

# Research Article

# **Reaction Kinetics of Sodium Bentonite with Different Acid** Systems: An Experimental Study

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Discovering the characteristics of the reaction kinetics of acid systems (hydrogen fluoride (HF), hydrochloric acid (HCl), and CH<sub>3</sub>COOH) at different concentrations with sodium bentonite can provide experimental support for optimising formulations used in removing plugs through acidification. By utilising a spectrophotometer and acid-base titration, changes in contents of Si, Al, and H<sup>+</sup> concentration when sodium bentonite reacted with different acid systems (HF, HF, HCl, and HF and CH<sub>3</sub>COOH) at different concentrations (5%, 10%, and 15%) for different reaction times (1, 2, 4, 8, 12, and 24 h) at 45°C were measured. Based on this, a reaction kinetics model of H<sup>+</sup> was fitted and reaction mechanisms of HF with sodium bentonite after adding HCl and CH<sub>3</sub>COOH were analysed. The results demonstrated that the rate of dissolution of Al was high and the reaction reached equilibrium in 1 h. Si showed a fast dissolution cocurred, with a more stable dissolution rate and longer reaction time. Among the three acids tested, it was HF that mainly reacted with sodium bentonite, rather than other forms, such as H<sup>+</sup>, F<sup>-</sup>, and HF<sub>2</sub><sup>-</sup>. The addition of HCl could promote the reaction, while CH<sub>3</sub>COOH inhibited the reaction. The research results provide experimental support for optimising the formulation of such acid solutions.

#### 1. Introduction

Discovering the kinetic characteristics of reactions of different acid systems with clay minerals and carbonate minerals can provide accurate experimental parameters for formulation optimisation. At present, the research methods for kinetics of acid-rock reactions mainly include static and dynamic acid-rock reactions [1].

The research method of static acid-rock reaction kinetics is as follows: the static acid-rock reaction is used to measure changes in Si and Al elements concentration at different temperatures after different reaction times by placing reactants in acid solution, for example, put montmorillonite, illite, and kaolinite statically in HF, soil acid system, carbonic acid, and other solutions to test the changes in the concentration of Si and Al elements and calculate the reaction rate of Si and Al elements, moreover combining reaction kinetic equations to explore its dynamic characteristics [2–4]. This method has a simple experimental design and is easy to operate, but it cannot simulate the state of flow of acid solutions in formation.

The research methods of dynamic acid-rock reaction kinetics include rotating disk method and parallel plate method. The former is used to measure changes in  $H^+$  concentration at different temperatures and pressures and allows calculation of the reaction rate by rotating the core in an acid solution. This method can better simulate the environment for acidifying cores, while the differences in the core specimens can result in different experimental results owing to their innate variability in situ [5–7]. The latter is

used to cut cores into rock plates of the same size, in which acid solution flows in the artificial cracks [8], thus measuring changes in  $H^+$  concentration of acid solution at the outlet. It mainly focusses on the changes in flow conductivity of artificial cracks after the acid-rock reaction [9] and entails a relatively complex process for preparing the samples, and the test is slow.

The acidity of different acid solutions is different, which results in different reaction rates and degrees of reaction when different acid solutions react with clay minerals, and may also generate negative effects such as precipitation [10–12]. The aim of this study is to ascertain the changes in reaction rates of HF with sodium bentonite before and after adding hydrochloric acid (HCl) and CH<sub>3</sub>COOH [13,14]. Sodium bentonite reacted with different acid systems (HF, HCl, and CH<sub>3</sub>COOH) to measure changes in concentration and find the reaction kinetics; moreover, based on changes in Si and Al elements and H<sup>+</sup> content, reaction mechanisms were discussed, expecting to lay an experimental foundation for optimising the formulations of different acid solutions.

### 2. Experimental

The bentonite used in this reaction is produced by Lin'an District, Hangzhou City, Zhejiang Province. The sodiumbased bentonite produced in Lin'an, Zhejiang Province, was used, and its chemical composition was mainly aluminosilicate by XRD. The chemical equation was  $M_{\nu}Al_{w}Si_{x}O_{y}(OH)_{z}$ , where M was metal cations such as Na<sup>+</sup> and Mg<sup>2+</sup>.

