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Study and Optimization of the Effect of Temperature, Acid Concentration, and Rock Grain Size on the pH of Carbonate Reservoir Acidizing

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ABSTRACT

After the carbonate reservoir acidizing and the damaged wellbore stimulating, the pH of the environment has particular importance in reducing corrosion during production. In this study, the pH change after the calcium carbonate and hydrochloric acid reaction was modeled, and the optimum pH after the reaction was determined. Also, the effect of temperature HCl concentration and calcium carbonate grain size on final pH was investigated. According to the findings, an increase in temperature causes an increase in final pH. The effect of concentration is against temperature, and pH decreases with increasing concentration. Also, the grain size of calcium carbonate particles has an insignificant effect on pH alteration. Hence, the maximum pH in all grain sizes occurs at 70 ºC and 1.95 wt.% HCl and equals 6.7. The R square adjusted R square and predicted R square of the models are acceptable values and show that experimental data agrees with prediction data.

Introduction

In many cases, oil and gas production from wells due to the formation damage and reduced permeability in the vicinity of the wellbore is below the appropriate level, and the flow of oil into the well is reduced. Damage, which disrupts the oil layers' natural conditions, reduces production, and increases costs, causes premature abandonment of wells. Well-stimulation methods are usually used to solve these problems and increase production. One of the practical and common ways to solve this issue is wellbore acidizing [1-3]. Hydrochloric acid is the most common acidizing fluid due to its low cost and high efficiency [4] and because HCl generates chloride salts, which are highly soluble in the aqueous phase and dissolve minerals like calcite [5-6]. HCl concentration in acidizing is in the range of 5 – 28 wt.% commonly 15 wt.% [7].

Many parameters affect reservoir acidizing, including temperature and acid concentration. Nowadays, due to increasing attention to unconventional sources of hydrocarbons, the use of

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acidizing for well stimulation at high temperatures has increased [8-9]. In many researches, the temperature is considered an important design parameter in the reservoir acidizing, and its effect on acidizing efficiency was investigated [10-15]. Most of these researchers presented that the optimum injection rate and the acid volume increase due to increasing temperature.

The HCl-base acidizing fluid causes problems, including corrosivity, when combined with crude oil in production. This problem becomes more significant at various temperatures and acid concentrations [16]. Hence, determining pH after the reaction in different temperatures and HCl concentrations is essential in preventing corrosion in production.

In reservoir acidizing, pH after the reaction was not noticed. The importance of this matter is when we intend to produce from the reservoir after the acidizing operation. If the environment is acidic, it will cause damage to equipment, corrosion, and such problems during production from the reservoir. Therefore, it is essential to check the pH after the acidizing process, and the more neutral environment after the reaction, the more ideal the conditions are. In this study, the effect of temperature, HCl concentration, and grain size on pH after the reaction of hydrochloric acid with calcium carbonate has been investigated.

Material and methods

Material

HCl 15 wt. % was chosen since the most typical acid concentration in carbonate reservoir acidizing is 15 wt.%, also known as regular acid [17]. To perform the reaction of hydrochloric acid and calcium carbonate, the concentration of the reacted acid was calculated from equation 1 [18].

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

After calculating the acid concentration, the amount of calcium carbonate for the reaction was obtained according to the mass dissolution equations. Using stoichiometric calculation from the reaction between calcium carbonate and hydrochloric acid, the amount of calcium carbonate that reacts with HCl is 10.27 g. Hence The amount of calcium carbonate was considered equal to 10 g, which is less than the actual value obtained from the mass dissolution calculations to limit the reaction by calcium carbonate. This concentration was used to examine the effect of temperature.

Table 1. HCl concentrations

Hydrochloric Acid Concentration (wt.%)	Increased Water (mL)	Total volume (mL)	Initial pH
6	104.8	125	0.9
9	63.06	83.35	0.75
12	42.23	62.5	0.64
15	29.73	50	0.56
18	21.4	41.67	0.5
21	15.44	35.72	0.45
24	10.98	31.25	0.39
27	7.50	27.78	0.31
30	4.73	25	0.16
33	2.45	22.73	0.06

In the following, hydrochloric acid in various concentrations was used to acidize the prepared sections and study the effect of acid concentration. The concentrations used in the experiments are illustrated in Table 1.

We used three types of meshes, including numbers 20, 30, and 40, to determine the grain size of carbonate particles, and using that, the sizes 230, 377, and 774 µm were investigated. After meshing the calcium carbonate powder, the obtained powders were prepared using a press machine into thin sections for the impending experiments.

