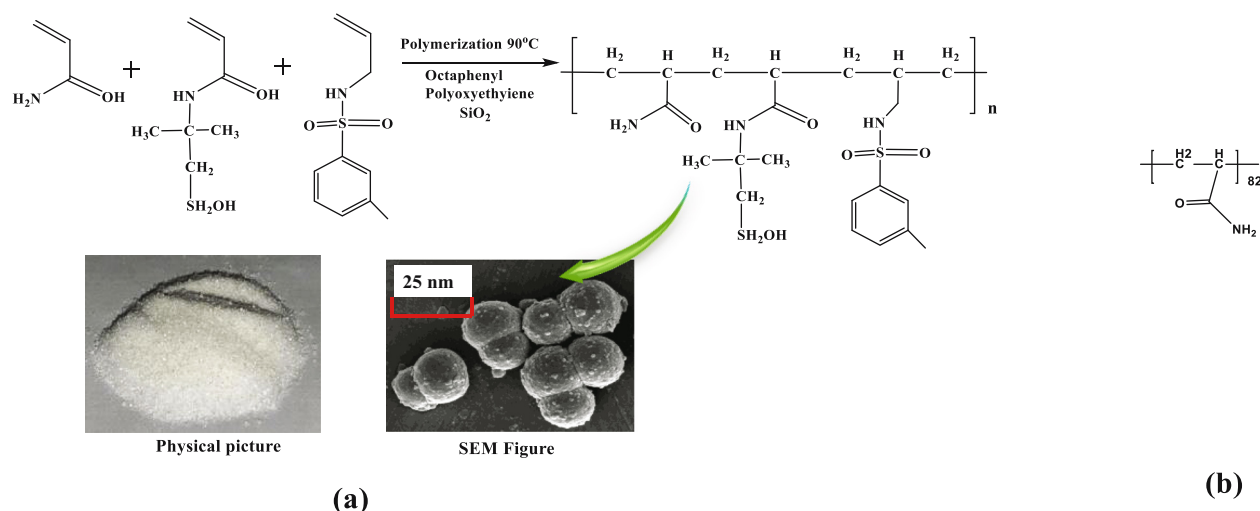


Figure 2: Preparation process and SEM microscopic images of nano-silica gelling agent CTG-1 and commercially available gel structure.

device through the piston at the bottom of the tank. A three-way valve was connected to the flow path of the deionized water. The three-way valve can make the acid gelling agent enter the dissolving device to mix with the deionized water evenly by the operation of a hydraulic pump. It is then transferred to another temporary storage tank, where it is pressurized or heated to simulate the conditions of carbonate rock reservoirs. The acid solution that reaches a certain temperature and pressure is pushed into the capillary tube by the constant speed pump, and the fluid viscosity and friction coefficient under different conditions were measured, post which the acid solution enters the core displacement instrument to realize the acid filtration loss of the carbonate rock reservoir.

2.3 Preparation of nano-silica gelling agent CTG-1

12.7 g of nano-silica with a particle size of 15–30 nm and 60 mL of ethanol were taken in a two-necked flask, and it was placed in a constant temperature heating furnace at 78°C for continuous heating. 20 mL of *N*-allyl-*p*-toluenesulfonamide, 25 mL of propylene amide, and 30 mL of 2-acrylamide-2-methylpropanesulfonic acid were poured into a two-necked flask, and 50 µg octylphenol polyoxymethylene ether was added, and stirred at 90°C for 3 h. Then, it was extracted with toluene after cooling, the extracts were dried at 105°C. During the drying process, a viscous white solid can be obtained that it is the target substrate, the nano-silica gelling agent. The principle and process for synthesizing the agent are shown in

Figure 2a. The molecular weight of CTG-1 is 5,902, and the number of amide groups in the molecule (39) can be calculated according to the following formula.

$$\text{Number of amide groups}(n) = 3 \times \frac{\text{Compound total molecular weight}(M_t)}{\text{Basic unit molecular weight}(M_b)}, \quad (1)$$

where n is the number of basic units of a compound, M_t is the total molecular weight of the compound, and M_b is considered as the molecular weight of the basic unit of the compound.

2.4 Preparation and performance evaluation of acid solution

9 g of the prepared gelling agent CTG-1 was taken and put in a container, then the deionized water was added to the device as shown in Figure 1 and certain pressure was exerted. Then, a constant pressure pump was used to mix the nano-silica gelling agent with the gelling agent. Pressured deionized water was mixed evenly, and then the corrosion inhibitor and clay stabilizer were added, the mixture was fully stirred, and the acid system of carbonate rock reservoir was prepared.

After adding the acid solution system into the performance evaluation device of reservoir acid solution as shown in Figure 1, the evaluation of the apparent viscosity and friction reducing performance of the reservoir acid solution was first carried out, the equations (2) and (3) were used to calculate apparent viscosity and friction-reducing properties of acid solutions [11,14].

$$\eta = \frac{\tau_w}{\dot{\gamma}_w} = \frac{D\Delta p/(4L)}{8v/D}, \quad (2)$$

$$\varepsilon = \frac{\Delta p}{p_{\text{initial}}}. \quad (3)$$

In equation (2), η is the viscosity of the liquid to be measured, mPa s; τ_w is the shear stress, Pa; $\dot{\gamma}_w$ is the shear rate, s⁻¹; D is the diameter of the capillary, m; L is the length of the capillary, m; v is the volume flow of the liquid to be measured, m s⁻¹; and Δp is the pressure difference at both ends of the capillary, Pa. In equation (3), p_{initial} is the pressure at the inlet of the capillary, Pa; ε is the friction-reducing rate, %.

As shown in equation (2), when evaluating the apparent viscosity of the acid fluid in the reservoir, the friction-reducing rate of carbonate rock reservoirs can also be studied based on equations (2) and (3) at the same time. After the reservoir acid flows out of the capillary, it can continue to enter the reservoir core in the core displacer at a certain pressure until there are no longer any changes in the flow velocity at the core outlet. The exertion of pressure was stopped; the fluid loss capacity of the acid was calculated by using the filtration coefficient of equation (4) [15–17].

$$C = 0.005 \frac{m}{A}. \quad (4)$$

In equation (4), C is the filtration coefficient of the acid solution, m min^{1/2}; m is the slope of the filtration curve of filtration volume V and $t^{1/2}$, m³ min^{1/2}; A is the area of transversal surface of shale core, m².

3 Results and analysis

3.1 Chemical structure characterization of nano-silica gelling agent CTG-1

Microscopic SEM and ¹H-NMR was mainly used for the chemical characterization of nano-silica gelling agent CTG-1 in this research. As shown in Figure 2 of SEM, each synthesized nano-silica gelling agent is microscopically composed of particles with a diameter of 25 nm. There were a few protrusions on the surface of the particle, which are different side chains as shown in Figure 2. In this study, the chemical structure of the product is characterized by ¹H-NMR. ¹H-NMR (400 MHz, CDCl₃) δ : 0.94 (m, 1H), 0.99 (m, 1H), 1.18, 1.25, 1.48 (m, 14H), 2.27 (q, 32H), 2.58, 2.83 (s, 24H), 3.09 (s, 18H), 4.20 (m, 24H), 7.43 (s, 8H), 7.55 (s, 8H), 7.73 (s, 8H), and 7.70 (s, 8H). All the hydrogen groups of the silica gelling agent in Figure 2 were exhibited in the ¹H-NMR spectrum as shown in Figure 3, indicating that the nano-silica gelling agent of this study has been successfully synthesized.