The different acid solutions are as follows: HCl, HF, CH<sub>3</sub>COOH, and equally mixed HCl and HF, HF and CH<sub>3</sub>COOH, HCl and CH<sub>3</sub>COOH, and HCl, HF, and CH<sub>3</sub>COOH, and so on (expressed as HCl+HF, HF+CH<sub>3</sub>COOH, HCl+CH<sub>3</sub>COOH, and HCl+HF+CH<sub>3</sub>COOH herein). Different acid solutions to 3% sodium bentonite solution are added; the concentrations are 5%, 10%, and 15%; solutions reacted at different temperatures (1 h, 2 h, 4 h, 8 h, 12 h, and 24 h), filtered, and tested the concentration of Si and Al elements and reaction kinetic parameters generated in the liquid phase [15].

2.1. Measurement of Si and Al Element Concentration in the Liquid Phase. The specific method is as follows: when different acid solutions with different concentrations (5%, 10%, and 15%) are reacted with 3% sodium bentonite to the test time (1 h, 2 h, 4 h, 8 h, 12 h, and 24 h), the supernatant is pipetted from the reaction flask and filtered with a filter paper. The Shanghai Youke 721 spectrophotometer was used to calibrate the absorbance corresponding to different concentrations of Si and Al element solutions using ammonium molybdate spectrophotometry and chrome azurite spectrophotometry, and the standard curve corresponding to the absorbance was plotted [16] (Figure 1).

2.2. Test of Reaction Kinetic Parameters. According to the mass action principle, at constant temperature and pressure, the reaction rate is positively correlated with  $m^{th}$  power

product of the concentrations of each substance. Therefore, the reaction rate in the above experiment is expressed as follows:

$$J = KC^m, \tag{1}$$

where *J*, *K*, and *C* represent the chemical reaction rate (mol/(L·s)) at a given time, the constant  $((mol/L)^{1-m}/s)$  of reaction rate, and the concentration  $(mol/(L\cdots))$  in acidification at a given time, respectively, and *m* indicates the reaction order and is dimensionless.

Taking the logarithm of both sides of equation (1),

$$\lg J = \lg K + m \lg C. \tag{2}$$

A logarithmic relationship diagram can be made, and the reaction order and reaction rate constant in the reaction kinetics can be obtained based on the slope and intercept of the diagram.

Therefore, it is necessary to test the acid concentration and  $H^+$  reaction rate when the acid solution reaches the dissolution/analysis equilibrium at the initial (5%, 7%, 10%, 13%, and 15%) concentration and then calculate the reaction order and reaction rate. Constant, the reaction kinetic equation [17] is obtained. Among them, since the Si element in the sodium-based bentonite used in this experiment accounts for 71.79%, the time for the acidification reaction to reach the dissolution/analysis equilibrium can be obtained according to the dissolution/analysis equilibrium time of the Si element in the liquid phase.

First, the acid concentration is tested after the reaction. The specific test method is as follows: for the sample that has reached the reaction time, 3 mL of the supernatant is filtered and taken and diluted with distilled water 10 times. 1 mol/L NaOH solution is used for acid-base neutralization titration. The pH meter records the pH of the solution. When it shows a pH of 7.00, the titration is completed. The volume of the NaOH solution is recorded, and the acid concentration after the reaction is calculated.

As CH<sub>3</sub>COOH, HF was weak acid, it was not completely ionised in water, and its concentration could change with the consumption of H<sup>+</sup> in the experimental process. And HF and SiO<sub>2</sub> could generate strong acid H<sub>2</sub>SiF<sub>6</sub> (fluorosilicic acid) in water (formula (3)), which could interfere with the measurement of H<sup>+</sup> in liquid solution after reaction. By indirectly measuring the amount of remaining HF to calculate and exclude H<sup>+</sup> produced by fluorosilicic acid, the H<sup>+</sup> concentration in the sample liquid phase that participates in the reaction is tested:

$$SiO_2 + 6HF = H_2SiF_6 + 2H_2O$$
(3)

The test method was as follows: for samples do not containing HF in the reactive acids, the acids solution concentration before the reaction is subtracted from the acid solution concentration after the reaction to obtain the H<sup>+</sup> concentration changes during the sample reaction and calculate the reaction rate. For samples containing HF in reactive acids, a certain volume of supernatant was taken for an erosive experiment on a slide. According to changes in mass before and after erosion on the slide, the residual HF



