

The Effect of Decompression on the Dissolution Reaction of Calcium Carbonate

Makoto Takahashi^{*1}, Tomonori Nagaya¹, Takaya Suzuki¹, Yuki Yogo¹, Tatsunosuke Omi¹, Masahiro Tahashi², Sadao Ohkido³, Yukio Inoue⁴, Satoshi Yamaguchi⁵

¹Department of Applied Chemistry, College of Engineering, Chubu University, Matsumoto-cho 1200, Kasugai, Aichi 487-8501, Japan

²Department of Electronic Engineering, College of Engineering, Chubu University, Matsumoto-cho 1200, Kasugai, Aichi 487-8501, Japan

³Teacher-training Course, Chubu University, Matsumoto-cho 1200, Kasugai, Aichi 487-8501, Japan

⁴Showa Water Industries Co., Ltd., 2-1 Souden Higashimati, Gifu-city, Gifu 502-0843, Japan

⁵Daiyu Incorporated, 4-27-6 Kozone, Touonaka, Ohsaka 561-0813, Japan

^{*1}thinfilm@isc.chubu.ac.jp; ²tahashi@isc.chubu.ac.jp; ³sohki871533@kfa.biglobe.ne.jp; ^{4,5}y.inoue@showa-water.co.jp

Abstract-Calcium carbonate (CaCO₃) is one of the main components of mineral scale. Removing this CaCO₃ scale is very important in many fields of the industry, such as the boiler, the air conditioner, the oil well drilling and so on. In this paper, CaCO₃ was dissolved under various decompression conditions (1.0, 0.50, and 0.20 atm) and studied the relationship between the decomposition efficiency and acid concentration under various decompressions. It was found out that when the proton concentration was near the stoichiometric ratio for the dissolution reaction ($\text{CaCO}_3 + 2\text{H}^+ \longrightarrow \text{Ca}^{2+} + \text{H}_2\text{O} + \text{CO}_2(\text{gas})$), decomposition efficiency increased significantly with decreasing pressure. This phenomenon was explained by the Le Chatelier's Law, stirring effect due to the ascent of CO₂ bubbles, and the cavitation effect of CO₂ bubbles.

Keywords- Calcium Carbonate; Mineral Scale; Dissolution Reaction; Decompression Effect

I. INTRODUCTION

Calcium carbonate (CaCO₃) is one of the main components of mineral scales (along with MgCO₃ and CaSiO₄) that form on heat exchangers and inside pipes. This mineral scale causes various problems. For, scale formation inside water pipes inhibits the flow of water and is a major cause of pipe burst [1-3]. The thermal conductivities at room temperature of calcium carbonate and calcium silicate are 0.5~1 and 0.05 W/(m·K), respectively [4]. These thermal conductivities are much smaller than those of metals, such as Cu (401 W/(m·K) at 27°C) or Fe (80.2 W/(m·K) at 27°C) [4], thus scales formed on the metal of a heat exchanger decreases the heat exchange efficiency [5, 6], and thereby reduces production and economy. In the past two decades, interest in environmental problems with the goal of saving energy and minimizing environmental load has increased. This has elevated the importance of studying scale and its effects.

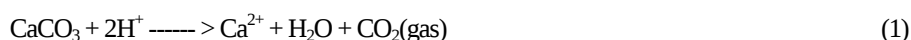
Research on scale, especially mineral scale which primarily consists of calcium carbonate, has been conducted in various industrial fields. This research can be classified into three themes:

(Theme 1) The formation reaction and its mechanism of calcium carbonate in the liquid phase [7-10].

(Theme 2) Developments of scale inhibitors and methods for preventing calcium carbonate scale [11-17].

(Theme 3) Developments in technology for scale removal [18-20].

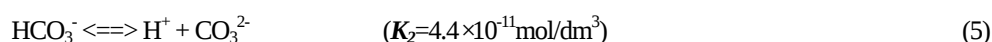
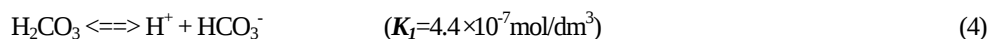
Most research papers have dealt with themes 1 and 2, while fewer have tackled theme 3. Calcium carbonate is removable as it dissolves with acid according to the following overall reaction (1). Research into scale removal technology has been performed by many companies with the development results primarily published as patents [21-24].



Using water treatment reagents and scale removal technology developed by a co-worker [25]. In general, >10 wt% HCl solution or >30-40 wt% organic acid solution (e.g., citric acid, glycolic acid) is used to remove calcium carbonate scale. Reducing the consumption of these inorganic or organic acids in scale dissolution will lead to a reduced environmental load and improved human safety, as well as an increase in economic efficiency. However, merely decreasing the total amount or concentration of the reagent will slow the dissolution and

extend reaction time and labor needed. Therefore, new methods are desired for the dissolution of calcium carbonate.

Reaction (1) represented above refers to the dissolution of calcium carbonate using hydrochloric acid. In this case, the velocity of the dissolution reaction can be considered to be the velocity of the formation of CO_2 gas. Oppositely, the formation reaction of CaCO_3 scale can be considered as follows:



The dissolution reaction of CaCO_3 scale can be regarded as the inverse reaction of this CaCO_3 scale formation reaction. The velocity and the total amount of $\text{CO}_2(\text{gas})$ formation observed in the dissolution reaction is proportional to the difference between the saturated concentration of H_2CO_3 in the bulk solution, which obeys Henry's law, and the concentration of H_2CO_3 near the surface of CaCO_3 scale. Therefore, if the partial pressure of CO_2 in the gas phase can be kept low during the dissolution reaction, this difference in concentrations can be maintained as a large value. As a result, the fast velocity of the CaCO_3 scale dissolution may be maintained. This investigation tried to confirm this idea. In order to reduce the partial pressure of CO_2 gas in the reaction system, the total pressure of the reaction system was reduced using a rotary pump and dissolved chalk. The chalk was used as CaCO_3 scale substitute and was dissolved in 1.0 wt% HCl solution under 0.1 atm. Fig. 1 compares the appearance of the solutions under 1 atm with reaction times of (a) 0.5 min and (b) 5 min, and under 0.1 atm with reaction times of (c) 0.5 min and (d) 5 min. When the chalk was dissolved under 1 atm, a big amount of small bubbles formed on the sample surface and the solution was transparent at the reaction start 0.5 min later (Fig. 1(a)). At 5 min (Fig. 1(b)), the solution became cloudy but a large lump of chalk was clearly observed. In contrast, when the chalk was dissolved under 0.1 atm, many large bubbles were generated and the solution was cloudy at the reaction start 0.5 min later (Fig. 1(c)). At 5 min (Fig. 1(d)), the solution became cloudier and most of the sample was dissolved with the remainder observed as a small amount of powders on the bottom of the beaker. These results indicate that, whit CaCO_3 scale dissolution under pressure lower than 1 atm, a rapid dissolution rate can be maintained so that the scale dissolution can finished in a smaller amount of time. No attempts have been made to estimate the effects of decompression on the dissolution of calcium carbonate scale.