3.2 Influence of gelling agent content on the properties of acid solution

To compare the excellent performance of nano-silica gelling agent CTG-1 on acid solution, this study took the commercially available gelling agent as a control, the

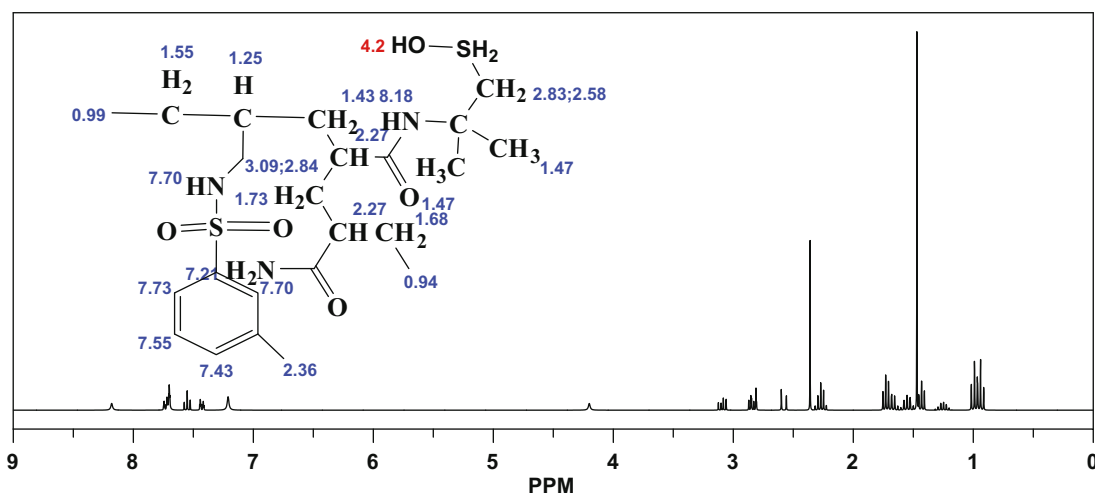


Figure 3: ¹H-NMR spectrum of nano-silica gelling agent.

influence of gelling agent contents on apparent viscosity, friction-reducing rate, and filtration coefficient of acid solution was studied under carbonate rock reservoir conditions at 180°C, 20 MPa, and 170 s⁻¹. As shown in Figure 4, the gradual addition of the gelling agent content will gradually increase the apparent viscosity of the reservoir acid and the friction-reducing rate of the reservoir, proportional relationship. When the nano-gelling agent was not added, the acid viscosity and the friction-reducing rate of the reservoir were 8 mPa s and 30%, respectively. When the nano-gelling agent was less than 0.4%, the viscosity and friction-reducing rate of acid fluid did not change significantly with the content of the agent, but the two increased significantly after the addition of more than 0.4% nano-gelling agent. At the content of 0.6%, the viscosity and friction-reducing rate of acid fluid could reach 25 mPa s and 71%, respectively.

A minor increase in apparent viscosity and friction-reducing rate, with values of only +4 mPa s and 10%, was shown when the content of nano-gelling agent increased from 0 to 0.4%. However, when the content of nano-gelling agent increased from 0.4 to 0.6%, the increase in apparent viscosity and friction-reducing rate of the acid solution jumped greatly, becoming 25 mPa s and 71%, with increments of 13 mPa s and 31%, respectively. However, the increase in apparent viscosity and friction-reducing rate of the commercially available gelling agent was only +2 mPa s and 5% when it increased from 0 to 0.4%. When it increased from 0.4 to 0.6%, the viscosity value and friction-reducing rate were only 14 mPa s and 42%, which are much lower than that of nano-silica gelling agent under the same conditions.

Table 1: Effect of gelling agent content on acid fluid loss coefficient of carbonate rock reservoirs

Gelling agent content (%)		0	0.20	0.40	0.60	0.80
Nano gelling agent CTG-1	Filter loss coefficient/	4.0	4.1	4.3	4.5	4.8
Commercially available gelling agents	(10 ⁻² m ³ min ^{1/2})	5.9	6.2	6.6	7.2	7.9

In addition, as shown in Table 1, the filtration coefficient of the acid solution with the same content of nano-silica gelling agent was significantly lower than that of the commercially available gelling agent. At the content of 0.6%, the filtration coefficients of the two were $4.5 \times 10^{-2} \text{ m}^3 \text{ min}^{1/2}$ and $7.2 \times 10^{-2} \text{ m}^3 \text{ min}^{1/2}$, respectively. Under the same conditions, the nano-silica gelling agent exhibited better performance than the commercially available gelling agent, showing more excellent properties in reducing the filtration loss of acid fluid in carbonate rock reservoirs.

The differences in the apparent viscosity, friction-reducing rate, and filtration capacity of the acid solution caused by the type and content of the gelling agent can be considered to be caused by the differences in the number and distribution of the amide groups of the gelling agent [18–21]. Figure 5 is a schematic diagram showing the molecular structures of the commercially available gelling agent and the nano-gelling agent CTG-1. First, the nano-silica gelling agent contains multiple amide groups and

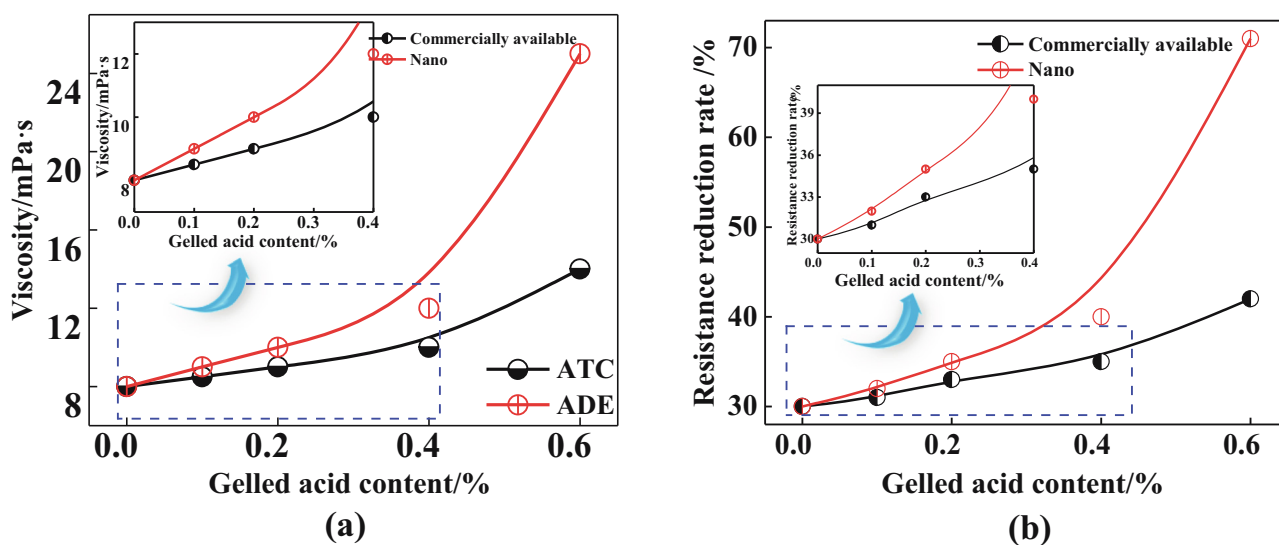


Figure 4: Influence of gelling agent addition on acid viscosity, friction-reducing rate, and filtration coefficient. (a) Effect of chemical content on fluid viscosity; (b) effect of chemical content on resistance reduction rate.