FIGURE 1: Standard curve of absorbance of (a) Si element and (b) Al element.

content after reaction of the samples was calculated and the amount of HF consumed in the reaction was obtained; furthermore, the H<sup>+</sup> content and concentration of H<sub>2</sub>SiF<sub>6</sub> fluorosilicic acid produced by the sample were calculated. The acid solution concentration before the reaction is subtracted from the acid solution concentration after the reaction and the H<sup>+</sup> concentration in the generated H<sub>2</sub>SiF<sub>6</sub> to obtain the H<sup>+</sup> concentration change during the sample reaction, and the reaction rate is calculated.

# 3. Experimental Results and Analysis

3.1. Analysis of the Changes in the Si and Al Elements in the Liquid Phase under Different Reaction Times. The changes in Si and Al contents after reaction of sodium bentonite with different acids at 45°C for different times are shown in the figure.

As presented in the Figures 2(a)-2(c), the dissolution of Si and Al elements in different acid solutions had the following characteristics:

(1) Effect of reaction time on dissolution

It can be seen from the figure that, with increasing reaction time, dissolution of Si rapidly rises in the first 2 h, then slows down from 2 to 4 h, and finally tends to be stable or grows slowly in the later stage of testing. Dissolution of Al rapidly increases in the first 1 h and shows fluctuations within a certain range thereafter.

(2) Effect of acid type and concentration on dissolution ① Dissolution of Si element: the acid solution containing no HF has less dissolution amount than the acid solution containing HF. In acids types without HF, the reaction will reach equilibrium at 1 h and will stabilize in the later stages. The order of dissolution amount is HCl>HCl+CH<sub>3</sub>COOH> CH<sub>3</sub>COOH, and the amount of dissolution in a 5% acid solution is less than those in 10% and 15% acid solutions; however, there is a small difference in the

amount of dissolution of Si in 10% and 15% acid solutions. In acids types containing HF, when using HF acidification, the concentration of 5% concentration rose at 0~1 h and 10% and 15% concentration rose fastest at 0~2 h; then, the rising rate decreased and reached the maximum dissolution amount at 4 h, and the dissolution amount at 4~24 h gradually lowers and reaches equilibrium. When using HF + CH<sub>3</sub>COOH acidification, the concentration of Si element increased slowly under different acid solution concentrations, the dissolution amount reached the maximum value in 4 h, and the concentration did not decrease in the later period. When using HCl+HF acidification, the increase rate of Si element concentration was greater than that of most other acid types. Under different concentrations, the dissolution rate gradually decreased at 0~1 h AND 1~2h, reached the maximum dissolution rate at 2~4 h, and then stabilized. The dissolution amount is greater than all other acid types when 5% and 10% concentrations are acidified. Compared with 5% concentration HCl and HF, the mixed acid solution of 10% HCl and CH<sub>3</sub>COOH has a higher Si element formation rate and a larger dissolution amount, indicating that HCl can promote the acidification of HF. When using HCl+HF+CH<sub>3</sub>COOH acidification, the increase rate of Si element concentration was slightly lower than that of HCl, HF, and HCl + HF. The dissolution amount increased steadily at 0~4 h, and it decreased slightly at 4~8 h, reaching the maximum dissolution rate and becoming steady. The dissolution amount of 15% HCl+HF+CH<sub>3</sub>COOH is not much different from that of 10% HCl + HF, but the reaction is more stable and the dissolution time is longer.

② Dissolution of Al element: the dissolution amount of Al element of different types of acids is different; HF,  $HF + CH_3COOH$ ,  $HCl + CH_3COOH$ , and  $HCl + HF + CH_3COOH$  are larger, while HCl,



FIGURE 2: Continued.



FIGURE 2: Variation of Si and Al elements with different concentrations of different acidified sodium bentonites overtime: (a) 5% acid Si and Al elements change with time; (b) 10% acid Si and Al elements change with time; (c) 15% acid Si and Al elements change with time.

CH<sub>3</sub>COOH, and HCl+HF are smaller. The concentration of acid solution had little effect on the change in the amount of Al dissolution.