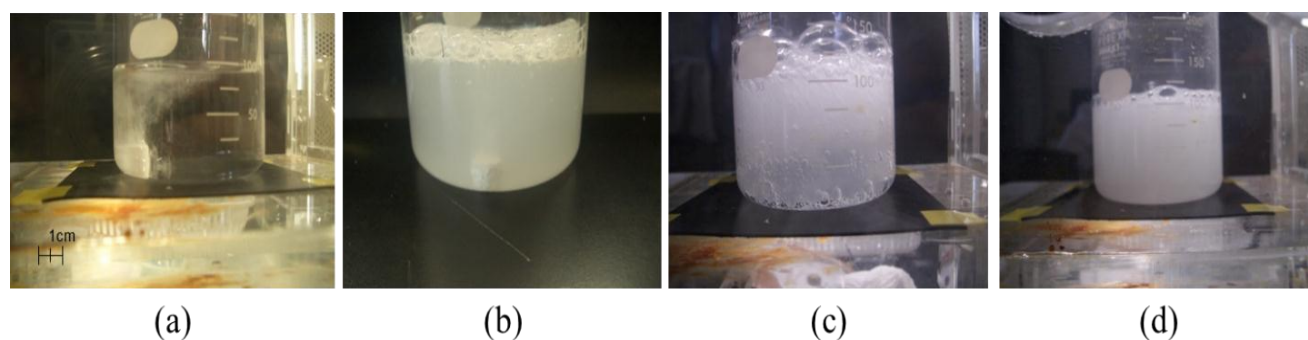


Fig. 1 Comparison of a solution in a beaker under (a), (b) 1 atm and (c), (d) 0.1 atm for various reaction times.

Reaction times: (a) 0.5 min (at 1 atm), (b) 5 min (at 1 atm), (c) 0.5 min (at 0.1 atm), (d) 5 min (at 0.1 atm)

Dissolution solution: 1.0 wt% (0.27 mol/L) HCl solution 100 mL, Sample: CaCO_3 (Chalk) (purity > 90 %) 0.50 g

The main purpose of this work is to develop a new method for the dissolution of calcium carbonate scale that has reduced impact on the environment and human health. Calcium carbonate was dissolved with diluted hydrochloric acid, which worked well in scale removal work, under various decompression conditions and semi-quantitatively examined the effects of decompression on the dissolution of calcium carbonate scale.

II. EXPERIMENT

A. Materials

In these experiments, commercial chalk (purity: >90%, minimum guarantee purity: >85%, diameter: 11 mm, density: 1.7 ± 0.1 g/mL) without a polymer coating, purchased from Hagoromo Bunngu Co. Ltd., was used as a substitute for calcium carbonate (CaCO_3) scale samples. After the chalk was cut to a suitable size, it was dried in a drying oven at 70°C for 24 h. After drying and cooling in the desiccator, 0.500 ± 0.005 g chalk samples were made by polishing with emery paper (#1000 and 2000). The weight of the sample was measured with an electronic balance (Shimadzu Corporation, AY-220).

Diluted hydrochloric acid solutions (concentration: 0.50, 1.00, and 2.50 wt%) were prepared from concentrated hydrochloric acid (reagent chemical, 36 wt%) and ultrapure water. The densities of the diluted hydrochloric acid solutions were in the range between 1.00 [g/mL] (0.10 wt% HCl) and 1.01 [g/mL] (2.50 wt% HCl).

The sucking filtration was done with qualitative filter paper (Toyo Roshi Kaisha, Ltd., No. 4A, nominal rating: $1\mu\text{m}$). The pH values of filtrates were measured by a pH meter (HORIBA, Ltd., F-21 pH meter).

B. Experimental Setup and Procedure

Fig. 2(a) provides a schematic diagram of the experimental setup, which was composed of the vacuum desiccator (size: $210 \times 210 \times 210$ mm/mm/mm, volume: 9.26 L) with a vacuum gauge, a 200 mL beaker, and a vacuum pump (ULVAC, PD-52, exhaust speed: 50 L/min).

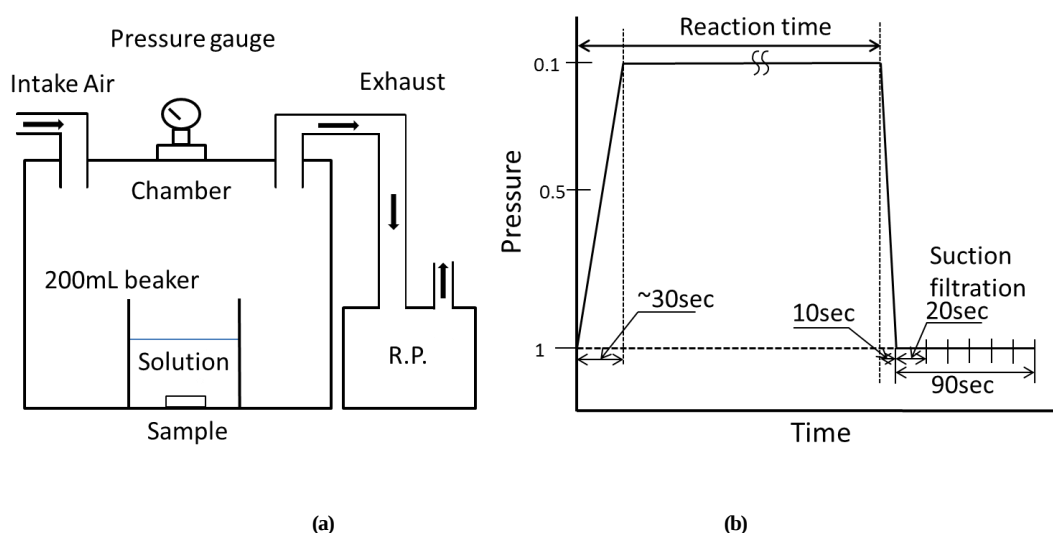


Fig. 2 Schematic diagrams of (a) the experimental system and (b) the experimental time schedule

The experimental procedure is described as follows, with the schematic time schedule shown in Fig. 2(b).

- (1) Place the beaker with 100 ml diluted hydrochloric acid into the vacuum desiccator.
- (2) Put the sample into the beaker.
- (3) Decompress the desiccator until the predetermined pressure is reached.

The pressure in the desiccator reached the predetermined value within 30 sec.

The predetermined pressures were 1 atm, 0.50 atm, and 0.10 atm.

