

LIMESTONE NEUTRALIZATION OF ACID SOLUTIONS CONTAINING DISSOLVED IRON

KATSUJI NODA, SHIGEO UCHIDA AND MICHIIHIKO MIYAZAKI

Department of Chemical Engineering, Shizuoka University, Hamamatsu 432

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Experimental data on the effects of operating conditions such as pH, particle diameter, concentration of limestone, presence of dissolved iron ions, and species of sparged gases on the neutralization rates of acid waters containing metal ions by limestone have been obtained and investigated from thermodynamic and kinetic points of view. The concentrations of dissolved ions in the solution at a given pH and the rates of dissolution are explained respectively by an equilibrium model and a model based on an instantaneous reversible reaction of calcite and hydrogen ion. This rate model shows good agreement with the experimental data.

Introduction

Neutralization of acid waters containing iron ions has been practiced using inexpensive lime. However, the cost of treatment by lime is now significant inasmuch as its price has recently increased. Attention has therefore been paid to the use of limestone, which is less expensive than lime. Important aspects of the use of limestone are its lower reactivity and the inhibition of the process by precipitates on limestone in the presence of large quantities of sulfate (when neutralizing sulfuric acid) and/or metal ions.

To develop a kinetic model for the estimation of the dissolution rate of limestone, some experimental and theoretical studies have been reported. Uchida *et al.*¹¹⁾ measured the rate of dissolution of pulverized limestone into acid solutions and showed that the data obtained were explained by a model in which a diffusion process involving hydrogen ion and dis-

solved calcium carbonate was assumed to be a rate-controlling step. Barton and Vatanatham¹⁾ showed that the dissolution of limestone was described by a shrinking-particle model and that the rate of neutralization of sulfuric acid by limestone was controlled by hydrogen ion diffusion in the pH range of 2 to 6. Rochelle *et al.*^{2,10)} reported a model which was constructed by assuming instantaneous equilibria in the boundary layer around a CaCO₃ particle for all diffusing species except CO₂. Volpicelli *et al.*¹²⁾ measured the neutralization rate of acid waters containing aluminum ions by limestone and showed that the limestone dissolution rate was limited by the diffusion at the solid-liquid interface, and that the precipitation of aluminum hydroxide and the CO₂ desorption were also rate-determining steps. Volpicelli *et al.*¹³⁾ also measured the dissolution rate of limestone into a waste water containing sulfuric acid from a sugar plant, and showed that to achieve adequate neutralization rate it was necessary to have a surface area above a certain value that seemed to be about

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400–450 m⁻¹ in the solution. In recent work with lime, Jenke *et al.*⁶⁾ studied the neutralization of acidic waste waters containing various base metals and analyzed the process by computer simulation.

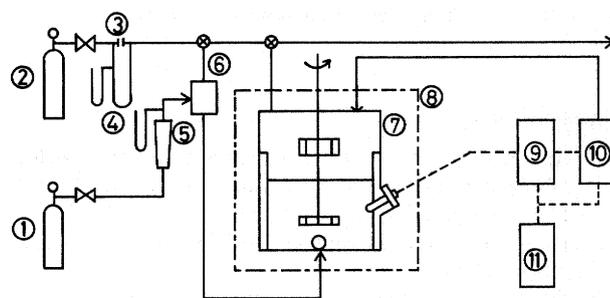
The purpose of this work is to simulate the dissolution rate of limestone over a wide range of pH values from the initial state to equilibrium. Two experimental methods, the pH-stat method and the pH-drift method, are employed to obtain data on the neutralization rate of acid waters containing iron ions by limestone. Experimental variables are the pH, the particle diameter, the concentration of limestone, the presence of dissolved iron ions, and the kinds of sparged gases.