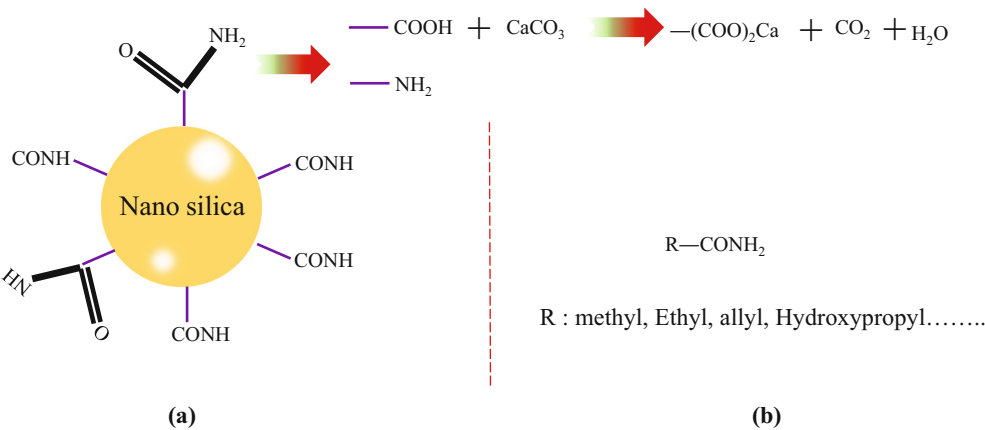


Figure 5: Comparison of molecular structures and functional differences of two acid gelling agents. (a) Structure of nano silica gelling agent and reaction mechanism; (b) structure of commercially available gelling agents.

sulfonic acid groups. The amide groups can be hydrolyzed with H₂O molecules into carboxylic acid and sulfonic acid, which can easily interact with sodium carbonate in carbonate rock reservoirs, achieving better acidification of the reservoir. The change in the liquid acidity pH value with the reaction time of the two systems in Table 2 can reveal this reason. At the beginning, a large number of amide groups were arranged on the nano-silica surface of the gelling acid CTG-1, which could hydrolyze more carboxylic acids. And with the prolongation of reaction time, the more the carboxylic acid hydrolyzed, the more significant is the decrease in the pH value of the system. These carboxylic acids can achieve acid–base reactions with more calcium carbonate in the subterranean formation to achieve reservoir acidification and plugging removal.

However, after 0.4% commercial gelling acid was added to the system, the pH value only dropped from 6.4 at the beginning to 5.5 after 20 min, which was significantly lower than that of the CTG-1 under the same acidification time. The commercially available gelling agent contains only one amido group, which is relatively not active to form carboxylic acid and sulfonic acid with calcium carbonate and other substances, thus weakening the ability to acidify the reservoir [22,23]. In addition,

more amide groups in the nano-silica gelling agent can form a grid-like structure with calcium carbonate, thereby increasing the viscosity and friction-reducing rate of the acid solution in the capillary fractures of the reservoir. Second, most of the amido sulfonic acid groups in the nano-silica gelling agent molecules are distributed around the nano-silica molecules and are distributed in a circular shape, which can achieve calcium carbonate from more corners and larger areas to reservoir rocks, ultimately enhancing the acidification effect and friction reducing performance.

3.3 Influence of reservoir pressure on the properties of acid solution

Carbonate rock reservoirs are differentially pressured with the burial depth of reservoirs. Figure 6 shows the tendency of variations in the acid fluid rheology, fluid loss reduction ability, and friction-reducing rate under different reservoir pressure conditions. In Figure 6, the apparent viscosity of the reservoir acid added with the two gelling agents, respectively, increased slightly with the increase in reservoir pressure [24]. When the reservoir pressure under 0.6% nano-gelling acid increased from 10 to 30 MPa, the apparent viscosity of the reservoir acid increased from 18 to 32 mPa s. The friction-reducing rate also increased from 66 to 79%. Under the pressure variation conditions of the same reservoir, the apparent viscosity of the acid solution containing the commercially available gelling agent only increased from 12 to 19 mPa s, and the friction-reducing rate only increased from 40 to 46%. Under the same condition of pressure variation in the reservoir, the nano-gelling agent exhibits better performance of viscosity increase

Table 2: Effect of gelling agent content on acid fluid loss coefficient of carbonate rock reservoirs

Mixing time (min)		0	5	10	15	20
Nano gelling agent	pH of reservoir acid	6.4	6.1	5.8	5.4	5
CTG-1/0.4%						
Commercially available gelling agents/0.4%		6.4	6.3	6.1	5.8	5.5

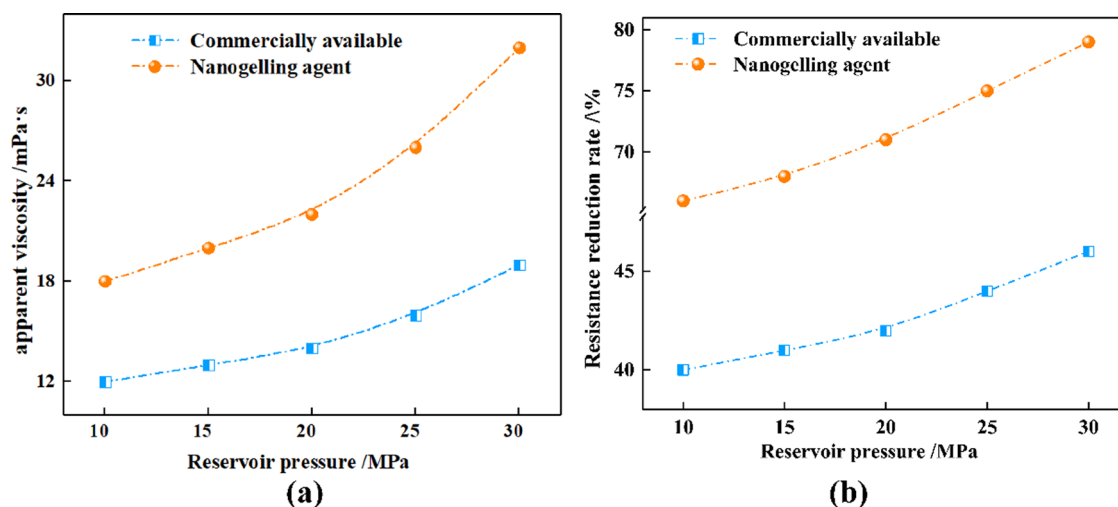


Figure 6: Variation in apparent viscosity and drag reduction rate of acid solution with reservoir pressure for different gelling agents: (a) Effect of reservoir pressure on fluid viscosity; (b) effect of reservoir pressure on resistance reduction rate.

and friction-reducing ability than the commercial gelling agent. In addition, with the increase in pressure in carbonate rock reservoir, the apparent viscosity and friction-reducing rate of acid fluid increased significantly.

First, compared with the simpler single amide group structure of commercial gelling agents, there are a large number of amide groups in the nano-gelling agent molecules, and the amide groups are distributed around the surface of nano-silica which act as side chains. As the pressure of the reservoir gradually increases, the distance between the amide group and the water molecule is squeezed and becomes smaller, and the amide group is more likely to be hydrolyzed to form amines and carboxylic acids [25–28]. The carboxylic acid formed can react with a large number of reservoir rocks, and the side chains of the same nanoparticle or different nanoparticles can also be entangled with each other, thereby increasing the apparent viscosity and friction-reducing rate of the reservoir acid. In addition, as the reservoir pressure continues to increase, the distance between the gelling agent and water molecules decreases, and the interaction becomes more intense, resulting in a rapid increase in the friction-reducing rate and viscosity. The influence of viscosity and friction-reducing rate on oil-field working fluid is consistent.