- (4) The dissolution reaction occurred over a predetermined period.

The predetermined periods (reaction times) were 3, 5, 7, 10, and 15 min.

- (5) After the completion of the reaction, the pressure was raised to 1 atm.

- (6) The solution was filtered by suction. The pH value of the filtrate was measured by the pH meter.

(7) The undecomposed residue left on the filter was washed by 10mL ultrapure water by suction filtration. This procedure was repeated five times, after which the pH value of the filtrate was about 7. The pH value check was performed using pH litmus paper. (The filtration and washing operations were finished within about 1 min.)

(8) The washed sample was dried in a drying oven at 70°C for 24 h.

(9) The undecomposed residue was weighted using the electronic balance.

(10) The efficiency of the dissolution reaction was calculated by following equation.

$$\eta(\text{efficiency}) = (W_0[\text{g}] - W_{\text{res}}[\text{g}]) / W_0[\text{g}] \times 100 \quad (7)$$

where W_0 is the original weight of the chalk [g], and W_{res} is the weight of the residue left on the filter [g].

When > 5 wt% HCl solutions were used, the dissolution reaction with fast reaction rate was progressing during the filtration and we could not obtain data with good reproducibility. Therefore, in order to obtain data with good reproducibility, HCl solutions were used, their concentration were lower than 2.5 wt%. The experiments were repeated 5~7 times under the same conditions. The efficiency of dissolution reaction shown in the figures is the average values and the size of the characters in the figure shows the range of the experimental error.

III. RESULTS

Fig. 3 shows the relationship between the reaction time and the efficiency of the dissolution reaction observed using solutions containing various HCl concentrations under 1 atm (open system): (a) 2.5 wt% (0.693 mol/L)(Δ), (b) 1.0 wt% (0.275 mol/L)($\square$), and (c) 0.5 wt% (0.132 mol/L)($\circ$). For the 2.5 wt% HCl solution (Fig. 3(a)), the dissolution efficiency increased rapidly with increasing reaction times, and at about 9 min the efficiency reached 85 %, which was the guaranteed minimum purity of CaCO_3 in the chalk. For 1.0 wt% HCl solution (Fig. 3(b)), the dissolution efficiency linearly increased until 7 min, and then gradually increased. The dissolution efficiency reached 80% at 15 min. For 0.5 wt% HCl solution (Fig. 3(c)), the dissolution efficiency gradually increased and reached 38% at 15 min. These results were as expected, due to the fact that when CaCO_3 or metals are dissolved with acid, the rate of the dissolution increases with an increasing concentration of the acid solution used. Fig. 4 represents the relationship between the reaction time and the efficiency of the dissolution reaction observed using various concentrations of HCl solutions under various pressures: (a) 1.0 atm ($\blacklozenge$), (b) 0.5 atm ($\square$), and (c) 0.1 atm (Δ) (closed system). Fig. 4(1) represents the relationship between the reaction time and the efficiency of the dissolution reaction observed using 2.5 wt% (0.693 mol/L) HCl solution. The result of Fig. 4(1)(a) is the same as that of Fig. 3(a). For the pressure of 0.5 atm (Fig. 4(1)(b)) the dissolution efficiency increased more rapidly and reached 85% at 7 min. When the reaction occurred under 0.1 atm (Fig. 4(1)(c)), the dissolution efficiency reached 85% in less than 3 min. From these results, it was found that the end of the dissolution reaction occurred earlier from 9 min to 3 min when pressure was decreased from 1 atm to 0.1 atm. When the dissolution reactions occurred under decompression, lumps of the sample disintegrated into numerous small grains within 3 min after the beginning of the decompression. This disintegration became remarkable as the pressure of the system was lowered from 0.5 atm to 0.1 atm. After the reaction, all reaction solutions were filtered and divided into non-reactant (the residual substance) and reaction solution. In these experiments, the residual substances left on the filter were a mixture of very small particles and the powder with filtrates being transparent.

Fig. 4(2) shows the relationship between the reaction time and the efficiency of the dissolution reaction using 1.0 wt% (0.275 mol/L) HCl solution. The result of Fig. 4(2)(a) is the same as that of Fig. 3(b). For the pressure of 0.5 atm (Fig. 4(2)(b)), the dissolution efficiency increased faster than that under 1 atm, and reached 85% at 15 min. For 0.1 atm (Fig. 4(2)(c)), the dissolution efficiency linearly increased and the efficiency reached 85% at 5 min. According to these results, it was found that the end of the dissolution reaction occurred earlier, from over 15 min down to 5 min when the pressure was decreased from 1 atm to 0.1 atm. In these experiments, the same phenomena observed in Fig. 4(1)(b) and 4(1)(c) occurred. The samples disintegrated into numerous smaller grains at 7 min from the beginning of decompression. This disintegration became remarkable as the pressure of the system was lowered. After the reaction, all reaction solutions were filtered and divided into non-reactant (the residual substance) and reaction solution (filtrate). At a reaction time of 5 min (at 0.1 atm), the residual substance left on the filter changed as lump $\rightarrow$ powdery mixture of a few smaller grains and powder $\rightarrow$ powder, as the pressure was decreased from 1 atm to 0.1 atm. In these experiments, all filtrated solutions were transparent.

Fig. 4(3) shows the relationship between the reaction time and the efficiency of the dissolution reaction observed using 0.5 wt% (0.132 mol/L) HCl solution. The result of Fig. 4(3)(a) is the same as that of Fig. 3(c). For the pressure of 0.5 atm (Fig. 4(3)(b)), the dissolution

efficiency increased linearly until 7 min. The values of the dissolution efficiency at each time frame were larger than those observed at 1 atm, and reached 65% at 15 min. For 0.1 atm (Fig. 4(3)(c)), the dissolution efficiency linearly increased until 7 min, and then it increased more gradually and reached 80% at 15 min. According to these results, the dissolution efficiency at a reaction time of 15 min increased from 38% to 80% when pressure was reduced from 1 atm to 0.1 atm. At the reaction time of 5 min, the residual substances changed in the following way, as the pressure decreased from 1 atm to 0.1 atm:

Lump $\rightarrow$ mixture of small grains and powder $\rightarrow$ mixture of smaller grains and powder

In these experiments, all filtrated solutions were transparent and their pH values were lower than $\text{pH} = 1.5 \pm 0.2$.

