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Investigation of the Effect of Temperature and Grain Size on the Kinetic of Hydrochloric Acid and Calcium Carbonate Reaction as a Simulation of Wellbore Acidizing

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ABSTRACT

In this study, the significance of temperature within the range of 25 to 70 degrees Celsius and the particle size of calcium carbonate at 237 µm, 348.5 µm, and 497.5 µm on the hydrochloric acid reaction rate with calcium carbonate stone was deliberated. The slow reaction rate helps a retarded action, and therefore, HCl penetrates deeper, and the zones farther from the wellbore will be affected by the acidizing. Therefore, the exploration of variables influencing the reaction rate holds considerable significance. The reaction rate is controlled by influential factors such as temperature and particle size, where the effect of these two factors is discussed in detail. According to the empirical findings, the reaction rate exhibits an upward trend as temperature rises and as the size of calcium carbonate particles decreases. It is worth mentioning that the highest and lowest reaction rates were observed at temperatures of 70 and 25 degrees Celsius, and with calcium carbonate particle sizes of 237 and 497.5 micrometers, respectively. Consequently, this research, considering the examined parameters and the obtained results, contributes to a better understanding and more efficient design of the acidizing process.

Introduction

In many fields, oil and gas production is below the desired level due to damage of the formation and reducing permeability in the vicinity of the wellbore. Well-stimulation methods are usually used to solve these issues and increase production. One of the effective and common methods for solving these issues is wells acidizing [1- 4]. The possibility of inorganic sediments along the well is very high. Depending on the wellbore condition and the composition of the reservoir water, different types of these sediments may occur that the most common sediments are calcium carbonate, iron carbonate, calcium sulfate, barium sulfate, strontium sulfate, and