In addition, the filtration coefficient of the reservoir acid added with the continuous increase in the reservoir pressure, and the filtration reduction ability continued to improve. The filtration coefficients of the two acid solutions containing nano-gelling agent and commercial gelling agent, respectively, decreased from 4.7×10^{-2} and $7.5 \times 10^{-2} \text{ m}^3 \text{ min}^{1/2}$ at 10 MPa to 2.3×10^{-2} and $5.9 \times 10^{-2} \text{ m}^3 \text{ min}^{1/2}$

at 30 MPa. The reductions of the two were 2.4×10^{-2} and $1.6 \times 10^{-2} \text{ m}^3 \text{ min}^{1/2}$. The ability of the nano-gelling agent to reduce the filtration loss of the acid solution was evidently improved with the increase in pressure in the reservoir, which is mainly related to the reaction rate of the acid solution and the number of amide groups.

The above speculation can be verified by the change trend of pH of acid system with reservoir pressure. It can be shown from Table 3 that the increase in reservoir pressure reduces the distance between the amide group and the water molecule, which leads to an enhanced ability of the amide group to be hydrolyzed to carboxylic acid. The increase in the content and number of carboxylic acids in the solution also reduces the pH of the acid solution. The pH decrease of the solution with increase in the reservoir pressure increases the reactivity of the carboxylic acid with the rock, which in turn triggers the results in Figure 6. Furthermore, since the nanoparticle surface of CGT-1 occupies more amide groups, a large amount of hydrolysis of amide groups and a rapid increase in pH can be achieved from various positions close to

Table 3: Effect of reservoir pressure on acid fluid loss coefficient of carbonate rock reservoirs

Reservoir pressure (MPa)		0	4	8	12	16
Nano gelling agent	pH of	6.4	6.3	6.0	5.7	5.3
	reservoir					
CTG-1/0.4%	acid	6.4	6.3	6.2	6.0	5.7
Commercially available gelling agents/0.4%						

water molecules. However, commercially available PAM does not have nanostructures and cannot rapidly decrease the pH of the solution under increased pressure.

Figure 7 is a schematic diagram showing the difference of acidification position and effect of acid solution in carbonate rock salt reservoir under different pressure conditions. It can be seen from the results in Figure 7 that in the low-pressure reservoir, the low-pressure acid fluid flowed slowly in the porosity system and fracture, thus making longer the retention time in the fractures or pores. The reaction with calcium carbonate leads to the formation of vugs in the low-pressure reservoirs. Acidification and fracturing cannot be achieved at the fracture cusp, which also leads to a significant increase in filtration loss under low pressure. However, in the high-pressure reservoir shown in Figure 7, due to the high pressure of acid solution in the fractures of carbonate rock reservoirs, the cusp of fracture was rapidly pressured. The minimum fracturing initiation pressure of the reservoir can be quickly reached, thereby quickly achieving the initiation and expansion of fractures. In certain parts of the reservoir, the acid solution had a short retention time, a vertical acidification phenomenon occurs when the low pressure cannot be formed. The amide group in the agent can be more decomposed into carboxylic acid, achieving excellent acidification and reduction of filtration loss.

3.4 Influence of reservoir temperature on acid viscosity, friction-reducing rate, and filtration coefficient

The temperature resistance of acid solution used in carbonate rock reservoirs has also become a key indicator for

evaluating its excellent performance. At the same time, the reservoir temperature also significantly changes the viscosity, friction-reducing rate, and filtration coefficient of the acid solution. Figure 8 shows the changes in viscosity, friction-reducing rate, and fluid loss coefficient of the acid solution when the reservoir temperature was increased from 160 to 200°C. The viscosity of the acid solution containing gelling agent gradually decreased with the increase in reservoir temperature. When the reservoir temperature was 160°C, the viscosity of acid solution containing the two gelling agents was 28 and 18 mPa s, respectively. However, the viscosity of the acid solution, respectively, changed to 23 and 10 mPa s, when the temperature raised to 200°C. The viscosity of the acid solution containing the commercially available gelling acid was reduced by 8 mPa s, while that of the nano-gelling acid was only 5 mPa s. From equations (1) and (2), both the friction-reducing rate and viscosity of the acid solution were related to the pressure difference between the two sections of the capillary. The friction-reducing rate is positively correlated with the acid viscosity.

In addition, the filtration coefficient of acid solution increased with the increase in the reservoir temperature. Under the same conditions, the acid filtration coefficient of commercially available gelling acid increased from 6.8×10^{-2} to $7.8 \times 10^{-2} \text{ m}^3 \text{ min}^{1/2}$ when the reservoir temperature increased from 160 to 200°C, with an increment of $1 \times 10^{-2} \text{ m}^3 \text{ min}^{1/2}$. At this time, the filtration coefficient of acid solution with nano-gelling agent increased from 4.4×10^{-2} to $4.8 \times 10^{-2} \text{ m}^3 \text{ min}^{1/2}$, and the nano-gelling agent showed better temperature resistance than the commercial gelling agent.

The microscopic mechanism that the fluid loss coefficient of acid solution increases with reservoir temperature can be explained by the Arrhenius equation [16,29]:

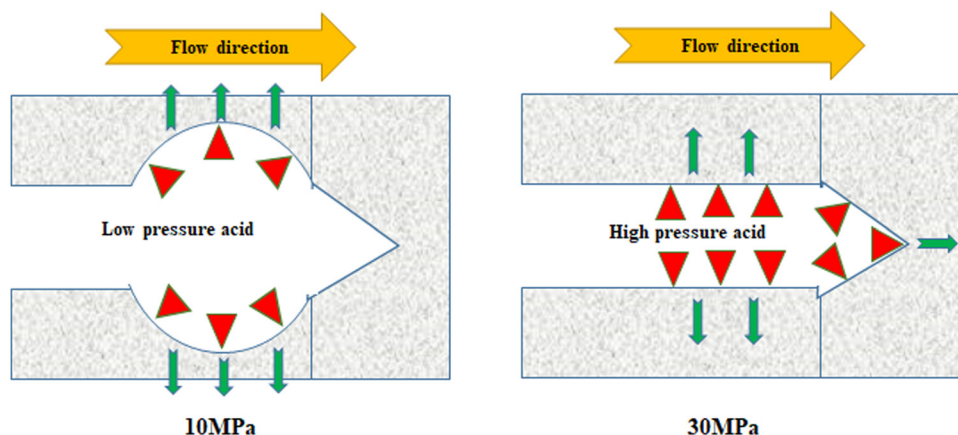


Figure 7: Acidification position and effect of acid in carbonate rock reservoirs under different pressures: (a) 10 MPa of reservoir pressure; (b) 30 MPa of reservoir pressure.