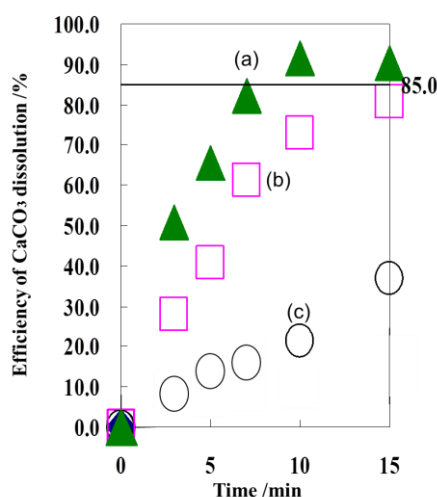


Fig. 3 The relationship between the efficiency (η) of the CaCO_3 dissolution reaction and the reaction time with the various concentrations of HCl solution under 1 atm at room temperature. HCl concentration: (a) 2.5 wt% (0.693 M) (Δ), (b) 1.0 wt% (0.275 M) ($\square$), (c) 0.5 wt% (0.132 M) ($\circ$)

Sample: 0.500 g CaCO_3 (0.0045 mol)

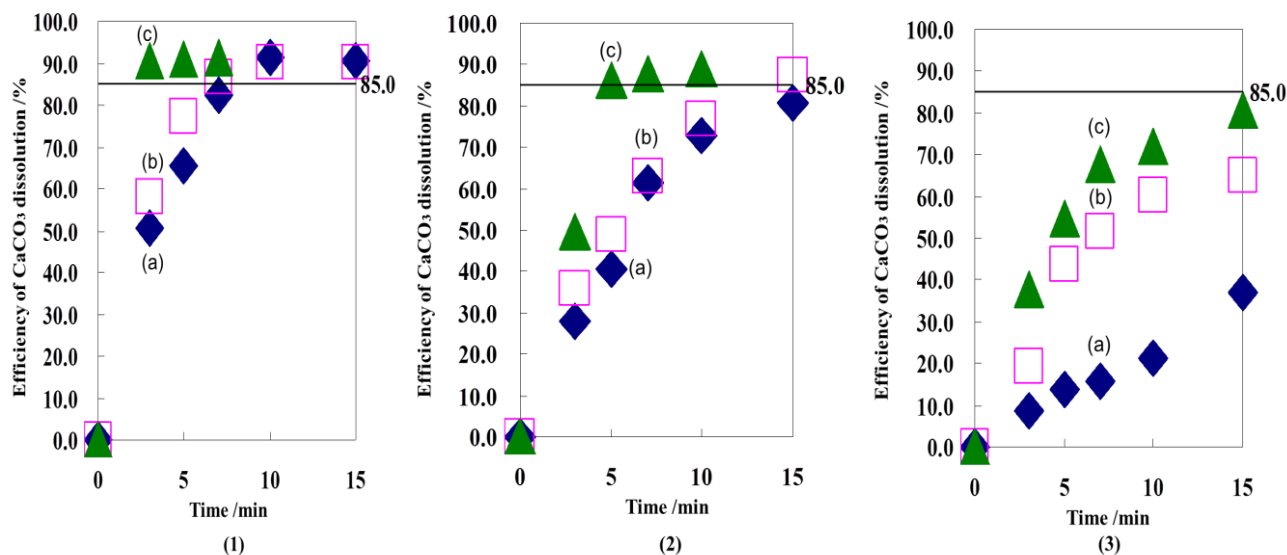


Fig. 4 The relationship between the efficiency (η) of the CaCO_3 dissolution reaction and the reaction time with various concentration of HCl solutions under various pressures.

HCl concentration: (1) 2.5 wt% (0.693 M), (2) 1.0 wt% (0.275 M), (3) 0.5 wt% (0.132 M) Pressure: (a) 1 atm ($\blacklozenge$), (b) 0.5 atm ($\square$), (c) 0.1 atm ($\blacktriangle$)

Sample: 0.500 g CaCO_3 (0.0045 mol)

The results obtained in these experiments indicate that when the calcium carbonate is dissolved with an acid solution under reduced pressure, the total amount of acid used for the dissolution can be decreased while maintaining a high dissolution velocity. Diminishing the total

amount of acid used will reduce the negative impact on the environment and on human health.

IV. DISCUSSION

The results obtained in our experiments are summarized as follows:

(1) The dissolution rates of calcium carbonate in diluted HCl solution increased with reduced pressure. Especially, when the proton concentration nears the stoichiometric ratio, the decompression effects become more evident. The efficiency of the dissolution reaction with 0.5 wt% HCl increased from 38% (at 1 atm) to 80% (0.1 atm) at a reaction time of 15 min.

(2) The disintegration of the lump of calcium carbonate became noticeable as the pressure of the system was lowered from 1.0 atm to 0.1 atm.

The dissolution reaction of the calcium carbonate solid with the acid solution is a heterogeneous reaction. It is well known that the velocity of a heterogeneous reaction depends on the concentration of the reactant, the surface area of the solid sample, the stirring speed of the solution, and the temperature. However, the effect of decompression on the reaction rate has not been discussed. Here, we examine why the dissolution rate increases with reduced pressure in the reaction system. We discuss possible reasons from three viewpoints:

- (1) Promotion of the dissolution reaction due to Le Chatelier's Law;
- (2) The stirring effect due to an increase in the ascent speed of bubbles;
- (3) An increase in the surface area of the solid sample due to its disintegration by the cavitation effect.

(Promotion of the dissolution reaction due to Le Chatelier's Law)

In our experiment, all filtered solutions were transparent and their pH values were less than 2 ($\text{pH} < 2$). These results indicated that the species of carbonic acid (H_2CO_3) in the solution was H_2CO_3 , and not HCO_3^- , because of the acid dissociation constant of carbonic acid ($\text{H}_2\text{CO}_3 \rightleftharpoons \text{H}^+ + \text{HCO}_3^-$, $K_1 = 4.4 \times 10^{-7} \text{ [mol/dm}^3\text{]}$). Thus, the dissolution reactions are considered to be as follows:



Reaction (9) is the acid-base reaction and its rate is fast under our experimental condition ($\text{pH} < 2$). Reactions (11) and (10) are the reverse reactions of the dissolution reaction and the hydration reaction, respectively. It is known that the concentration of the solute cannot be higher than its saturated concentration. In our experiment (the reaction generating carbon dioxide gas), when the concentration of the solute (H_2CO_3 in this experiment) in the interface layer on the surface of the solid sample becomes higher than the saturated concentration of carbonic acid (H_2CO_3) in the bulk solution. Therefore, the rates for reactions (10) and (11) are also fast. Fig. 5 shows a schematic of the mass transfer and reactions in our experimental system. The pressure in the reaction chamber was controlled by the vacuum pump (exhaust velocity $V \text{ [L/min]}$ at 1 atm) and the intake valve. Therefore, the mass balance of gas molecules per unit time can be expressed as in Eq. (12).

$$n_{\text{gas}}(\text{cham}) = n_{\text{gas}}(\text{in}) + n_{\text{gas}}(\text{gen}) - n_{\text{gas}}(\text{ex}) \quad (12)$$

$n_{\text{gas}}(\text{cham})$ is the total mole number of gas in the chamber per unit time [mol/sec], $n_{\text{gas}}(\text{in})$ is the mole number of the intake gas per unit time [mol/sec], $n_{\text{gas}}(\text{gen})$ is the mole number of molecules generated by the reaction per unit time [mol/sec], and $n_{\text{gas}}(\text{ex})$ is the mole number of exhaust gas per unit time [mol/sec].