1. Experimental

A schematic diagram of the apparatus used in this study is shown in Fig. 1. The dissolution of limestone was carried out in a stirred tank with a gas sparger located at the bottom. During the experiments, a gas was bubbled into the liquid in the tank. The main part of the tank consisted of a Pyrex glass bottle of 142 mm diameter and 293 mm height, equipped with 8 baffles of 10 mm width. Two 8-blade impellers of 70 mm diameter were used for mixing the gas and the liquid at a constant speed of 6.5 s⁻¹. The gases to be sparged were supplied from cylinders of N₂, O₂, and CO₂ and mixed in a gas mixer to the desired concentration. The rate of sparged gas was 2.0 × 10⁻⁵ m³/s, and the liquid volume was 1.5 × 10⁻³ m³. The temperature of the liquid in the stirred tank was maintained at 298 ± 1 K.

An acid water containing given concentrations of sulfate and iron ions was prepared in the stirred tank. When a given amount of limestone with prescribed particle diameter was put into that solution, an experimental run was begun.

Two experimental methods, the pH-stat method and the pH-drift method, were employed. In the former, the rate of dissolution was measured by the titration of sulfuric acid solution. During the titration, the rate of addition of acid was continuously adjusted to maintain the pH of slurry at the desired constant value throughout. In the latter method, the pH of the slurry increased gradually according to the dissolution of limestone and the pH was continuously monitored. The rate of neutralization was determined by the pH change with time or the change in total calcium in the solution. In both methods, samples were taken from the tank by a transfer pipet and analyzed as follows. The concentrations of total calcium and iron ions were determined by an atomic absorption spectrophotometer. The ferrous ions were determined by the phenanthroline method. For the concentration of carbon dioxide in the gas phase, samples were drawn by a microsyringe and injected



1: O₂ or CO₂ cylinder
2: N₂ cylinder
3: Orifice
4: Manometer
5: Flow meter
6: Gas mixer
7: Bubble-agitated vessel
8: Constant-temperature bath
9: pH meter
10: pH stat
11: Recorder

Fig. 1. Experimental apparatus

Table 1. Limestone composition (weight %)

Ignition loss	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Total
43.30	0.26	0.24	0.16	54.96	0.51	99.43

into a gas chromatograph. The composition of limestone used in this study is shown in Table 1.

2. Equilibrium

In the bulk liquid phase, it is assumed that all components are in equilibrium with one another, and that dissolved CO₂ is also in equilibrium with the gas. However, these components are not in equilibrium with solid phase and dissolution of limestone continues to saturation. At saturation these components are in equilibrium with solid phase and their concentrations can be calculated from the solubility products.

The concentrations of each ion and ion pair are calculated from chemical equilibrium constants and initial conditions. These equilibrium constants are cited from the literature.^{8,9)}

It is necessary to estimate the activity coefficients of ions for the calculation of equilibrium concentrations. The extended Debye-Hückel equation used to calculate them is given as follows⁹⁾:

$$\log \gamma = \frac{Az^2 \sqrt{I}}{1 + aB \sqrt{I}} \quad (1)$$

where I is an ionic strength defined by:

$$I = (1/2) \sum C_i z_i^2 \quad (2)$$

The activity coefficients of molecules (ion pairs) are given by Eq. (3)³⁾:

$$\log \gamma = 0.076 I \quad (3)$$

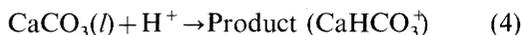
The concentration of each species can be calculated by an iteration method from the chemical equilibria

and some constraints (mass balance, pH, P_{CO_2}).

3. Kinetics

It has been reported by some investigators^{1,11} that the limestone dissolution rate is limited by the diffusion at the solid-liquid interface. The rate-controlling species has been considered to be hydrogen ion. However, their models can be applied to the middle range of pH (about 3–5).

Uchida *et al.*¹¹ simulated the neutralization of sulfuric acid with limestone, assuming that the following reaction (Eq. (4)) is instantaneous and irreversible (Fig. 2) and that all other reactions are in equilibrium.



The rate of dissolution was expressed as:

$$Rd = K_s \left(1 + \frac{[H^+]}{[CaCO_3]_{sat}} \right) [CaCO_3]_{sat} \quad (5)$$

where the diffusion coefficients of all species are assumed to be equal. The model of Uchida *et al.* explains the dissolution rate well in the pH range of about 3 to 5. However, Eq. (5) is not applicable to the condition near equilibrium with the solid $CaCO_3$. Therefore, Eq. (5) may be modified as follows.