0.1 M NaOH was used for acid-base titration. All of the using materials, such as hydrochloric acid, calcium carbonate powder, and NaOH, are provided by MERCK Germany.

Methods

Experimental

This manuscript has two sections, a) investigate the effect of temperature and grain size and b) investigate the acid concentration and grain size on pH changes.

A water bath or Bain-marie was used to adjust the effective temperature of the reaction for the first aim of this work. This device adjusts the desired temperature in a specific time interval, and the temperature range of the device is from room temperature to 100 degrees Celsius. To start work, first, the steel vessel is filled with deionized water, and the convective movement of heat in the water prevents the direct heat of the flame and causes a uniform and controllable heat in Bain-marie. After reaching the desired temperature, the experiments were performed according to the design experiment table. The pH after the reaction was performed by a digital pH meter model Multi Meter CP-500L from the Korean company ISTECK with a measurement accuracy of 0.01 and a relative error of 0.02.

In the second part, the temperature is constant, and the acid concentration will be changed, so the reaction is performed in a laboratory water bath placed on a magnetic stirrer to keep the reaction temperature constant. The stirrer at 700 rpm is also used to establish the hydrostatic equilibrium of the reaction. It should be noted that the mole of HCl involved in the reaction is constant, and the concentration changes by adding deionized water. Calcium carbonate limits the reaction, so the amount of used HCl is more than the amount of calculated HCl with stoichiometric equations of calcium carbonate consumed in the reaction completely.

HCl and calcium carbonate reaction is shown in Eq. 2 [19]. According to the equation, CO2 gas increases in the reaction; therefore, the end of the reaction equals the end of gas exit from the system.

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

Model

Design-Expert 12.0.3.0 was used to model and optimize the pH change discussed in the article. The response surface was implemented to study the effect of the factors on final pH; the design type and design model were considered I-optimal, and Quadratic, respectively. The model's factors are grain size and temperature in the first modeling (a) and grain size and acid concentration in the second modeling (b), and the response is the final pH of the reaction. All factors were converted to a number between -1 to 1 using conversion functions and are reported in Tables 2 and 3 for a) temperature and grain size and b) acid concentration and grain size modeling, respectively.

Table 2. Model factors in the first modeling

Factor	Name	Unit	Type	Min	Max	Coded Low	Coded High	Mean	Std. Dev.
A	Temperature	ºC	Numeric	25.00	70.00	-1 ↔ 25.00	+1 ↔ 70.00	47.50	14.61
B	Grain size	µm	Numeric	230.00	774.00	-1 ↔ 230.00	+1 ↔ 774.00	460.33	233.70

Table 3. Model factors in the second modeling

Factor	Name	Units	Type	Min	Max	Coded Low	Coded High	Mean	Std. Dev.
A	Concentration	Mol/L	Numeric	1.95	10.7	-1 ↔ 1.95	+1 ↔ 10.77	6.36	2.86
B	Grain size	µm	Numeric	230.0	774.0	-1 ↔ 230.00	+1 ↔ 774.00	460.33	233.70

Results and Discussion

The necessary tests were designed using Design-Expert software to study and model the effect of temperature, acid concentration, and grain size on the final pH. The factors and responses are reported in Tables 4 and 5 to investigate models (a) and (b).In model (a), the first factor is the temperature in the range of 25-70 ^oC, and the second factor is grain size determined by discussed meshes. Similarly, in the model (b), the first factor is the HCl concentration in the 6-33 wt.%, and the second factor is grain size. The system's pH was measured using a digital pH meter, and the results are listed in Tables 4 and 5 after finishing the sections acidizing.

Table 4. designed experiments using software and experimental responses for model (a).

	Factor 1	Factor 2	Response 1	
Run	A: temperature	B: Grain size	pH	
	Deg C	micron	Experimental	Predicted
1	25	230	6.14	6.15
2	25	377	6.12	6.15
3	25	774	6.12	6.15
4	30	230	6.21	6.20
5	30	377	6.21	6.20
6	30	774	6.22	6.20
7	35	230	6.25	6.25
8	35	377	6.26	6.25
9	35	774	6.25	6.25
10	40	230	6.32	6.30
11	40	377	6.33	6.30
12	40	774	6.33	6.30
13	45	230	6.36	6.36
14	45	377	6.37	6.36
15	45	774	6.36	6.36
16	50	230	6.4	6.42
17	50	377	6.4	6.42
18	50	774	6.41	6.42
19	55	230	6.47	6.49
20	55	377	6.47	6.49
21	55	774	6.48	6.49
22	60	230	6.55	6.55
23	60	377	6.55	6.55
24	60	774	6.55	6.55
25	65	230	6.64	6.62
26	65	377	6.64	6.62
27	65	774	6.63	6.62
28	70	230	6.7	6.70
29	70	377	6.7	6.70
30	70	774	6.7	6.70