Our experiments were performed under constant low pressure (P_{cham} [atm]) and in a chamber with a constant volume (V_{cham} [L]). If the gas and the solution are considered as the ideal state, the mole number of the gas $n(\text{cham})$ which exists in the chamber per unit time can be calculated:

$$n_{\text{gas}}(\text{cham}) = P_{\text{cham}} \cdot (V_{\text{cham}} / (R \cdot T)) \quad (13)$$

R is the gas constant ($0.08205 \text{ [atm} \cdot \text{L} \cdot \text{mol}^{-1} \cdot \text{T}^{-1}]$) and T is the absolute temperature [K].

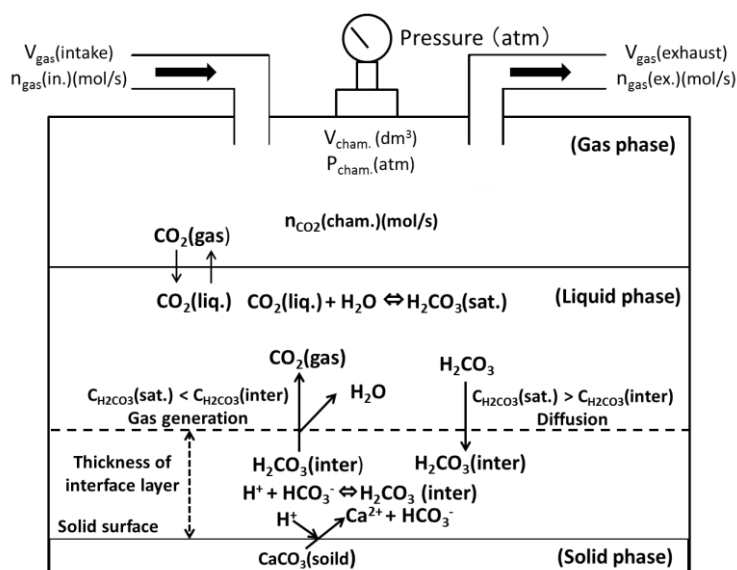


Fig. 5 Schematic diagram of the reactions and mass transfer process in the experimental system

$n_{\text{gas}}(\text{ex})$ can be calculated using the following equation:

$$\begin{aligned} n_{\text{gas}}(\text{ex}) &= P(1\text{atm}) \cdot V_{\text{gas}}(\text{exhaust}) \left[\frac{\text{L}}{\text{min}} \right] / (60[\text{sec}] \times R \cdot T) \\ &= \frac{V_{\text{gas}}(\text{exhaust})}{60R \cdot T} \quad [\text{mol/sec}] \end{aligned} \quad (14)$$

$V_{\text{gas}}(\text{exhaust})$ is the exhaust velocity of the vacuum pump at 1 atm [L/min].

When Eq. (13) and Eq. (14) are substituted into Eq. (12), Eq. (15) is obtained.

$$\begin{aligned} n_{\text{gas}}(\text{in}) + n_{\text{gas}}(\text{gen}) &= n_{\text{gas}}(\text{cham}) + n_{\text{gas}}(\text{ex}) \\ &= P_{\text{cham}} \cdot \left(\frac{V_{\text{cham}}}{R \cdot T} \right) + \frac{V_{\text{gas}}(\text{exhaust})}{60R \cdot T} \quad [\text{mol/sec}] \end{aligned} \quad (15)$$

$n_{\text{gas}}(\text{gen})$ is expressed as follows,

$$n_{\text{gas}}(\text{gen}) = n_{\text{H}_2\text{O}}(\text{gen}) + n_{\text{CO}_2}(\text{gen}) \quad (16)$$

$n_{\text{H}_2\text{O}}(\text{gen})$ is the mole number of water evaporating from the solution per unit time [mol/sec].

If the evaporation rate of the water is fast and the chamber is in the saturated steam pressure, $n_{\text{H}_2\text{O}}$ can be calculated as follows:

$$n_{\text{H}_2\text{O}}(\text{gen}) = \frac{P_{\text{H}_2\text{O}} \cdot V_{\text{cham}}}{R \cdot T}$$

$P_{\text{H}_2\text{O}}$ is the saturated steam pressure [atm] at T [K], and $n_{\text{CO}_2}(\text{gen})$ is the mole number of CO_2 released from the dissolution reaction per unit time [mol/sec].

The results shown in Fig. 4(1)-4(3), when the pressure decreased from 1 atm to 0.1 atm, the dissolution efficiency (η) increased linearly until about 7 min. These results implied that the dissolution rates were regarded as constant until about 7 min. Thus, $n_{\text{gen}}(\text{CO}_2)$ can be estimated from the time dependence of the dissolution efficiency.

$$\eta(\text{dissolution efficiency})(\%) = \frac{n_{\text{CaCO}_3}(\text{dis})}{n_0(\text{CaCO}_3)} \times 100 \quad (17)$$

$n_{\text{CaCO}_3}(\text{dis})$ is the mole number of dissolved CaCO_3 in a reaction time, and $n_0(\text{CaCO}_3)$ is the mole number of the initial CaCO_3 .

$$n_{\text{CO}_2}(\text{gen}) = n_{\text{CaCO}_3}(\text{dis}) = \left(\frac{\eta}{100}\right)n_0(\text{CaCO}_3)$$

Therefore, $n(\text{in})$ can be calculated from Eq. (18):

$$n_{\text{gas}}(\text{in}) = n_{\text{gas}}(\text{cham}) + n_{\text{gas}}(\text{ex}) - n_{\text{gas}}(\text{gen}) \quad (18)$$

$$\frac{P_{\text{cham}} \cdot V_{\text{cham}}}{R \cdot T} + \frac{V_{\text{gas}}(\text{exhaust})}{60R \cdot T} - \frac{P_{\text{H}_2\text{O}} \cdot V_{\text{cham}}}{R \cdot T} - n_{\text{CO}_2}(\text{gen})$$

To control the pressure in the chamber, the gas supplied to the chamber is air. Air includes 0.035 mol% CO_2 . Therefore, the mole number of CO_2 molecules ($n_{\text{CO}_2}(\text{cham})$) that are in the chamber at unit time, can be calculated by Eq. (19):

$$n_{\text{CO}_2}(\text{cham}) = n_{\text{CO}_2}(\text{gen}) + n_{\text{gas}}(\text{in})\chi(\text{CO}_2) \quad (19)$$

$\chi(\text{CO}_2)$ is the mole fraction of CO_2 in air: $\chi(\text{CO}_2) = 0.00035$.