The reaction expressed by Eq. (4) is assumed to be an instantaneous, reversible reaction and to be second-order with respect to the forward reaction and first-order with respect to the reverse reaction.

The rate of this reaction is given by⁷:

$$Rd = K_s \left(1 + \frac{(D_{H^+}/D_{CaCO_3})[H^+]}{[CaCO_3]_{sat} + (D_{H^+}/D_{CaHCO_3^+})/K} \right) \times ([CaCO_3]_{sat} - [CaCO_3]) \quad (6)$$

where

$$K = \frac{[CaHCO_3^+]}{[H^+][CaCO_3]} \quad (7)$$

If it is assumed that the diffusivities of all components are equal and $K \gg 1$ (when $CaCO_3$ may be an ion pair, $K = 2.5 \times 10^8$), then Eq. (7) is simplified to:

$$Rd = K_s \left(1 + \frac{[H^+]}{[CaCO_3]_{sat}} \right) ([CaCO_3]_{sat} - [CaCO_3]) \quad (8)$$

The total amount of calcium at equilibrium with solid $CaCO_3$ and that in the bulk solution at the given pH are employed as the values of $[CaCO_3]_{sat}$ and $[CaCO_3]$. Since the amount of calcium, $[CaCO_3]_{sat}$, varied with that of sulfate even at constant pH, the initial amount of sulfate is used in this calculation. The initial pH was adjusted by the total amount of sulfates.

Although the difference between Eq. (5) and Eq. (8) is not significant below pH of about 4, it becomes

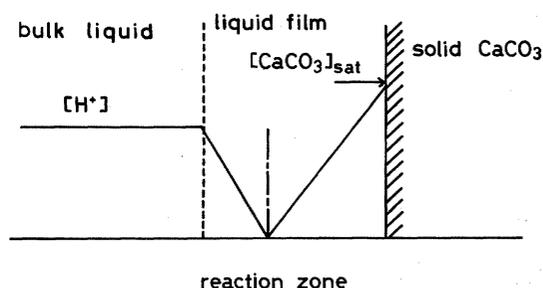
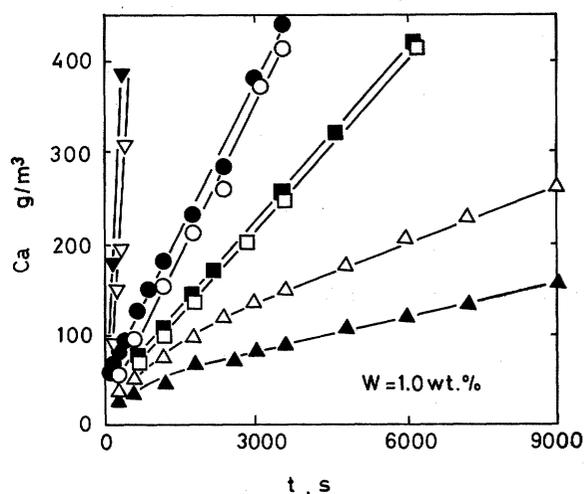


Fig. 2. Concentration profiles of key components around solid-liquid interface (instantaneous irreversible reaction)



Key	pH	CO ₂ (%)	Fe ³⁺ (g/m ³)	d _p (μm)
●	4	0	0	324
▲	5	0	0	324
○	4	20	0	324
△	5	20	0	324
■	4	0	0	547
▼	3	0	0	547
□	4	0	100	547
▽	3	0	100	547

Fig. 3. Effects of CO₂ or Fe³⁺ on dissolution rate of limestone (pH-stat)

important above pH of about 5.

4. Results and Discussion

The experimental results by means of the pH-stat method are shown in Fig. 3. The difference in dissolution rate with and without iron ions is not significant in that method, because the concentration of iron ions in the solution is definitely determined by the pH value. Therefore, the dissolution rate is affected just at the pH where iron hydroxide precipitates.