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iron sulfide. Sedimentation of reaction products in the carbonate rocks acidizing cannot be a major problem because the acid reaction products with the formation are soluble in water. However, in the case of sandstone acidizing, the situation is different [5]. There are two types of acidizing to be performed on carbonate reservoirs, which are distinguished by pressure and injection rate. The operation in which the injection rate is lower than the fracturing pressure is called matrix acidizing. The first purpose of matrix acidizing is to improve the flow rate from the affected zone near the wellbore. This can be done by solving rocks near the wellbore [6]. The most common solution for acid fracturing and matrix acidizing in carbonate reservoirs is a 15wt% hydrochloric acid solution [7]. Temperature is one of the factors that effect on kinetic of acid reaction. Measuring well temperature is a requirement for designing the acidizing process. Changing the fluid flow regime due to the rheological properties of the fluid has a significant effect on the temperature distribution of the wellbore. However, deep wells with high bottom-hole temperatures can change fluid viscosity performance, affect the acid-rock reaction, and limit the stimulating effects of acidizing. Numerous studies have been conducted to predict the temperature of the wellbore and formation; however, a few researches have been done on the thermal properties of fluids and fluid flows and their effect on the dissolution of organic and inorganic materials during the injection process. Medeiros et al. investigated the heat transfer that occurred during matrix acidizing. They showed that the method's efficiency in eliminating damage to the formation is strongly dependent on the reaction temperature, and the kinetics of the chemical reactions between the injected acid and the minerals in the rock are very temperature sensitive. Therefore, the temperature is an important factor in the matrix acidizing that can accelerate or slow down chemical reactions [8]. Lyons et al. proposed a new thermal acid fracturing model that uses the Boltzmann method to simulate reactions transfer. This method incorporates precise hydrodynamics and solid/liquid reaction kinetics. Temperature changes are performed using the finite-difference technique [9]. Guo et al. proposed an approach to study wellbore heat transfer and predict wellbore temperature distribution concerning fluid rheological effects. They found that the change in fluid flow regime due to the rheological properties of the fluid had a significant effect on the temperature distribution of the well. In 2008, Cheng and colleagues explored the use of organic acids and organic acid mixtures with hydrochloric acid for carbonate reservoir acidizing. Hydrochloric acid, commonly used, has limitations due to its reactivity and corrosion issues. Organic acids offer advantages like delayed reactions and reduced corrosion, but their low dissolution capacity may restrict penetration. Mixing HCl with organic acids provides an opportunity to optimize penetration and enhance reservoir stimulation. Essential data for designing such treatments includes reaction kinetics, carbonate dissolution capacity, product solubility, and the HCl-to-organic acid ratio's impact [10]. Shembre and colleagues investigated the mechanism of reservoir damage at elevated temperatures. They conducted quantitative studies on the impact of temperature on surface forces that lead to particle displacement and migration. Their research focused on understanding how surface forces and temperature influence particle migration. Reactions occurring within porous media's pore walls depend on various factors, including mineralogy of the porous medium, fluid concentration, chemical composition, pH, and temperature. Experimental results demonstrated that with increasing temperature, particle migration occurs under conditions of alkaline pH and moderate salinity [11].Yu and colleagues conducted experiments on the reaction kinetics between acid and dolomite rock in carbonate reservoir acidizing. Using a new acid can lead to significant errors in determining injection parameters like injection rate, volume, and pumping schedule in a carbonate reservoir acidizing plan, as dissolution rates and other parameters are not estimated. Therefore, for designing an acidizing plan in carbonate reservoirs, the impact of the acid consumed on the rock-acid reaction kinetics must be considered. The consumed acid is defined as the acid that reacts with the rock and produces reaction products such as calcium and magnesium ions during the reaction [12]. Bazin and colleagues investigated the acidizing of fractured reservoirs. In their research, they examined the effects of various variables such as gravity, different acid concentrations, reaction temperature, and reservoir pressure on reaction rates. They demonstrated that at a 15% by weight hydrochloric acid concentration, the reaction rate increases in fractured reservoirs. Furthermore, to consider the effect of gravity, they injected hydrochloric acid with different concentrations in the direction of Earth's gravity and concluded that the reaction rate increases compared to injecting acid into fractures that are oriented opposite to the direction of gravity [13]. Taylor and colleagues conducted various experiments to investigate the reaction rate of hydrochloric acid with dolomite reservoir rock. They tested a range of hydrochloric acid concentrations from 0.2% by weight to 17% by weight at a temperature of 85 degrees Celsius. Their research revealed that the reaction rate is proportionate to the composition of the rock and the type of reservoir rock [14]. Kalya and colleagues investigated the impact of fluid temperature in the acidizing process for carbonate reservoir matrices. They emphasized the need to understand how temperature affects various formations and injection fluids, as many carbonate reservoirs now have elevated temperatures. The effect of temperature on wormhole formation varies based on the reaction kinetics. For instance, in limestone acidizing, higher temperatures increase the required acid volume, while on dolomite rock, the temperature effect is more complex and depends on injection rate [15].

In this study, we investigated the effect of temperature and particle size on the reaction rate of hydrochloric acid and calcium carbonate to find the effect and interaction of these factors on the reaction rate. The temperature ranges were selected according to the boiling point and the volatility of the acid. The particle size was measured at three levels by three meshes.

Material and Methods

Material

HCl 15 wt.% was used because in carbonate reservoir acidizing, the most common acid concentration is 15 wt.%, called regular acid. The HCl 15 wt.% was made from HCl 37 wt.%, provided by MERCK Germany. According to equation 1, to obtain HCl 15 wt.% of HCl 37 wt.%, increase the amount of 20.27 ml of 37 wt.% acids with 29.73 ml of deionized water to a volume of 50 ml [16]. The properties of HCl are listed in Table 1.

$$\frac{C_f}{C_i} * V_f = V_r \tag{1}$$

where C_f, C_i, V_f, and V_r are final acid concentrations (wt.%), initial acid concentrations (wt.%), final volume (ml), and required acid volume (ml).

Table 1. Properties of HCl used in research

Density	1.19 g/cm3 (20 °C)
pH value	<1 (H_2 O, 20 °C)
Vapor pressure	190 KPa (20 °C)
Assay (alkalimetric)	37.0 - 38.0 %

The chemical reaction between HCl and CaCO3 is as following:

$$2HCl + CaCO_3 \rightarrow CaCl_2 + CO_2 + H_2O \tag{2}$$

To perform the reaction, the amount of calcium carbonate, which reacts completely with 15 wt.% hydrochloric acid, is equal to 12.52 g due to the stoichiometric relation. Considering that we want to consider calcium carbonate as the limiting agent for the reaction, we chose 10.5 g of the selected calcium carbonate. The values required to perform the reaction are given in Table 2.