The partial pressure of CO_2 gas in the chamber ($P_{\text{CO}_2}(\text{cham})$) can also be calculated.

$$P_{\text{CO}_2}(\text{cham}) = n_{\text{CO}_2}(\text{cham})R \cdot T/V_{\text{cham}} \quad (20)$$

The values of η , $n_{\text{CaCO}_3}(\text{dis})$, and $n_{\text{CO}_2}(\text{gen})$ are shown in Table 1, and the values of the calculated $n_{\text{CO}_2}(\text{cham})$, $P_{\text{CO}_2}(\text{cham})$, and $C(\text{H}_2\text{CO}_3)$ are shown in Table 2. $C_{\text{H}_2\text{CO}_3}(\text{sat})$ is the saturated molar concentration of carbonic acid in the solution, which can be calculated with Henry's law:

$$C_{\text{H}_2\text{CO}_3}(\text{sat}) \left[\frac{\text{mol}}{\text{dm}^3} \right] = K \cdot P_{\text{CO}_2}(\text{cham}) \quad (21)$$

K is the Henry's law constant: $K = 0.032 [\text{mol} \cdot \text{L}^{-1} \cdot \text{atm}^{-1}]$ at 298 K [26].

TABLE 1 THE LIST OF η , $n_{\text{CaCO}_3}(\text{dis})$, AND $n_{\text{CO}_2}(\text{gen})$ AT 3 min UNDER 0.5 atm AND 0.1 atm

	0.5 atm	0.1 atm
η (with 2.5wt% HCl)	0.819 ± 0.020	(0.90~0.85)
η (with 1.0wt% HCl)	0.542 ± 0.033	0.844 ± 0.006
η (with 0.5wt% HCl)	0.381 ± 0.012	0.558 ± 0.011
$n_{\text{CaCO}_3}(\text{dis})(2.5\text{wt}\%) [\text{mol}]$	$(3.69 \pm 0.09) \times 10^{-3}$	$(4.05 \sim 3.8) \times 10^{-3}$
$n_{\text{CaCO}_3}(\text{dis})(1.0\text{wt}\%) [\text{mol}]$	$(2.44 \pm 0.15) \times 10^{-3}$	$(3.80 \pm 0.03) \times 10^{-3}$
$n_{\text{CaCO}_3}(\text{dis})(0.5\text{wt}\%) [\text{mol}]$	$(1.71 \pm 0.06) \times 10^{-3}$	$(2.51 \pm 0.05) \times 10^{-3}$
$n_{\text{CO}_2}(\text{gen})(2.5\text{wt}\%) [\text{mol}/\text{sec}]$	$(1.23 \pm 0.03) \times 10^{-5}$	$(2.13 \sim 2.25) \times 10^{-5}$
$n_{\text{CO}_2}(\text{gen})(1.0\text{wt}\%) [\text{mol}/\text{sec}]$	$(0.813 \pm 0.05) \times 10^{-5}$	$(1.27 \pm 0.01) \times 10^{-5}$
$n_{\text{CO}_2}(\text{gen})(0.5\text{wt}\%) [\text{mol}/\text{sec}]$	$(0.570 \pm 0.02) \times 10^{-5}$	$(0.837 \pm 0.016) \times 10^{-5}$
$n(\text{in}) [\text{mol}/\text{sec}]$	0.212	0.060
$n(\text{in})(\text{CO}_2) [\text{mol}/\text{sec}]$	7.41×10^{-5}	2.10×10^{-5}

TABLE 2 THE VALUES OF THE CALCULATED $n_{\text{CO}_2}(\text{cham})$, $P_{\text{CO}_2}(\text{cham})$, AND $C(\text{H}_2\text{CO}_3)$ AT 3 min UNDER 0.5 atm AND 0.1 atm

	0.5atm	0.1atm
$n_{\text{CO}_2}(\text{cham})(2.5\text{wt}\%)[\text{mol}]$	$(8.64 \pm 0.03) \times 10^{-5}$	$(4.23 \sim 4.35) \times 10^{-5}$
$n_{\text{CO}_2}(\text{cham})(1.0\text{wt}\%)[\text{mol}]$	$(8.22 \pm 0.05) \times 10^{-5}$	$(3.37 \pm 0.01) \times 10^{-5}$
$n_{\text{CO}_2}(\text{cham})(0.5\text{wt}\%)[\text{mol}]$	$(7.98 \pm 0.02) \times 10^{-5}$	$(2.94 \pm 0.01) \times 10^{-5}$
$P_{\text{CO}_2}(\text{cham})(2.5\text{wt}\%)[\text{atm}]$	$(2.28 \pm 0.01) \times 10^{-4}$	$(11.2 \sim 11.5) \times 10^{-5}$
$P_{\text{CO}_2}(\text{cham})(1.0\text{wt}\%)[\text{atm}]$	$(2.17 \pm 0.01) \times 10^{-4}$	$(8.90 \pm 0.01) \times 10^{-5}$
$P_{\text{CO}_2}(\text{cham})(0.5\text{wt}\%)[\text{atm}]$	$(2.11 \pm 0.01) \times 10^{-4}$	$(7.76 \pm 0.01) \times 10^{-5}$
$C(\text{H}_2\text{CO}_3)(2.5\text{wt}\%)[\text{mol/L}]$	$(7.52 \pm 0.04) \times 10^{-6}$	$(3.69 \sim 3.80) \times 10^{-6}$
$C(\text{H}_2\text{CO}_3)(1.0\text{wt}\%)[\text{mol/L}]$	$(7.16 \pm 0.03) \times 10^{-6}$	$(2.94 \pm 0.01) \times 10^{-6}$
$C(\text{H}_2\text{CO}_3)(0.5\text{wt}\%)[\text{mol/L}]$	$(6.96 \pm 0.04) \times 10^{-6}$	$(2.56 \pm 0.01) \times 10^{-6}$

The saturated molar concentration of carbonic acid in the air at 1 atm is 1.12×10^{-5} [mol/L]. The results portrayed in Table 2, show that the saturated molar concentration of carbonic acid decreases as the pressure in the chamber is reduced. It was also found that the saturated molar concentration of carbonic acid decreases with a decrease in the acid concentration under constant pressure. These results indicate that the decompression effect of the saturated concentration of carbonic acid becomes larger as the acid concentration in the solution decreases. Therefore, when the reaction system is decompressed, the saturated concentration of carbonic acid in the solution decreases rapidly so that the reverse reaction is suppressed. The dissolution reaction of calcium carbonate proceeds toward dissolution at a fast rate (Le Chatelier's law).