The partial pressure of CO₂ influences the dissolution rate to a lesser extent in the lower pH range. In this range almost all dissolved CO₂ exists in the form of H₂CO₃ and the dissolution rate is considered to be controlled by the hydrogen ion transfer. However, in

the range of higher pH the dissolved CO_2 is converted to HCO_3^- and the solubility of CO_2 in molecular plus ionic forms is very high compared with that at lower pH. In addition to hydrogen ion transfer controlling, the effect of the other components resulting from dissolved CO_2 on the dissolution rate seems to be significant. This effect on limestone solubility can be seen from the equilibrium calculation. Toprac and Rochelle¹⁰⁾ and Chan and Rochelle²⁾ have reported that the effect of partial pressure of CO_2 on the dissolution rate varies between pH 4 and 5. In this work, that result is also observed, as shown in Fig. 3.

The effect of pH on the dissolution rate at the initial stage is shown in Fig. 4. The effect on dissolution of limestone concentration in the slurry is very important since the rate per unit surface in the slurry may be almost constant irrespective of limestone diameter and concentration in the range of these experimental conditions. It is assumed here that the limestone particles are spherical and that the calculated surface area per unit volume of solution ranges from about 20 to 160 m^{-1} .

The solid line in Fig. 4 shows the calculated values according to Eq. (8). Uchida *et al.*¹¹⁾ employed the saturated concentration of CaCO_3 at $P_{\text{CO}_2}=0$ in pure water as $[\text{CaCO}_3]_{\text{sat}}$. In the present work, $[\text{CaCO}_3]_{\text{sat}}$ is calculated from the initial condition as mentioned above. In the low pH range under about 4, this choice is not so important because the dissolution rate is hydrogen ion diffusion controlling. However, in the high pH range (about 6) up to saturation, the value of $[\text{CaCO}_3]$ is important for the dissolution rate.

In Fig. 4, the solid line is calculated assuming that the dissolution rate constant K_s is $2.7 \times 10^{-3} \text{ m/s}$, although this value is greater than that given by Harriot's correlation.⁴⁾ This may be considered due to the fact that the diffusivity of hydrogen ion is much greater than that of any other species and the effect of P_{CO_2} on the saturated concentration of CaCO_3 . It is seen from Fig. 4 that Eq. (8) may represent the dissolution rate behavior well despite the model equation's simplicity.

The experimental results obtained by the pH-drift method are shown in Fig. 5. As in the pH stat method, the dissolution rate is greatly affected by the limestone concentration in the slurry.

Figure 6 shows a comparison of the concentration profiles of components from the equilibrium calculation with the experimental results. Concentration of calcium in Fig. 6 shows the total calcium, including such forms as Ca^{2+} and CaSO_4 , under the condition of no iron ion and N_2 sparged. The concentration of ferrous ions is suddenly lowered at about pH 6, because of oxidation of ferrous ion by the sparged O_2 gas. The rate of ferrous ion to ferric ion by oxygen has been reported by Higuchi *et al.*⁵⁾ as follows:

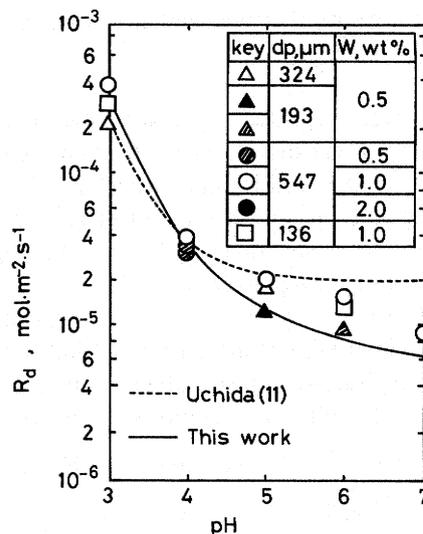


Fig. 4. Dissolution rate of limestone into acid solution—Comparison of calculated values with data (pH-stat, N_2 gas sparged, no iron ion)