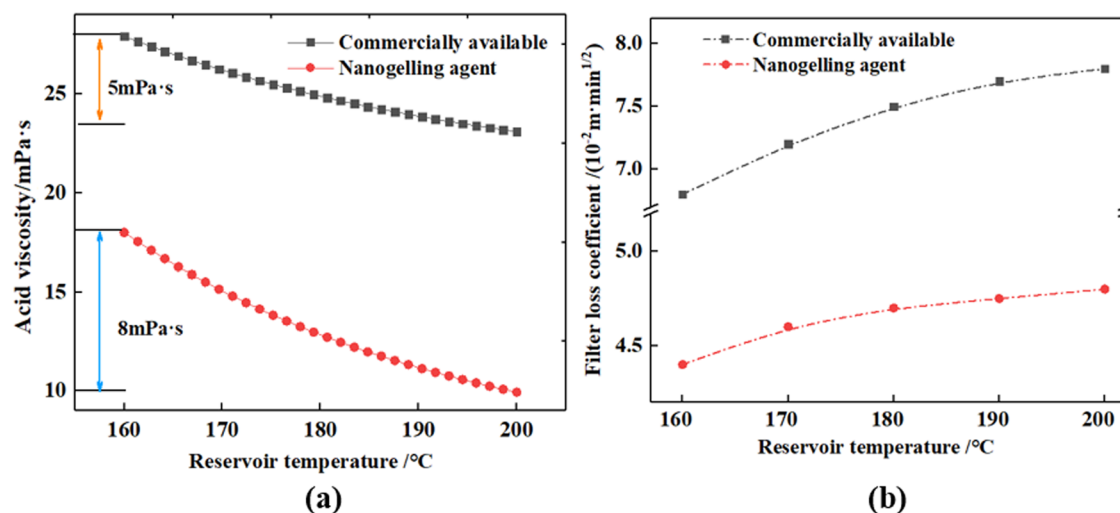


Figure 8: Influence of reservoir temperature on viscosity and friction-reducing rate of different acid solutions: (a) effect of reservoir temperature on fluid viscosity; (b) effect of reservoir temperature on resistance reduction rate.

$$\eta = A_v \exp(E_f/R_g T). \quad (5)$$

where η is the fluid viscosity of the reservoir acid, mPa s; E_f is the activation energy, J mol^{-1} , which is independent of temperature; A_v is the prefactor, dimensionless; and R_g is the molar gas constant, $\text{J mol}^{-1} \text{K}^{-1}$. None of E_f , A_v , and R_g changes with reservoir temperature. Figure 9 showed the action mechanism of nano-silica gelling agent at different reservoir temperatures. Molecules in the acid solution move more violently due to the high temperature of

the reservoir, and the amide groups in the gelling agent are hydrolyzed rapidly as a result. Nano-gelling agents containing multiple amide groups can react with calcium carbonate more quickly at the cusp of reservoir fractures, thereby achieving more beneficial acidification, avoiding the expansion of filtration failure effects [30–32]. As the temperature increases, new amide-containing side chain hydrolysis is involved in the acidification of carbonate rock reservoirs. The commercially available gelling agent

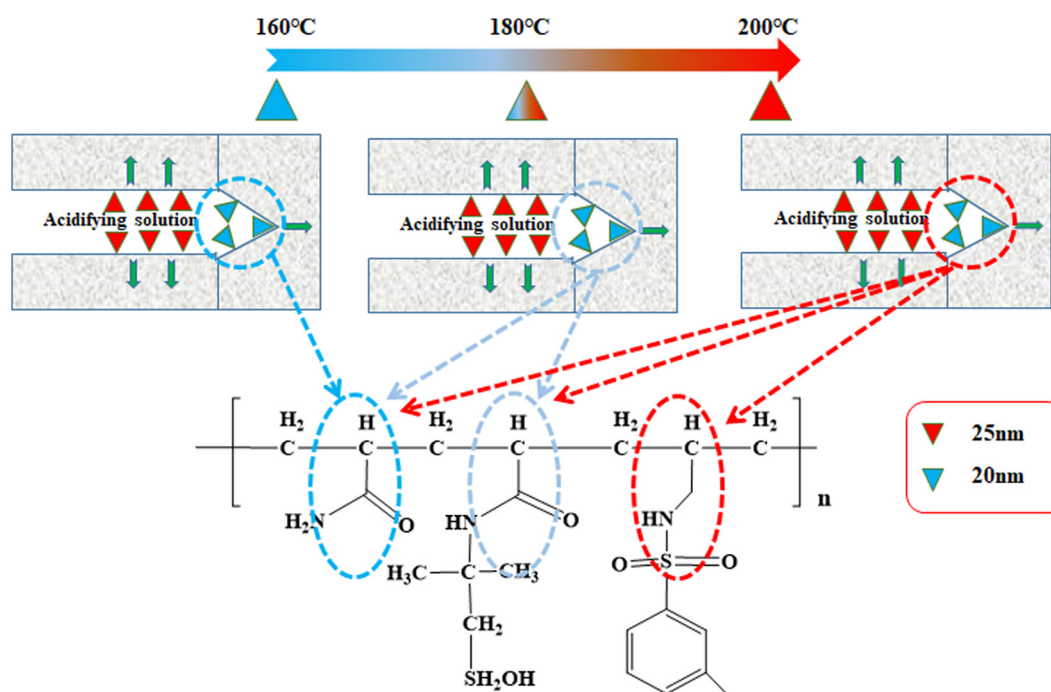


Figure 9: Action mechanism of nano-silica gelling agent at different reservoir temperatures (with dimensions).

Table 4: Effect of reservoir temperature on acid fluid loss coefficient of carbonate rock reservoirs

Reservoir temperature (°C)		160	170	180	190	200
Nano gelling agent	pH of reservoir acid	6.6	6.5	6.3	6	5.5
CTG-1/0.4%						
Commercially available gelling agents/0.4%		6.7	6.6	6.5	6.3	6

with only one amide group cannot be rapidly acidified at the fracture cusp, therefore the acid cannot be rapidly acidified in carbonate rock reservoir fractures, and the fluid loss increases.

This can be verified by the pH values of two different gelling acid liquids in Table 4 as a function of reservoir temperature to verify the above inference. The increase in reservoir temperature accelerates the molecular activation ability, which facilitates the rapid hydrolysis of the amide group to carboxylic acid in contact with water. However, the special nanostructure of CTG-1 can increase the hydrolysis ability of the amide group, causing the pH value of the liquid to be significantly lower than that of the commercially available gelling acid.

3.5 Influence of shear rate on acid viscosity, friction-reducing rate and filtration coefficient

The acid fluid shear rate also affects its rheology and filtration capacity during the acidizing fracturing process

of carbonate storage tanks [15,33,34]. As shown in Figure 10, the viscosity of the acid solution at low shear rate is significantly higher than that of the fluid at high shear rate, and the viscosity of acid solution decreases from 27 to 25 mPa s when the shear rate increases from 160 to 170 s⁻¹. The friction-reducing rate also decreases from 75 to 71% at 170 s⁻¹. At this time, the acid solution containing the commercially available gelling agent reduces the friction-reducing rate from 54 to 42%, and the viscosity decreases from 21 mPa s down to 14 mPa s. Nano-silica gelling agents exhibit better shear resistance than commercial gelling agents.

In addition, the filtration coefficient of the acid solution containing nano-silica gelling agent also increased from $4.4 \times 10^{-2} \text{ m}^3 \text{ min}^{1/2}$ at 160 s⁻¹ to $4.5 \times 10^{-2} \text{ m}^3 \text{ min}^{1/2}$ at 170 s⁻¹ which is much lower than the increase caused by commercially available gelling agent. There are many amide functional groups on the surface of the nano-silica gelling agent, which can be hydrolyzed from different angles and interact with the calcium carbonate in the carbonate rock reservoir, resulting in the formation of many interaction bonds to fix each other on the rock surface. Many interaction bonds are entangled with each other, which also realizes the excellent shear resistance of the acid solution containing nano-silica gelling agent. However, the commercially available gelling agent itself contains only one amide group, which can only be hydrolyzed alone and interact with the calcium carbonate in the reservoir. It has a weak grip on the surface of the reservoir and cannot be entangled with each other, therefore it has a small shear resistance [35–38].