(Stirring effect due to the increase of the ascent speed of bubbles)

Many bubbles were generated when the chamber was decompressed. Therefore, it is necessary to consider the stirring effect caused by the ascent of the bubbles. The ascent speed of a bubble (U) can be calculated from the balance of the gravity, buoyancy and drag (D) using the following equation:

$$m \cdot \left(\frac{dU}{dt} \right) = -V_{\text{bubble}} \cdot \rho(\text{gas}) \cdot g + V_{\text{bubble}} \cdot \rho(\text{solution}) \cdot g - D \quad (22)$$

m is the mass of the bubble, V_{bubble} is the volume of the bubble, g is the gravitational acceleration, $\rho(\text{gas})$ is the density of gas, and $\rho(\text{solution})$ is the density of the solution.

In this equation, since the density of the gas $\rho(\text{gas})$ is much smaller than that of the solution $\rho(\text{solution})$, i.e., $(\rho(\text{gas}) \ll \rho(\text{solution}))$, then the gravity of the bubble can be neglected. Therefore, Eq. (22) is rewritten as

$$m \cdot \left(\frac{dU}{dt} \right) = V_{\text{bubble}} \cdot \rho(\text{solution}) \cdot g - D \quad (23)$$

When considering the ascent speed of bubbles, their size and shape are very important factors. J. Matsumoto and a co-worker reported the relationship between the diameter, shape, and drag of an air bubble in pure water [27]. They reported that when the diameter of the bubble is smaller than 2 mm, the shape of the bubble is approximately a sphere and the Reynolds number (Re) is much smaller than 1 ($Re \ll 1$). In our experiment, bubble diameters observed in Fig. 1 were smaller than 0.2 mm. Therefore, the bubble shape can be considered spherical and the drag coefficient (C_D) is computed as follows:

$$C_D = \frac{24}{Re} = \frac{24 \cdot \nu}{U \cdot d} \quad (24)$$

U is the ascent speed of the bubble [m/sec], S is the projection cross section of the bubble, $S = \pi \cdot d^2 / 4$ (where d is the diameter of the bubble), and ν is the kinematic viscosity of the solution.

In this experiment, it is assumed that the viscosity of the solution is approximately the same as that of water. The buoyancy of the bubble F_b is expressed as follows:

$$F_b = \rho(\text{solution}) \cdot g \cdot V_{\text{bubble}} = \pi \cdot \rho(\text{solution}) \cdot d^3 \cdot g / 6 \quad (25)$$

The bubble rises at speed U under the condition that the buoyancy F_b is equal to the drag D ($F_b = D$). Therefore, the ascent speed is expressed using Eq. (24) and Eq. (25).

$$U = (g \cdot d^2) / (18 \cdot \nu) \quad (26)$$

From Eq. (26), we must estimate the change of the bubble's volume or diameter with changes in pressure. In this experiment, the internal pressure (P_{in}) in the bubble is equal to the hydrostatic pressure $P(\text{hydrostatic})$.

$$P_{in} = P(\text{hydrostatic}) = P(\text{external pressure}) + P(\text{water pressure}) \quad (27)$$

Since the experiment was performed several centimeters under the water surface, $P(\text{water pressure})$ can be disregarded compared to $P(\text{external pressure})$ (1 atm = water depth about 10 m).

$$P_{in} = P(\text{external pressure}) = P$$

When the bubble, which consists of one gas type, exists in the solution, the gas species state's equation dissolved in the solution is the same equation with the non-dimensional Henry's coefficient H_0 :

$$\left(\frac{P}{H_0} \right) \cdot V_w = n_w \cdot R \cdot T \quad (28)$$

V_w is the volume of the liquid phase, n_w is the mol number of the gas species dissolved in the solution, H_0 = (the gas concentration in the gas phase [mol/L]) / (the gas concentration in the liquid phase [mol/L]).

The law of conservation of mass, when the reaction system is in a steady state, states that the sum of the mole number of the gas species in the bubble and the mole number of the gas species dissolved in the solution becomes a constant value.

$$P \cdot V_{\text{bubble}} + \left(\frac{P}{H_0} \right) \cdot V_w = n_{\text{total}} \cdot R \cdot T = (\text{constant}) \quad (29)$$

To estimate the relationship between the pressure and the volume of the bubble, Eq. (29) is totally differentiated.

$$d \left\{ P \cdot V_{\text{bubble}} + \left(\frac{P}{H_0} \right) \cdot V_w \right\} = V_{\text{bubble}} \cdot dP + P \cdot dV_{\text{bubble}} + \left(\frac{V_w}{H_0} \right) \cdot dP + \left(\frac{P}{H_0} \right) \cdot dV_w = 0 \quad (30)$$

In this equation, since the dependency of the liquid volume on the pressure is very small ($V_w = 0$), Eq. (30) is rewritten as follows:

$$V_{\text{bubble}} \cdot dP + P \cdot dV_{\text{bubble}} + \left(\frac{V_w}{H_0} \right) \cdot dP = 0 \quad (31)$$

$$\frac{dV_{\text{bubble}}}{dP} = - \left(\frac{V_{\text{bubble}}}{P} \right) - \left\{ \frac{V_w}{H_0 \cdot P} \right\}$$

Since $P \cdot V_{\text{bubble}} + \left(\frac{P}{H_0} \right) \cdot V_w = (\text{constant})$ (see Eq. (29)), the constant C is introduced.

$$C = P \cdot (V_{\text{bubble}} + V_w / H_0) \quad (32)$$

Using Eq. (32), Eq. (31) is rewritten as follows:

$$\frac{dV_{\text{bubble}}}{dP} = - \left(\frac{V_{\text{bubble}}}{P} \right) - \left\{ \frac{V_w}{H_0 \cdot P} \right\} = - \frac{C}{P^2} \quad (33)$$

Therefore, the volume change ΔV_{bubble} can be obtained by the integration over P_1 [atm] to P_2 [atm].

$$\Delta V_{gas} = - \int_{P_1}^{P_2} \left(\frac{C}{P^2} \right) dP = C \cdot \left(\frac{1}{P_2} - \frac{1}{P_1} \right) \quad (34)$$

Thus, the volume of the bubble at P_2 [atm] is expressed as follows:

$$V_2 = V_1 + \Delta V_{bubble} = V_1 \cdot \left[1 + \left(\frac{1}{P_2} - \frac{1}{P_1} \right) \right] \quad (35)$$

The expected values of the volume, projection cross section, ascent speed of the bubbles and exclusion volume occurring behind the bubble are summarized in Table 3. These results indicate that the bubble's volume and ascent speed increase with decreasing pressure in the chamber. A rising bubble in a solution causes a mixing of the solution. We estimate that the stirring effect by the rising bubble is strongly influenced by the exclusion volume behind the bubble per unit time. The results shown in Table 3 also indicate that the rising bubble's speed observed at 0.1 atm is about 4.6 times higher than that observed at 1 atm. When the pressure diminishes from 1 atm to 0.1 atm, the exclusion volume at 0.1 atm is about ten times larger than that at 1 atm. The increase in the exclusion volume with reducing pressure implies that a large stirring effect can be obtained with a reduction of the pressure in the chamber.