3.2. The Reaction Kinetics. At  $45^{\circ}$ C, Table 1 shows the acid concentration and H<sup>+</sup> reaction rate data when the reaction between HCl, HF, CH<sub>3</sub>COOH, and mixed acid with sodium bentonite reaches the dissolution/analysis equilibrium.

At 45°C, the logarithmic linear curves of  $\lg J$  and  $\lg C$  for the reaction of HCl, HF, CH<sub>3</sub>COOH, and mixed acids with sodium-based bentonite are shown in Figures 3(a) and 3(b), respectively.

According to the slope and intercept of the straight line in Figure 3, the reaction order and reaction rate constant of different types of acid and mixed acid acidified sodiumbased bentonite can be obtained. The calculation results are shown in Table 2.

As presented in Figure 3 and Table 2, among the three acids, it is HF that mainly reacts with sodium bentonite, while single HCl, single  $CH_3COOH$ , and  $HCl + CH_3COOH$  only react slightly with sodium bentonite: when HCl is added to HF, the reaction order and the constant of reaction rate increase, thus promoting the reaction. The addition of  $CH_3COOH$  causes the decrease of both reaction order and reaction rate constant.

3.3. Analysis. According to the above experimental research, it can be seen that HF reacts strongly with sodium bentonite. After the concentration of Si element reaches the maximum, it will decrease to a certain extent and then stabilize. After adding HCl,  $CH_3COOH$ , and other acid solutions in HF, Si element dissolves large differences in rate, dissolution, and reaction kinetics equations. Therefore, this article attempts

to discuss the reaction mechanism of HF and sodium bentonite from the perspective of ionisation equilibrium and the effects of HCl and  $CH_3COOH$  on the acidification of sodium bentonite by HF.

3.3.1. Reaction Mechanism of HF with Sodium Bentonite. HF solutions at a low concentration may have forms, such as HF molecules,  $F^-$ ,  $HF_2^-$ , and  $H^+$  [18], so it is necessary to know which form reacts with sodium bentonite. At 25°C, there is an ionisation balance of each form as follows:

HF ⇐ H<sup>+</sup> + F<sup>-</sup> K<sub>1</sub> = 
$$\frac{[H^+][F^-]}{[HF]} = 6.6 \times 10^{-4}$$
, (4)

$$2HF \rightleftharpoons H^{+} + HF_{2}^{-}K_{2} = \frac{[H^{+}][HF_{2}^{-}]}{[HF]^{2}} = 2.2 \times 10^{-3}, \quad (5)$$

where  $K_n$  (n = 1, 2) represents the constant of ionisation equilibrium; [H<sup>+</sup>], [F<sup>-</sup>], and [HF<sub>2</sub><sup>-</sup>] indicate the concentrations (mol/L) of H<sup>+</sup>, F<sup>-</sup>, and [HF<sub>2</sub><sup>-</sup>] in the solution, respectively; and [HF] denotes the concentration (mol/L) of unionised HF molecules.

According to the Vant' Hoff equation, the equilibrium constants  $K_1(T)$  and  $K_2(T)$  of the reaction separately are given by the following equation:

$$K_n(T) = K_n e^{\left[\Delta H_n / R\left(\left(1 / T_0\right) - (1 / T)\right)\right]}, \quad n = 1, 2,$$
(6)

where  $\Delta H_n$  (n = 1, 2) denotes the enthalpy change and its values in formulae (4) and (5) are -3,210 and -2,080 through reference to published data; *R* denotes the ideal gas constant (8.314472 J·K<sup>-1</sup>·mol<sup>-1</sup>); and  $T_0$  and *T* represent the reaction temperature and Kelvin temperatures at 0°C, respectively.