Table 5. designed experiments using software and experimental responses for model (b)

	Factor 1	Factor 2	Response 1	
Run	**A: Concentration**	**B: Grain size**	**pH**	
	(wt.%)	**micron**	**Experimental**	**Predicted**
1	1.95	230	6.69	6.72
2	2.93	230	6.59	6.61
3	3.92	230	6.37	6.38
4	4.89	230	6.17	6.04
5	5.87	230	5.65	5.58
6	6.85	230	4.87	5.01
7	7.84	230	4.24	4.32
8	8.81	230	3.49	3.52
9	9.8	230	2.69	2.60
10	10.77	230	1.57	1.58
11	1.95	377	6.68	6.72
12	2.93	377	6.57	6.61
13	3.92	377	6.37	6.38
14	4.89	377	6.15	6.04
15	5.87	377	5.67	5.58
16	6.85	377	4.89	5.01
17	7.84	377	4.25	4.32
18	8.81	377	3.48	3.52
19	9.8	377	2.7	2.60
20	10.77	377	1.56	1.58
21	1.95	774	6.7	6.72
22	2.93	774	6.6	6.61
23	3.92	774	6.36	6.38
24	4.89	774	6.19	6.04
25	5.87	774	5.66	5.58
26	6.85	774	4.88	5.01
27	7.84	774	4.27	4.32
28	8.81	774	3.47	3.52
29	9.8	774	2.68	2.60
30	10.77	774	1.58	1.58

According to Tables 6 and 7, the p-values of factor B (grain size), the interactions between grain size and temperature or acid concentration, and the interactions of grain size on itself are more than 0.05, so these terms are not significant, and we ignore them in the model.

Table 6. ANOVA for Quadratic model (a)

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	0.9284	5	0.1857	658.71	< 0.0001	Significant
A-temperature	0.8959	1	0.8959	3178.13	< 0.0001	
B-Grain size	5.000E-06	1	5.000E-06	0.0177	0.8952	Not significant
AB	1.281E-06	1	1.281E-06	0.0045	0.9468	Not significant
A^2	0.0035	1	0.0035	12.26	0.0018	
B^2	3.317E-06	1	3.317E-06	0.0118	0.9145	Not significant
Residual	0.0068	24	0.0003			
Cor Total	0.9351	29				

Table 7. ANOVA for Quadratic model (b)

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	86.10	5	17.22	2409.13	< 0.0001	significant
A-Concentration	78.25	1	78.25	10947.53	< 0.0001	significant
B-Grain size	0.0002	1	0.0002	0.0252	0.8751	Not significant
AB	0.0001	1	0.0001	0.0135	0.9084	Not significant
A^2	5.23	1	5.23	731.97	< 0.0001	significant
B^2	0.0000	1	0.0000	0.0060	0.9390	Not significant
Residual	0.1715	24	0.0071			
Cor Total	86.27	29				

Eq. 3 shows the relation between final pH and temperature (model a), and Eq. 4 shows the final pH and acid concentration relation (model b). The grain size was ignored in the equations because of its insignificant p-value.

$$pH = 5.94506 + 0.006613 * T + 0.000059 * T^2 \tag{3}$$

$$pH = 6.59778 + 0.178065 * M - 0.059818 * M^2 \tag{4}$$

According to Tables 8 and 9, R^2, adjusted $R^{2,}$ and predicted R^2 of both of the models have acceptable values and show that experimental data has good agreement with prediction data.

Table 8. Fit Statistics of the model (a)

Std. Dev.	0.0168	**R^2**	0.9928
Mean	6.40	**Adjusted R^2**	0.9913
C.V. %	0.2621	**Predicted R^2**	0.9879
		Adeq Precision	73.4243

Table 9. Fit Statistics of the model (b)

Std. Dev.	0.0798	**R^2**	0.9980
Mean	4.83	**Adjusted R^2**	0.9979
C.V. %	1.65	**Predicted R^2**	0.9977
		Adeq Precision	203.7089

Diagnostic plots, including the normal plot of residual and the predicted vs. actual plot, are demonstrated in Figs 1 and 2. The diagnostic plots aid in judging the model's adequacy and satisfactoriness [20]. According to Figs. 1a and 1b, The normal probability diagram shows how the residues follow a normal distribution.