Table 2. The values of the parameters required to carry out the reaction of hydrochloric acid and calcium carbonate

Calcium carbonate weight	10.5 g
Initial acid mole	0.2448 mol
Initial acid volume	50 ml
Initial acid concentration	4.896 M
HCl 37 % volume	20.27 ml
Mole of calcium carbonate	0.1049 mol

Mesh number 30-40, 40-50, and 50-80 with the mean size of 479.5, 348.5, and 237 µm was used to determine the particle size. To investigate the effect of temperature on the reaction rate between hydrochloric acid and calcium carbonate, a range of temperatures including 25, 30, 35, 40, 45, 50, 55, 60, and 70 degrees Celsius were selected for experimentation.

Methods

The reaction rate is determined by dividing the measured reaction duration by the moles of consumed calcium carbonate. Acid concentration is assessed through acid-base titration. In this titration process, 5 ml of the reaction solution is transferred to the desired container, followed by the addition of phenolphthalein, an indicator commonly used in acid-base titrations, with the quantity of 2 drops. A lower indicator concentration in the solution corresponds to more precise acid and base titration. Subsequently, a 0.1 M sodium hydroxide solution is introduced using an insulin syringe for titration. The titration reaches its endpoint when the purple color change in the solution stabilizes. The remaining acid concentration is then determined using Equation 3 [17]. According to the residual acid concentration, the amount of consumed acid concentration is obtained from the difference between the initial and residual acid concentration.

$$x_1V_1=x_2V_2 \tag{3}$$

where x_1, x_2, V_1, and V_2 are residual acid concentration (mol/L), sodium hydroxide concentration (mol/L), primary volume (ml), and the volume of sodium hydroxide used for titration (ml), respectively.

A system comprising a magnetic stirrer, a reaction vessel, an oil bath, and a thermometer was prepared to investigate the effect of temperature and the particle size of calcium carbonate, aiming to achieve the best performance with the least error. To assess the temperature, when hydrochloric acid reacts with calcium carbonate, an oil bath is utilized to control the temperature within the system while mixing it with a magnetic stirrer. Following stoichiometric calculations, the quantity of calcium carbonate is determined for three groups with different particle sizes. Initially, a preselected amount of calcium carbonate is placed in the reaction vessel, and the reaction vessel is positioned on the magnetic stirrer inside an oil bath. Once the vessel reaches the desired acid temperature, the acid is introduced onto the calcium carbonate, and the reaction time is measured using a chronometer. The end of the reaction is indicated by the appearance of the last bubble in the reaction vessel. It's worth noting that each experiment was repeated twice for result verification.

Results and Discussion

In Table 3, the results of the tests are listed in the grain size of 497.5 µm and the temperature range of 25-70 °C. The grain size was obtained according to the numbers 30 and 40 meshes; therefore, the average grain size between the two meshes is 495.5 µm. According to Table 3, with increasing temperature, the reaction rate becomes faster, and as a result, the concentration of acid consumed increases. According to the consumption of calcium carbonate, equal to 0.1049 moles, the reaction speed in each test was obtained by dividing the mole of calcium carbonate consumption by time. Also, with increasing temperature, the concentration of acid consumption increased, indicating the volatility of acid. Fig. 1 shows the effect of temperature on the reaction rate at 497.5 µm grain size. As a result, according to the mole of calcium carbonate consumption and the reaction time, it was observed that the reaction rate increases with increasing temperature in this grain size.