The above inferences can be obtained from the pH changes of different solutions at shear rates in Table 5. An increase in the shear rate can significantly reduce the pH

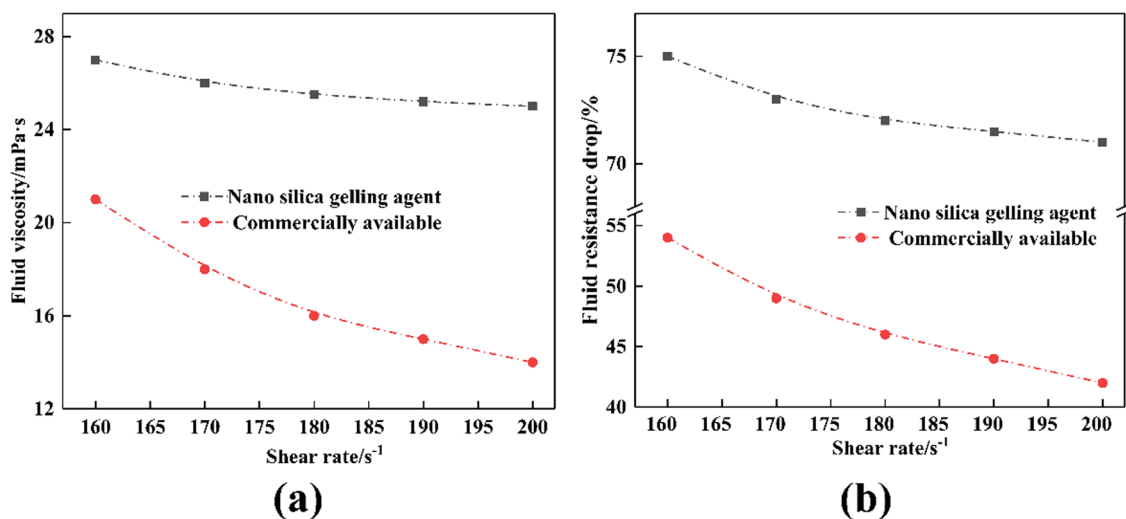
**Figure 10:** Effect of acid shear rate on apparent viscosity and friction-reducing rate: (a) effect of shear rate on fluid viscosity; (b) effect of shear rate on resistance reduction rate.

Table 5: Effect of shear rate on acid fluid loss coefficient of carbonate rock reservoirs

shear rate (s^{-1})		160	170	180	190	200
Nano gelling agent CTG-1/0.4%	pH of reservoir acid	6.7	6.6	6.4	6.1	5.7
Commercially available gelling agents/0.4%		6.8	6.7	6.6	6.4	6.2

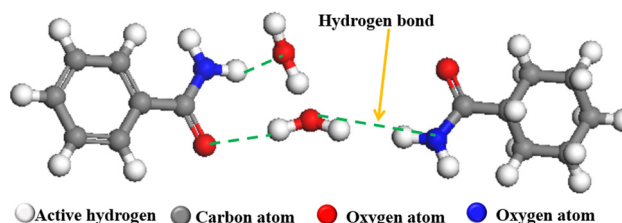
of the solution, which is mainly attributed to the significantly increased chance of the amide groups and water contacting each other due to shearing. CTG-1 can be hydrolyzed to carboxylic acid to a greater extent due to the large number of amide groups on the surface of nanostructures, which increases the probability of contact and reaction between carboxylic acid and rock calcium carbonate. However, a single molecule of commercially available chemicals cannot hydrolyze a large number of carboxylic acids at the same time, and the results are as shown in Figure 10 and Table 5.

3.6 Influence of nano-silica on acid viscosity, friction-reducing rate, and filtration coefficient

Table 6 shows the effect of adding different content of nano-silica on the viscosity friction-reducing rate and filtration coefficient of gelling acid. As shown in Table 6, when adding 4 g of nano-silica to prepare nano-silica gelling agent, the viscosity and filtration coefficient of acid solution are only 10 mPa s and $5.3 \times 10^{-2} m^3 min^{1/2}$, but after adding 12.7 g, the viscosity and filtration coefficient reached 27 mPa s and $4.5 \times 10^{-2} m^3 min^{1/2}$, respectively. The increase in nano-silica content helps to improve the viscosity and filtration capacity of the acid solution, which is mainly due to the adsorption of amide groups on the surface of nano-silica.

Table 6: Effect of nano-silica content on acid fluid loss coefficient and viscosity of carbonate rock reservoirs

Gelling agent content (g)		0	4	8	12	16
Nano gelling agent CTG-1	Filter loss coefficient/ $(10^{-2} m^3 min^{1/2})$	5.9	5.3	4.9	4.5	4.3
Commercially available gelling agents		5.9	5.8	5.4	4.9	4.8
Nano gelling agent CTG-1	Fluid viscosity/(mPa s)	8	10	16	27	31
Commercially available gelling agents		8	10	12	15	16

**Figure 11:** Intermolecular hydrogen bonding between guar gum and water molecules.

3.7 Filtration reduction mechanism

The microgrid theory is considered to be an important mechanism for improving the filtration performance of acidifying fluids in oil and gas reservoirs [39,40]. Polymer, water molecules, and rocks can form a large number of hydrogen bonds to build microscopic grids to improve the viscosity and filtration performance of acidifying fluids [41,42]. Intermolecular hydrogen bonds can be obtained by molecular dynamics simulations, as shown in Figure 11. In addition, equations (6) and (7) shows a calculation method of intermolecular hydrogen bond energy [43].

$$E = E_{AB}(\vec{R}_A + \vec{R}_B) - E_A(\vec{R}_A) - E_B(\vec{R}_B), \quad (6)$$

$$E_{AB} = a \frac{IP_A + IP_B}{2} \sigma + m, \quad (7)$$

where E is the intrinsic interaction energy, kJ; E_{AB} is the hydrogen bond energy, kJ; A and B are the atoms at both ends of a hydrogen bond; R_A and R_B are the coordinates of the atoms of monomers; E_A and E_B are the atomic energy, kJ; a and m are considered as constants, the latter shall be close to zero; σ is two-center shared electron number; and IP_X is the ionization potential of atom X.