The distribution diagram of actual values and predicted values are illustrated in Figs 2a and 2b and show that these values follow a normal distribution.

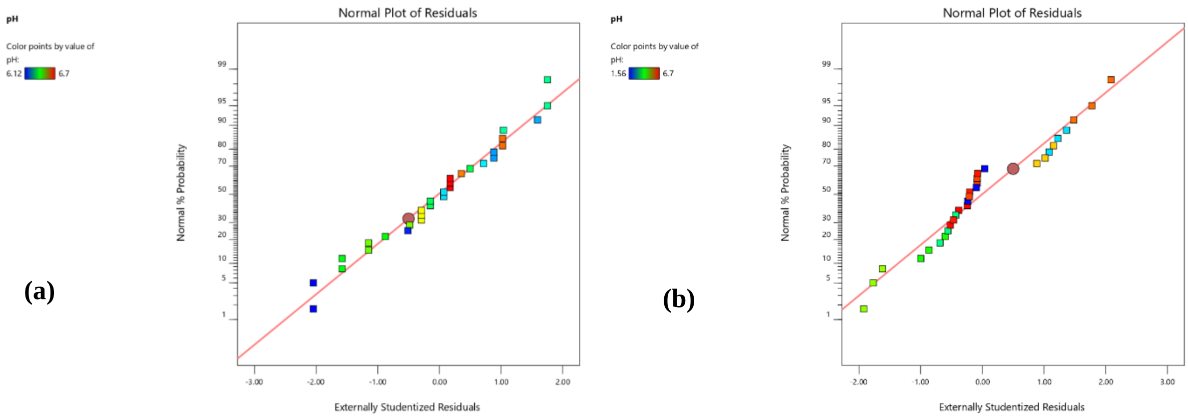

Fig. 1. The normal plot of residuals for (a) model a and (b) model b

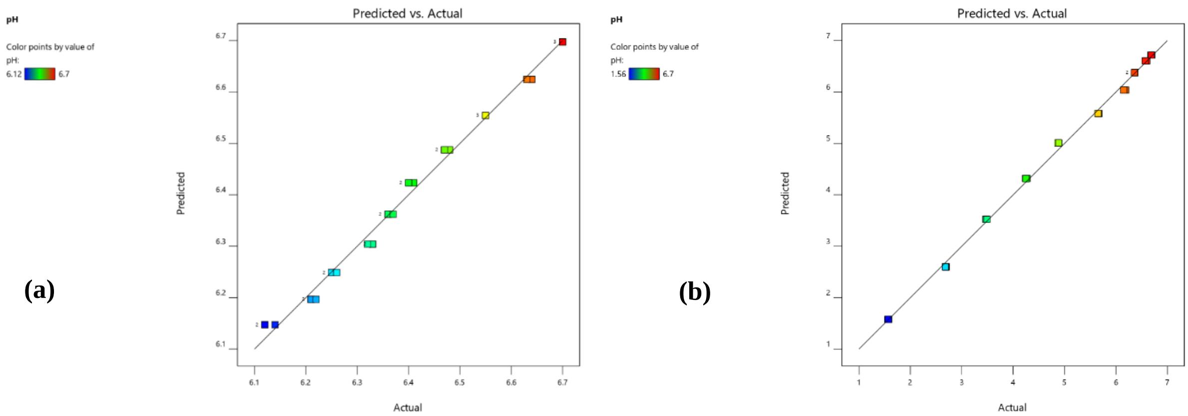

Fig. 2. Actual values vs. predicted values for (a) model a and (b) model b

The contour plot and 3D plot of pH change in the presence of temperature, acid concentration, and grain size are shown in Figs. 3 and 4. According to Figs. 3a and 4a, as the temperature increases, the final pH also increases, and the grain size does not significantly affect the final pH.

According to Figs 3b and 4b, the pH after the reaction decrease with increasing HCl concentration but in high concentration, pH decrease occurs faster than in low concentration; in other words, the slope of pH changes increases at high concentrations (Fig. 4b).

To achieve the aim of this research, the final pH was optimized, and the maximum pH equal to 6.7 occurred at the temperature of 70 °C in all grain sizes for model (a) and HCl concentration of 1.95 wt.% in all grain sizes for model (b).