Table 3 . The findings from the investigation of varying temperatures and particle sizes (specifically, 497.5 micrometers) on the reaction rate and the acid concentration consumed

Temprature (ºC)	Time (s)	Final acid Concentration (mol/L)	Rate (mol/s)
25	19/91	0/679	0/00526
30	19/21	0/669	0/00546
35	18/78	0/661	0/00558
40	18/34	0/653	0/00571
45	17/62	0/648	0/00595
50	17/09	0/641	0/00613
55	16/55	0/634	0/00633
60	16/13	0/627	0/0065
65	15/42	0/619	0/0068
70	14/97	0/615	0/007

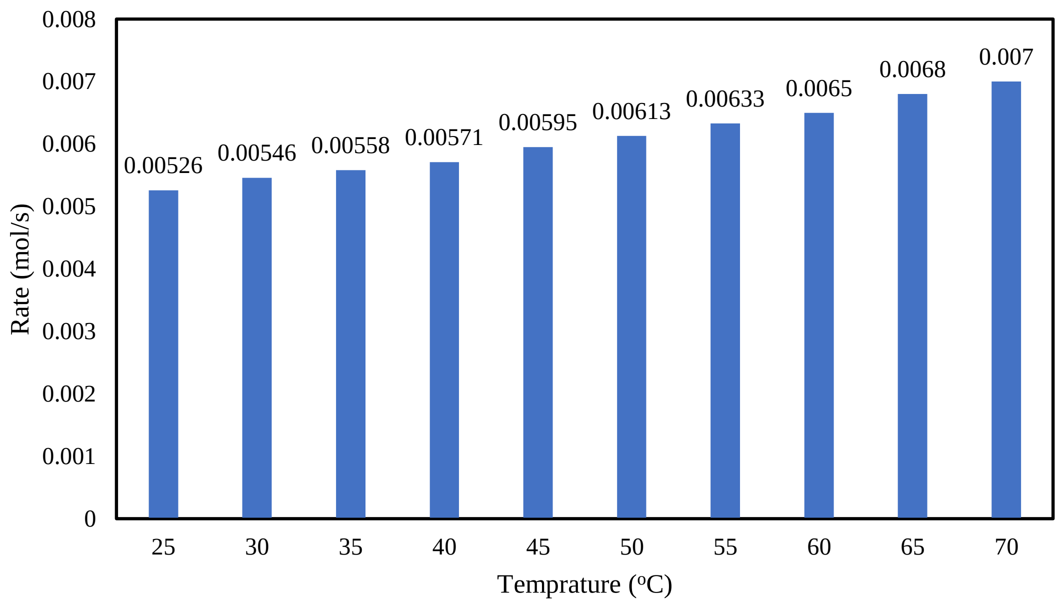

Fig. 1. The effect of temperature on the rate of reaction at 497.5 µm grain size

After that, the experiments were performed in an average grain size of 348.5 µm in the same temperature range of 25-70 ° C. This average grain size was obtained by number 40-50 meshes, which is smaller than the grain size used in the previous step. As expected, according to Table 4 and Fig. 2, the reaction time became shorter with increasing temperature, and as a result, the reaction rate increased concerning the moles of consumed calcium carbonate and the reaction time. Also, the concentration of consumed acid due to acid-base titration showed that the amount of consumed acid increases with increasing temperature.

Table 4. The findings from the investigation of varying temperatures and particle sizes (specifically, 348.5 micrometers) on the reaction rate and the acid concentration consumed

Temprature (°C)	Time (s)	Final acid concentration (mol/L)	Rate (mol/s)
25	19/65	0/675	0/00533
30	19/01	0/667	0/00551
35	18/67	0/662	0/00561
40	18/29	0/655	0/00573
45	17/59	0/649	0/00596
50	16/98	0/64	0/00617
55	16/45	0/632	0/00637
60	16/1	0/625	0/00651
65	15/39	0/618	0/00681
70	14/9	0/613	0/00704