When the content of nano-gelling acid or system pressure increases, a large number of intermolecular hydrogen bonds can be formed in unit space, and the grid density at this time increases significantly, which can cause the following two phenomena: (1) The favorable

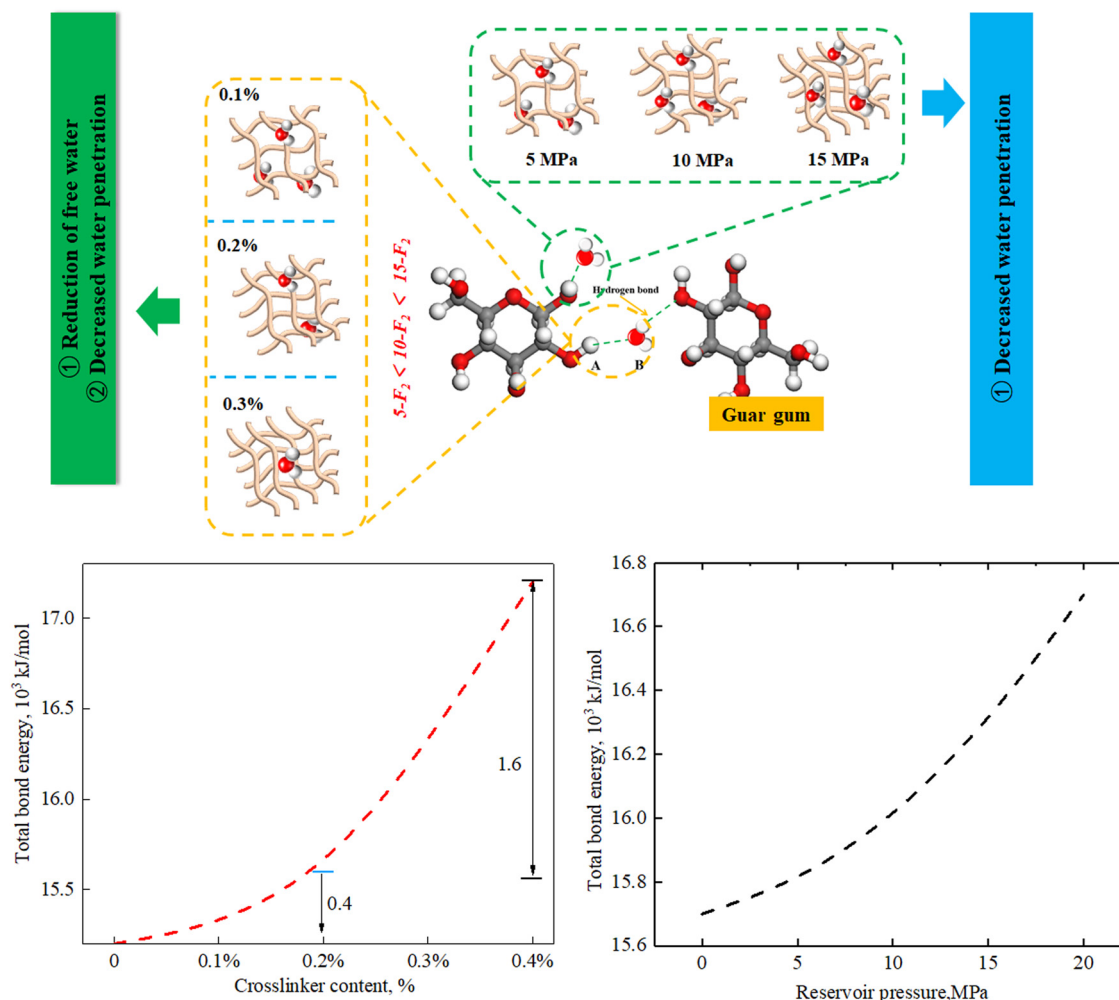


Figure 12: The filtration mechanism of guar gum fracturing fluid changes due to changes in content and pressure.

water molecules in the system decrease with the confinement of hydrogen bonds in the system; (2) Free water molecules also increase the mesh density and make it more difficult to permeate, reducing the fluid loss volume (Figure 12). The magnitude of the hydrogen bonds formed between the molecules in the guar gum fracturing fluid system has become an important microscopic factor affecting the filtration of the fracturing fluid, which is determined.

4 Conclusion

1) A nano-silica and amide-based compound are used as the base to prepare a new type of temperature- and shear-resistant nano-silica gelling agent CTG-1. The microscopic morphology and main functional group composition of the nano-gelling agent are characterized

by SEM and $^1\text{H-NMR}$ experimental methods. In addition, nano-silica gelling agent exhibits excellent fluid loss resistance to working fluids.

2) The integrated experimental device for acid rheology and filtration performance evaluation is used to investigate the effects of different gelling agent contents, reservoir temperature, reservoir pressure, and shear rate on acid viscosity, friction-reducing rate, and filtration loss. The influence law of the coefficient is compared, and the effect of the nano-gelling agent CTG-1 on the filtration performance was higher than that of the commercially available gelling agent under the same condition. CTG-1 showed an excellent temperature resistance and shear resistance. Synthesized nano-silica gelling agent exhibited significant anti-filtration efficiency for working fluids, and synthetic nano-silica gelling agent is not easy to penetrate into the fracture surface in reservoir fractures to achieve fracture compression.

- 3) The excellent rheology and friction-reducing rate of acid solution of nano-silica gelling agent are mainly based on the interaction of multiple amide groups and sulfonic acid groups in the molecule with water molecules and rocks. A large number of intermolecular hydrogen bonds are formed between the above groups to build a large number of microscopic grids, and a large number of water molecules are locked to avoid leakage through the crack surface.