HF in solution has a constant total mole number of fluorine, so

Acid composition	The initial concentration (%)	Amount of substance after reaction (mol/L)	Reaction speed (mol/s)
	5	0.518	$3.137 \times 10^{-8}$
	7	0.669	$3.378 \times 10^{-8}$
HCl	10	0.945	$4.147 \times 10^{-8}$
	13	1.362	$4.703 \times 10^{-8}$
	15	1.882	$5.794 \times 10^{-8}$
	5	0.330	$3.511 \times 10^{-7}$
	7	0.610	$5.814 \times 10^{-7}$
HF	10	0.733	$6.456 \times 10^{-7}$
	13	0.953	$7.792 \times 10^{-7}$
	15	1.799	$1.334 \times 10^{-6}$
	5	0.921	$9.563 \times 10^{-9}$
	7	1.183	$1.016 \times 10^{-8}$
CH₃COOH	10	1.505	$1.126 \times 10^{-8}$
	13	1.859	$1.192 \times 10^{-8}$
	15	2.390	$1.272 \times 10^{-8}$
	5	0.715	$1.660 \times 10^{-7}$
	7	0.793	$1.715 \times 10^{-7}$
HCl+HF	10	0.985	$2.138 \times 10^{-7}$
	13	1.410	$2.801 \times 10^{-7}$
	15	1.572	$3.171 \times 10^{-7}$
	5	0.610	$3.536 \times 10^{-8}$
	7	0.777	$4.090 \times 10^{-8}$
HCl+CH₃COOH	10	1.197	$4.861 \times 10^{-8}$
	13	1.565	$5.424 \times 10^{-8}$
	15	1.938	$6.165 \times 10^{-8}$
	5	0.550	$3.478 \times 10^{-7}$
	7	0.718	$3.792 \times 10^{-7}$
HF + CH <sub>3</sub> COOH	10	0.937	$4.320 \times 10^{-7}$
, second s	13	1.257	$4.813 \times 10^{-7}$
	15	1.599	$5.516 \times 10^{-7}$
HCl+HF+CH₃COOH	5	1.127	$2.492 \times 10^{-7}$
	7	1.346	$2.905 \times 10^{-7}$
	10	1.583	$3.534 \times 10^{-7}$
	13	1.855	$4.206 \times 10^{-7}$
	15	2.198	$5.102 \times 10^{-7}$

TABLE 1: Statistics of experimental data on the reaction of different types of acids with sodium bentonite.

$$[HF]_0 = [HF] + [F^-] + 2[HF_2^-],$$
(7)

By sorting formulae (4) to (7), concentrations of different forms of HF in solution are given by

where [HF]<sub>0</sub> denotes the initial concentration (mol/L) of HF.

$$\begin{cases} [HF] = \frac{-(K_1(T) + [H^+]) + \sqrt{(K_1(T) + [H^+])^2 + 8K_2(T) \cdot [H^+] \cdot [HF]}}{4K_2(T)}, \\ [F^-] = \frac{K_1(T) \cdot [HF]}{[H^+]}, \\ [HF_2^-] = \frac{K_2(T) \cdot [HF]^2}{[H^+]}. \end{cases}$$
(8)

When the  $H^+$  concentration in the solution changes, the reaction equilibrium shifts and concentrations of different forms of HF in the solution change: the concentration ratio

is used to represent the changes in concentrations in different forms under different  $H^+$  concentrations, as demonstrated in Figures 4(a)-4(c).



FIGURE 3: The relationship between the reaction rate of different acid solutions and sodium bentonite and the logarithm of multicomponent acid concentration: (a) logarithmic relationship between single acid and sodium bentonite; (b) logarithmic relationship between multi-component acid and sodium bentonite.

TABLE 2: Statistics of experimental results of acidified sodium bentonite in different acid systems.

Acid composition	Reaction order	Reaction rate constant	Reaction kinetic equation
HCl	0.47443	$4.19624 \times 10^{-8}$	$J = 4.19624 \times 10^{-8} C^{0.47443}$
HF	1.29106	$5.86665 \times 10^{-7}$	$J = 5.86665 \times 10^{-7} C^{1.29106}$
HAC	0.30961	$9.78566 \times 10^{-9}$	$J = 8.323 \times 10^{-7} C^{0.77913}$
HCl+HF	1.77476	$7.01068 \times 10^{-7}$	$J = 7.01068 \times 10^{-7} C^{1.77476}$
HCl+CH <sub>3</sub> COOH	0.45984	$4.49262 \times 10^{-8}$	$J = 4.49262 \times 10^{-8} C^{0.45984}$
HF + CH <sub>3</sub> COOH	0.43035	$4.43629 \times 10^{-7}$	$J = 4.43629 \times 10^{-7} C^{0.43035}$
$HCl + HF + CH_{3}COOH$	1.08723	$2.15021 \times 10^{-7}$	$J = 2.15021 \times 10^{-7} C^{1.08723}$



FIGURE 4: Variation in the proportion of different bodies in different concentrations of HF solution with pH: (a) 5% concentration HF; (b) 10% concentration HF; (c) 15% concentration HF.