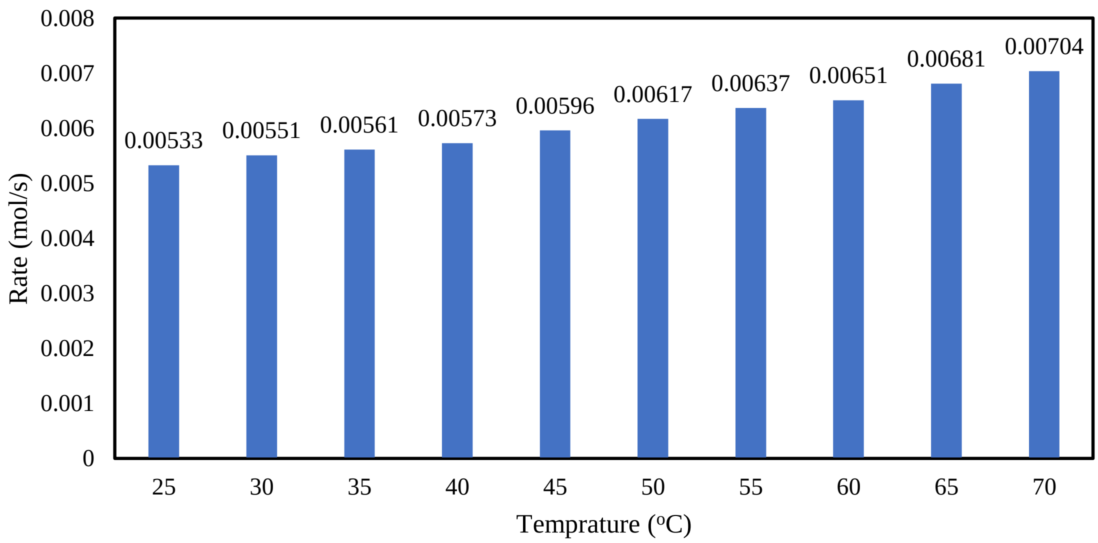

Fig. 2 The effect of temperature on the rate of reaction at 348.5 µm grain size

In the third step, the tests were performed in an average grain size of 237 µm and the same temperature range of 25-70 °C. Also, the particle size was adjusted using two meshes of 50 and 80, which are smaller than the previous grain sizes. As expected, and observed in previous experiments, in this grain size, with increasing temperature, the reaction time was shorter, and the amount of acid consumed was increased, and as a result, the reaction rate increased. Fig. 3 also shows the effect of temperature on the rate of reaction in this grain size, and according to the figure, the reaction rate has increased with increasing temperature. The result of this step is reported in Table 5.

Table 5. The findings from the investigation of varying temperatures and particle sizes (specifically, 237 micrometers) on the reaction rate and the acid concentration consumed

Temprature (ºC)	Time (s)	Final acid concentration (mol/L)	Rate (mol/s)
25	19/61	0/672	0/00535
30	18/95	0/661	0/00553
35	18/54	0/654	0/00565
40	18/25	0/649	0/00574
45	17/48	0/645	0/006
50	16/92	0/639	0/00619
55	16/41	0/632	0/00639
60	16/02	0/624	0/00654
65	15/29	0/619	0/00686
70	14/86	0/615	0/00705

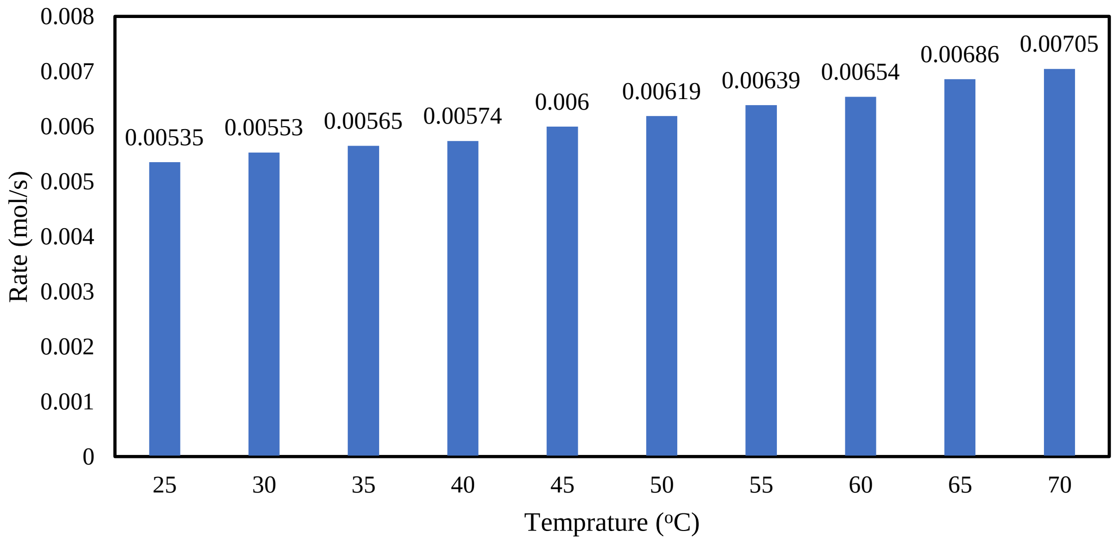

Fig. 3 The effect of temperature on the rate of reaction at 237 µm grain size

Fig. 4 is a general diagram showing the effect of temperature and grain sizes on the reaction rate. The figure shows that the reaction rate increases in all discussed grain sizes as the temperature increases. Depending on the figure, the smaller particle size at a constant temperature causes an increased reaction rate.