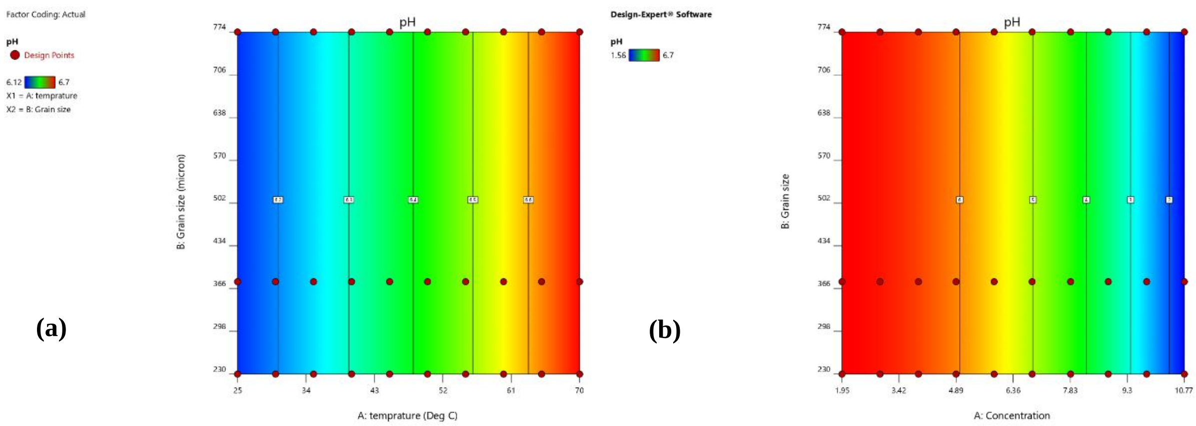

Fig. 3. contour plot of model (a) and (b)

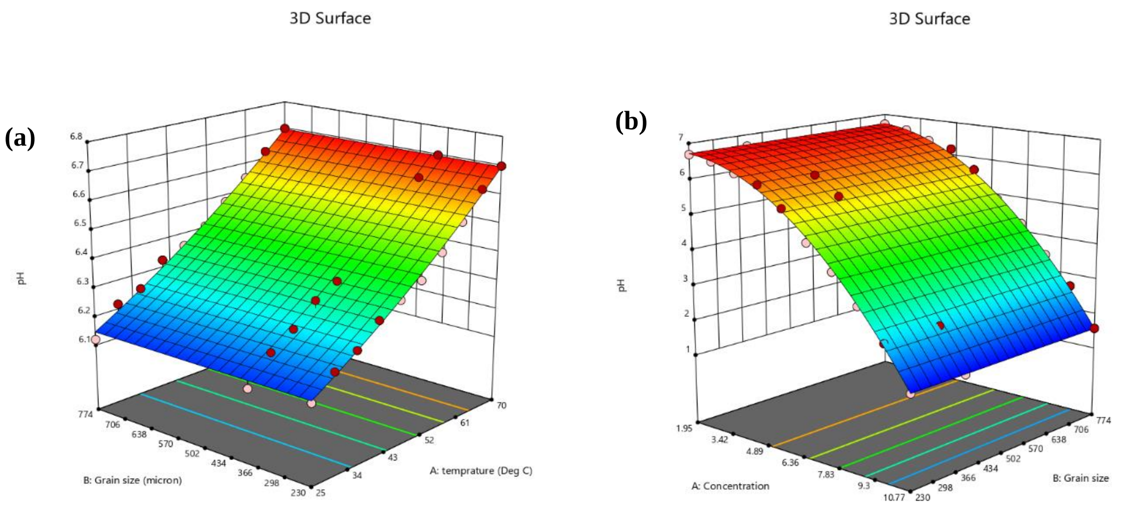

Fig. 4. 3D plot of the model (a) and (b)

Conclusion

To optimize the pH after carbonate reservoir acidizing, we investigate the effect of the temperature, HCl concentration, and grain size on the final pH of the environment. According to the result of experimental tests, two models for temperature and concentration were developed using design-expert software that represents the effect of these factors. According to the first model, pH increases with increasing temperature and does not depend on the grain size of calcium carbonate particles. Hence, The maximum pH occurs at 70 ^{o}C and equals 6.7. The second model shows a decrease in final pH with increasing HCl concentration, and the optimum pH occurs at 1.95 wt.% HCl and all grain sizes.

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Nomenclature

C_f	Final acid concentrations (wt.%)
C_i	Initial acid concentrations (wt.%)
V_f	Final volume (ml)
V_r	Required acid volume (ml)
T	Temperature (^{o}C)
M	Acid concentration (wt.%)

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