Time (h)	HF concentration		
	5%	10%	15%
1	3.39	2.63	1.98
2	3.41	3.16	2.65
4	3.43	3.20	3.11
8	3.43	3.21	3.20
1 2 4 8	5% 3.39 3.41 3.43 3.43	10% 2.63 3.16 3.20 3.21	

TABLE 3: Changes in pH of sodium bentonite and different concentrations of HF at different reaction times.

It can be seen from the figure that, when pH < 2, mainly HF molecules are present in the solution and the amount thereof gradually decreases with increasing pH. When pH > 3, there are few HF molecules present and the  $F^-$  content gradually increases in an exponential form, while the  $HF_2^-$  content first increases and then decreases. At a pH of 3, the  $HF_2^-$  content is maximised and then decreases thereafter.

In comparison with Figure 2, when sodium bentonite reacts with HF solution for  $1\sim2$  h, the rate of dissolution of Si is the fastest. At that moment, HF molecules in the solution dominate. As the pH increases to 3.11 to 3.43, the amount of dissolution of Si elements remains unchanged. In this case, F<sup>-</sup> and HF<sup>-</sup><sub>2</sub> are mainly found in the solution, indicating that HF molecules mainly react with sodium bentonite. Changes in pH during the reaction of sodium bentonite with HF of different concentrations over different times are demonstrated in Table 3.

Therefore, there are three reactions between sodium bentonite and HF solution: the first is a reaction with HF molecules to generate  $H_2SiF_6$ , as shown in formula (1), because the resulting  $H_2SiF_6$  is easily decomposed into HF molecules, and the second reaction involves decomposition of HF by  $H_2SiF_6$  that further reacts with sodium bentonite and  $H_2SiF_6$  reacts with metal cations to form a precipitate. In the third reaction, the aluminium-fluoride complexes generated in the first two reactions continue to react with aluminosilicate compounds present to generate fluorinecontaining complexes. When the pH reaches 3.04 to 3.48, the reaction stops.

The second and third reactions of sodium bentonite with HF solution can explain the reason why the dissolution amount of Si element reaches a maximum after HF acidification in Figure 2 and then stabilizes.

3.3.2. Effects of HCl and  $CH_3COOH$  on HF-Acidified Sodium Bentonite. Aluminosilicate in sodium bentonite is expressed as  $M_vAl_wSi_xO_y(OH)_z$ , where M represents a metal cation. In aluminosilicate, there are covalent bonds, such as Si-O, Si-OH, Al-O, and Al-OH and ionic bonds between metal cations (such as Na<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, and Fe<sup>2+</sup>) and aluminosilicate anions. Covalent bonds and ionic bonds in sodium bentonite can react with HF, and the strength of a majority of such covalent bonds is higher than that of the ionic bonds present. Breaking of covalent bonds is critical for acidifying sodium bentonite with HF [19] and the rate at which these bonds are broken determines the reaction rate.

Through comparison with dissolution rates and amounts of Si in HF, HCl+HF, and HF+CH<sub>3</sub>COOH solutions, the addition of HCl is found to promote the reaction between HF and sodium bentonite, while  $CH_3COOH$  inhibits the reaction between them. The difference between promotion and inhibition is caused by changes in H<sup>+</sup> concentration in the solution. The reason is as follows: HCl is a strong acid and can be completely ionised in water, while the ionisation constant of  $CH_3COOH$  is smaller than that of HF at the same temperature. H<sup>+</sup> (being without electrons) easily reacts with oxygen in lattice bonds of minerals to form intermediate products. Moreover, H<sup>+</sup> has strong field polarisation, thus making intermediate products unstable, so that the reaction occurs more easily.

By adding 5% HF of 30 mL to the samples of sodium bentonite, the pH is adjusted to 0.3, 0.4, and 0.5 using diluted HCl, so as to calculate dissolution rates at different times (1, 2, and 4h). The experimental results are presented in Figure 5.