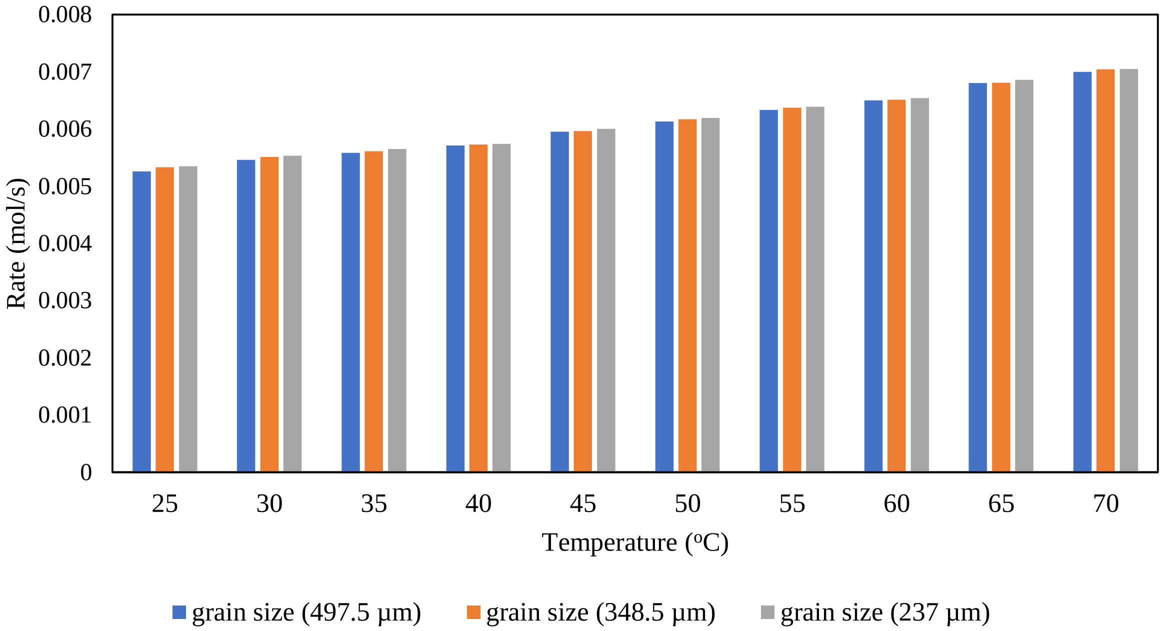

Fig. 4. Rate changes in presence of temperatures and grain sizes

Conclusion

A series of tests were conducted to study the effect of temperature and grain size on the reaction rate. The result showed that the reaction rate is not only a function of temperature but also depends on the grain size of the calcium carbonate particles, as a decrease in grain size while the temperature was held constant caused an increase in the reaction rate. In general, according to Fig. 4, increasing temperature and decreasing grain size cause an increase in reaction rate. In a way that the highest and lowest reaction rates were obtained at temperatures of 70 and 25 degrees Celsius and particle sizes of 237 and 497.5 micrometers of calcium carbonate, considering the results obtained, for the design of an acidizing program, the effect of the acid used on the kinetics of the rock-acid reaction should be taken into account. When the reaction of hydrochloric acid with calcium carbonate is carried out at a lower rate, hydrochloric acid can penetrate to a greater depth, affect areas farther from the wellbore, and reduce formation damage, resulting in increased well productivity. Based on the parameters examined in this study, it is suggested that other parameters that affect reaction kinetics, such as reservoir pressure, acid injection rate, different acid concentrations, and gravitational force, be investigated in future research.

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