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References

- [1] Xia L, Zhou M, Zhang L. Performance evaluation of amphoteric/anionic surfactants in cleaning fracturing fluids. *Oilfi Chem.* 2015;32(03):341–4.
- [2] Alzobaidi S, Lee J, Jiries S, Da C, Harris J, Keene K, et al. Carbon dioxide-in-oil emulsions stabilized with silicone-alkyl surfactants for waterless hydraulic fracturing. *J Colloid Inter Sci.* 2018;526(1):253–67.
- [3] Wang L, Yao B, Cha M. Waterless fracturing technologies for unconventional reservoirs-opportunities for liquid nitrogen. *J Nat Gas Sci Eng.* 2016;35(1):160–74.
- [4] Zhou M, Zhang J, Zuo Z. Preparation and property evaluation of a temperature-resistant Zr-crosslinked fracturing fluid. *J Ind Eng Chem.* 2021;96(1):121–9.
- [5] Li Q, Cheng Y, Ansari U, Han Y, Liu X, Yan C. Experimental investigation on hydrate dissociation in near-wellbore region caused by invasion of drilling fluid: Ultrasonic measurement and analysis. *Env Sci Poll R.* 2022;24:10153.
- [6] Aljawad MS, Aljulaih H, Mahmoud M. Integration of field, laboratory, and modeling aspects of acid fracturing: A comprehensive review. *J Pet Sci Eng.* 2019;181:106158.
- [7] Hou B, Zhang R, Chen M. Investigation on acid fracturing treatment in limestone formation based on true tri-axial experiment. *Fuel.* 2019;235:473–84.
- [8] Zhang R, Hou B, Zhou B. Effect of acid fracturing on carbonate formation in southwest China based on experimental investigations. *J Nat Gas Sci Eng.* 2020;73:103057.
- [9] Gou B, Guan C, Li X. Acid-etching fracture morphology and conductivity for alternate stages of self-generating acid and gelled acid during acid-fracturing. *J Pet Sci Eng.* 2020;200:108358.
- [10] Liu YF, Chen LL, Tang YF, Zhang XD, Qiu ZS. Synthesis and characterization of nano-SiO₂@octadecylbisimidazoline quaternary ammonium salt used as acidizing corrosion inhibitor. *Rev Adv Mater Sci.* 2022;61(1):186–94.
- [11] Li Q, Wang F, Forson K, Zhang J, Zhang C, Chen J, et al. Affecting analysis of the rheological characteristic and reservoir damage of CO₂ fracturing fluid in low permeability shale reservoir. *Env Sci Poll R.* 2022;24:9335.
- [12] Abdallah A, Antary T. Key discriminant factors affecting hotel owners and managers tendencies towards implementation of water conservation measures, and rainwater harvesting systems installation at hotels in Jordan. *Fresen Env Bull.* 2021;30(1):779–89.
- [13] Esmaeilirad N, Terry C, Kennedy H. Recycling fracturing flow-back water for use in hydraulic fracturing: Influence of organic matter on stability of carboxyl-methyl-cellulose-based fracturing fluids. *SPE J.* 2016;21(4):1358–69.
- [14] Fu LP, Ma QL, Liao KL, An JN, Bai JM, He YF. Application of Pickering emulsion in oil drilling and production. *Nanotech Rev.* 2022;11:26–39.
- [15] Li Q, Wang Y, Wang F, Xu N, Zhang C, Zhang J, et al. Factor analysis and mechanism disclosure of supercritical CO₂ filtration behavior in tight shale reservoirs. *Env Sci Poll R.* 2022;29(12):17682–94.
- [16] Zhao MW, Li Y, Xu ZL, Wang K, Gao MW, Lv WJ, et al. Dynamic cross-linking mechanism of acid gel fracturing fluid. *Colloid Surf A.* 2020;607:125471.
- [17] Cui GD, Ning FL, Dou B, Li T, Zhou QC. Particle migration and formation damage during geothermal exploitation from weakly consolidated sandstone reservoirs *via* water and CO₂ recycling. *Energy.* 2022;240:122507.
- [18] Zhao ZF, Qi TQ, Zhou W, Hui D, Xiao C, Qi JY, et al. A review on the properties, reinforcing effects, and commercialization of nanomaterials for cement-based materials. *Nanotech Rev.* 2020;9:303–22.
- [19] Li N, Dai J, Liu P. Experimental study on influencing factors of acid-fracturing effect for carbonate reservoirs. *Petroleum.* 2015;1(2):146–53.
- [20] Hong JQ, Zhang SF, Fang H, Xu XQ, Xie HL, Wang YT. Structural performance of textile reinforced concrete sandwich panels under axial and transverse load. *Rev Adv Mater Sci.* 2021;60:64–79.
- [21] Zhong HY, Kong XZ, Chen S, Grady B, Qiu ZS. Preparation, characterization and filtration control properties of cross-linked starch nanospheres in water-based drilling fluids. *J Mole Liq.* 2021;325:115221.
- [22] Zhong HY, Gao X, Zhang X, Qiu ZS, Zhao C, Zhang XB, et al. Improving the shale stability with nano-silica grafted with hyperbranched polyethyleneimine in water-based drilling fluid. *J Nat Gas Sci Eng.* 2020;83:103624.
- [23] Santhosh G, Sumaiya T. Sulphuric acid supported silica gel (H₂SO₄-SiO₂) as an efficient catalyst for one-pot multicomponent synthesis of pyrano [2,3-c]pyrazolamines under ultrasonication. *Mater Today Pro.* 2021;45(3):3762–8.
- [24] Moon B, Kim K, Park K, Seok C. Fatigue life prediction of tire sidewall using modified Arrhenius equation. *Mech Mater.* 2020;147:103405.
- [25] Honarvar B, Rahimi A, Safari M, Khajehahmadi S, Karimi M. Smart water effects on a crude oil-brine-carbonate rock (CBR)

- system: Further suggestions on mechanisms and conditions. *J Mol Liq.* 2020;299:112173.
- [26] Zeng WL, Zhao YX, Zheng HB, Poon CS. Improvement in corrosion resistance of recycled aggregate concrete by nano silica suspension modification on recycled aggregates. *Cem Concr Compos.* 2020;106:103476.
- [27] Abdollahi R, Esfandiyari H, Nadri Pari M, Davarpanah A. Conventional diverting techniques and novel fibr-assisted self-diverting system in carbonate reservoir acidizing with successful case studies. *Pet Res.* 2021;6(3):247–56.
- [28] Huang X, Gu LJ, Li SS, Du YF, Liu YL. Absolute adsorption of light hydrocarbons on organic-rich shale: An efficient determination method. *Fuel.* 2022;308:121998.
- [29] Chanda S, Bajwa DS. A review of current physical techniques for dispersion of cellulose nanomaterials in polymer matrices. *Rev Adv Mater Sci.* 2021;60:325–41.
- [30] Emamverdian A, Ding YL, Mokhberdoran F, Ahmad ZS, Xie YF. Determination of heavy metal tolerance threshold in a bamboo species (*Arundinaria pygmaea*) as treated with silicon dioxide nanoparticles. *Glob Eco Cons.* 2020;24:e01306.
- [31] Wang J, Ma R, Gu P. Chitosan modified silicon dioxide composites for the capture of graphene oxide. *J Phys Chem Solids.* 2020;147:109629.
- [32] Goyal S, Joshi P, Singh R, Rohan C. Applications and role of Nano-Silica particles on altering the properties and their usage for oil well cementing. *Mater Today Pro.* 2021;46(20):10681–6.
- [33] Liu JW, Wang SB, He L, Hu P, Gao Y. Preparation and properties of nano-silica hybrid hydrophobic associated polyacrylamide for polymer flooding. *J Pet Sci Eng.* 2021;208(Part B):109434.
- [34] Gunday ST, Cevik E, Yusuf A, Bozkurt A. Synthesis, characterization and supercapacitor application of ionic liquid incorporated nanocomposites based on SPSU/Silicon dioxide. *J Phys Chem Solids.* 2020;137:109209.
- [35] Pagolu R, Singh R, Shanmugam R, Kondaveeti S, Patel S, Kalia C, et al. Site-directed lysine modification of xylanase for oriented immobilization onto silicon dioxide nanoparticles. *Bioresour Technol.* 2021;331:125063.
- [36] Carchini G, Hussein IA, Al-Marri MJ, Mahmoud M, Shawabkeh R, Aparicio S. Ab-Initio Molecular Dynamics investigation of gas adsorption on α -quartz (001) for CO₂ enhanced natural gas recovery. *J Pet Sci Eng.* 2021;205(30):108963.
- [37] Liu F, Zhang CX, Li XQ, Zhnag ZX, Wang XW, Dai XD, et al. Investigation of the inhibition mechanism of polymer/nano-silica composite as shale inhibitor in water-based drilling fluids. *Colloid Surf A.* 2022;636:128099.
- [38] Ren Q, Wu MH, Weng ZS, Wang L, Zheng WG, Hikima Y, et al. Lightweight and strong gelling agent-reinforced injection-molded polypropylene composite foams fabricated using low-pressure CO₂ as the foaming agent. *J CO₂ Util.* 2021;48(7):101530.
- [39] Rui Z, Jiang J, Lu J, Randy M. An integrated technical-economic environmental assessment of CO₂ enhanced oil recovery. *Appl Energ.* 2019;247:190–211.
- [40] Li Q, Wang F, Wang Y, Forson K, Cao L, Zhang C, et al. Experimental investigation on the high-pressure sand suspension and adsorption capacity of guar gum fracturing fluid in low-permeability shale reservoirs: Factors analysis and mechanism disclosure. *Env Sci Poll R.* 2022;29:53050–62.
- [41] Wang Y, Zhang C, Xu N, Lan J, Jiang B, Meng L. Synthesis and properties of organoboron functionalized nanocellulose for crosslinking low polymer fracturing fluid system. *RSC Adv.* 2021;11(22):13466–74.
- [42] He Y, Cheng S, Sun Z, Chai Z, Rui Z. Improving oil recovery through fracture injection and production of multiple fractured horizontal wells. *J Energy Resour-ASME.* 2020;142(5):053002.
- [43] Wendler K, Thar J, Zahn S, Kirchner B. Estimating the hydrogen bond energy. *J Phys Chem A.* 2010;114(35):9529–36.