TABLE 3 THE VOLUME, DIAMETER, PROJECTION CROSS SECTION, RISING SPEED AND EXCLUSION VOLUME OF CO₂ BUBBLE UNDER 0.5 [atm] AND 0.1 [atm]

The pressure P_2	Volume	Diameter	Projection cross section	The rising speed	The exclusion volume behind the bubble
0.5atm	$2 \cdot V_1$	$1.26 \cdot d_1$	$1.59 \cdot S_1$	$1.59 \cdot U_1$	$2.53 \cdot (U_1 \cdot S_1)$
0.1atm	$10 \cdot V_1$	$2.15 \cdot d_1$	$4.64 \cdot S_1$	$4.64 \cdot U_1$	$21.53 \cdot (U_1 \cdot S_1)$

V_1 : the volume of the bubble at 1 atm d_1 : the diameter of the bubble at 1 atm

S_1 : the projection cross section of the bubble at 1 atm ($S_1 = (\pi/4)d_1^2$) U_1 : the rising speed of the bubble at 1 atm

(Increasing the surface area of the solid sample due to disintegration of the solid sample by the cavitation effect)

S. Ramadan and H. Idrissi reported that when CaCO₃ layers were dissolved with diluted hydrochloric acid, two population waves related to a release of CO₂ bubbles and CaCO₃ layer breaks were detected [28]. The first population wave had a peak frequency at 150 kHz and amplitude between 30 - 40 dB. The second population wave was observed at a frequency range from 230 to 260 kHz and its amplitude was greater than 40 dB. These two waves were ultrasonic waves. Therefore, in our experiment, it is believed that ultrasonic waves occur and that they affect the rate of the dissolution reaction (cavitation effect). Sound is a compression wave and the relationship between its sound power density I [W/m²], frequency f [1/sec], and amplitude A [m] is described by Eq. (36):

$$I = (2 \cdot \pi \cdot A \cdot f)^2 \cdot Z_0 / 2 \quad (36)$$

Z_0 is the specific acoustic impedance of the medium, $Z_0 = \rho \cdot c$.

In this relation, ρ is the medium's density [kg/m³] and c is the sound velocity [m/sec], where $c = \sqrt{K/\rho}$, and K is the medium's bulk modulus. The value of c (in water) = 1479 [m/s] (at 20°C) and $Z_0 = 1.48 \times 10^6$ [kg/(m²·s)] for water at 20°C,

$$I = \frac{p^2}{\rho \cdot c} \quad (37)$$

p is the sound pressure [N/m²].

When a bubble is generated, an ultrasonic wave occurs. We neglect the dependence of its sound power W_0 [W] on the pressure, and we assume that the site of the formation of gas is a point sound source and that the sound is propagated isotropically in the solution. The sound power density I_1 at a distance d_1 from the site of the formation of gas is expressed as follows:

$$I_1 = \frac{W_0}{(\pi \cdot d_1^2)} \quad (38)$$

Thus, the sound power density I_2 at an arbitrary distance d ($= a \cdot d_1$) from the site of gas formation can be expressed as follows:

$$I_2 = \frac{W_0}{(\pi \cdot d)^2} = \frac{W_0}{\pi \cdot (a \cdot d_1)^2} = \left(\frac{1}{a^2}\right) \cdot I_1 \quad (39)$$

In our experiment, the CO₂ gas formation's site approaches the surface of the solid sample with a decrease in the pressure in the chamber, because the saturated concentration of carbonic acid (H₂CO₃) diminishes with reduced pressure. Fig. 6 is a schematic showing the relationships between the position of gas formation, the saturated concentration of (H₂CO₃) in the bulk solution, and the pressure as a function of the distance from the solid sample surface. From Eq. (39), the sound power density varies as the inverse square of the distance. Therefore, if the gas formation's site approaches the surface of the sample, the sound power (equal to sound pressure) reached on the surface of the sample rapidly becomes larger and the solid sample collapses locally. Thus, the surface area and the reaction rate increase.

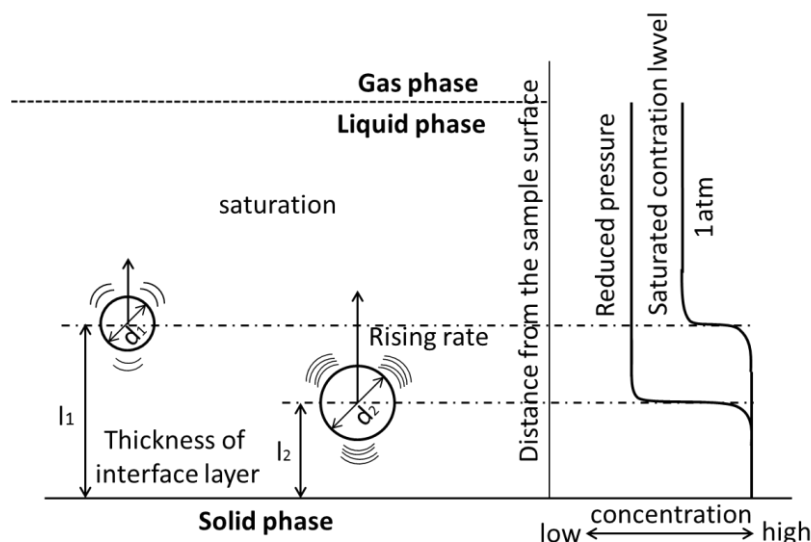


Fig. 6 Schematic diagram of the relationship between the site of bubble formation, volume of bubbles, saturated concentration and pressure in the chamber

V. CONCLUSION

Chalks were dissolved as a substitute for calcium carbonate (CaCO₃) scale samples with HCl solutions under various decompression states. Dissolution rates increased significantly with decreasing pressure. Especially, when the proton concentration nears the stoichiometric ratio for the dissolution reaction, the decompression effects become noticeable. The results of this study indicate that when calcium carbonate is dissolved with the acid solution under a reduced pressure, the total amount of the acid needed for the dissolution can be reduced while maintaining a high dissolution velocity. A decrease in the total amount of acid used reduces negative effects on the environment and human health. The increase in the dissolution velocity with decreased pressure is explained by Le Chatelier's Law, the stirring effects by rising bubble, and the cavitation effect.

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