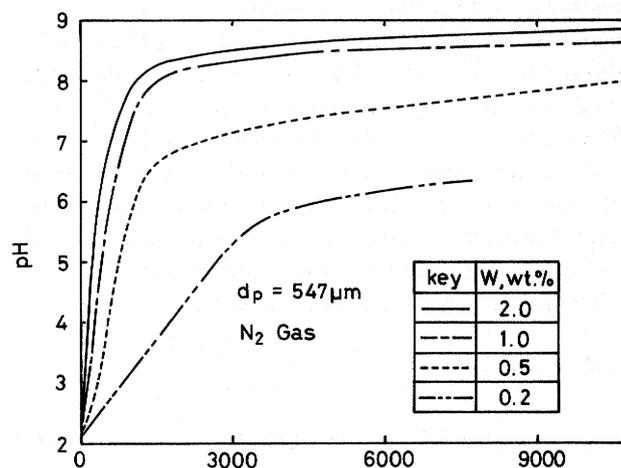


Fig. 5. Effects of slurry concentration on dissolution rate (pH-drift, no iron ion)

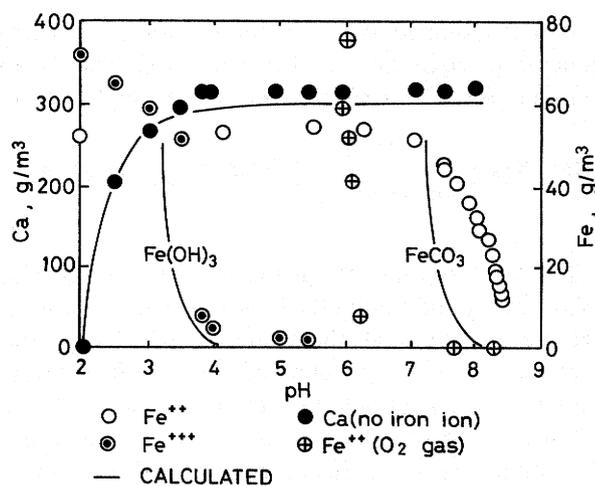


Fig. 6. Behavior of component by the pH-drift method, results from separate runs starting at pH 2 ($d_p=136 \mu\text{m}$, $w=1.0\%$, N_2 gas sparged)

$$\frac{-d[\text{Fe}^{2+}]}{dt} = Kr[\text{Fe}^{2+}][\text{O}_2(\text{aq.})][\text{OH}^-]^{1.33} \quad (9)$$

where

$$Kr = 3.1 \times 10^3 \text{m}^{2.33}/(\text{mol}^{2.33} \cdot \text{s}) \quad (10)$$

The rate of oxidizing Fe^{2+} to Fe^{3+} is shown in **Table 2**. Table 2 shows that appreciable oxidation of Fe^{2+} to Fe^{3+} takes place at about pH 6.

Conclusion

(1) The dissolution rate of CaCO_3 for the neutralization of acid water is affected by pH, particle concentration, particle diameter, and partial pressure of CO_2 .

(2) Only at the pH where metal ion precipitates does the dissolved metal ion (iron) affect the dissolution rate.

(3) A modified form of the model of Uchida *et al.* well correlates the dissolution rate up to the neutral range (pH 3 to 7).

(4) The behavior of ions in the solution is explained by the equilibrium model.

Nomenclature

A, B	= constants depending upon type of solvents and temperature in Eq. (1)	
a	= parameter corresponding to size of ion in Eq. (1)	
$[C_i]$	= concentration of species i	[mol/m ³]
D	= diffusivity	[m ² /s]
d_p	= mean diameter of solid particles	[μm]
I	= ionic strength	[mol/m ³]
K	= equilibrium constant	[m ³ /mol]
\tilde{K}_s	= dissolution rate constant	[m/s]

Table 2. Rate of oxidization of Fe^{2+} to Fe^{3+}

pH	5	6	7
$-d[\text{Fe}^{2+}]/dt$ [mol/(m ³ ·s)]	0.073	4.8	100

Kr	= reaction rate constant in Eq. (9)	[m ^{2.33} /(mol ^{2.33} ·s)]
P_{CO_2}	= partial pressure of carbon dioxide	[Pa]
Rd	= rate of dissolution of limestone	[mol/(m ² ·s)]
z	= charge of ion	
γ	= activity coefficient	

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