According to the calculation in Table 4, when the pH is between 0.3 and 0.4, the rate of change in the distribution (by proportion) of HF in the solution is 0.587%. Furthermore, rates of change in dissolution rates at 1 and 4 h are 3% and 3.06%, respectively. When the pH is between 0.4 and 0.5, the rate of change in the distribution (by proportion) of HF in the solution is 0.59% and those of the rates of dissolution are, separately, 1.37% and 2.21% at 1 and 4 h. This indicates that the addition of HCl to the solution exerts no influence on the proportional distribution of HF, while the dissolving capacity of HF increases significantly with increasing H<sup>+</sup> concentration.

At the same temperature, the degree of ionisation of CH<sub>3</sub>COOH is lower than that of HF. The addition of CH<sub>3</sub>COOH to the HF solution increases the pH of the solution while reducing its H<sup>+</sup> concentration. This results in HF molecules in the solution shifting towards the direction of ionising F<sup>-</sup> and HF<sup>-</sup><sub>2</sub> and their concentration decreases, thus reducing the rate of reaction.

3.3.3. Work That Can Be Continued in the Future. In the mixed acid, only different kinds of acids were mixed in equal proportions and the results were discussed under ideal conditions, and the effect of temperature on the reaction was not considered. In the next step, based on the research in this paper, experiments will be carried out with different proportions of mixed acids at different temperatures. Analyzing the effect of the product's isoionic effect on the reaction rate, and the effect of temperature on the reaction, the reaction activation energy is calculated and the change in H<sup>+</sup> concentration is observed.



FIGURE 5: Dissolution rate of HF to sodium bentonite under different pH conditions.

TABLE 4: The relationship between the proportion of HF in different pH values and the range of dissolution rate at different times.

pH interval	HF distribution ratio	1 h dissolution rate variation range	4 h dissolution rate variation range
0.3~0.4	0.9686~0.9629	30~29.1	32.7~31.7
0.4~0.5	0.9629~0.9573	29.1~28.7	31.7~31

# 4. Conclusions

The reaction between different acid systems and sodium bentonite was analysed, and the following conclusions are drawn:

- (1) By conducting reaction experiments on different acid systems (HCl, HF, CH<sub>3</sub>COOH, and mixed acids with different concentrations of 5%, 10%, and 15%) with sodium bentonite, changes in the rate and amount of dissolution of Si and Al were obtained. The results demonstrated that the amount of dissolution of Si in acid solutions containing HF rapidly increased, slowly increased, and then tended to be stable thereafter. The amount of dissolution of Si in acid solutions without HF was lower and reached a maximum within 1 h. The amounts of dissolution of Si in 10% and 15% acid solutions were similar. Al was quickly dissolved out in the first hour and then the amount of dissolution fluctuated within a certain range thereafter. The concentration of the acid solution exerted little influence on changes in the amount of dissolution of Al.
- (2) The reaction kinetics equations for the H<sup>+</sup> changes in seven acid types and sodium bentonite were calculated. The results showed that the main HF molecules reacted with sodium bentonite, and the single HCl, CH<sub>3</sub>COOH and HCl+CH<sub>3</sub>COOH reacted slightly with sodium bentonite.

(3) The reaction mechanism of sodium-based bentonite with HF and multicomponent acid and the reasons for the influence of HCl and CH<sub>3</sub>COOH on HF and sodium-based bentonite were revealed. The results show that there are three reactions between sodium bentonite and HF solution; one reaction reacts with HF to form H<sub>2</sub>SiF<sub>6</sub>, and the second is that H<sub>2</sub>SiF<sub>6</sub> decomposes HF molecules to further react with it. The third reaction is the first two generations of fluorine. The aluminum complex continues to react with the aluminosilicate. The reaction with sodium bentonite is mainly HF molecules; the reaction is inhibited by adding CH<sub>3</sub>COOH, and HCl is added to promote the reaction.

#### **Data Availability**

The data used to support the findings of this study are included within the article.

## **Conflicts of Interest**

The authors declare that there are no conflicts of interest.

# **Authors' Contributions**

Xiaoming Ni conceptualized the study, investigated the study, planned for resources, reviewed and edited the article, did project administration, and obtained funding acquisition. Yang Li was involved in methodology, curated the study, and wrote the original draft. Zhongcheng Li performed formal analysis and supervised the study. Zheng Zhao and Cixiang Yang validated the study. Zheng Zhao was responsible for visualization.

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