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Effect of the magnetic field on the growth rate of aragonite and the precipitation of $CaCO_3$

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ABSTRACT

A series of growth experiments of aragonite, which is a polymorph of calcium carbonate ($CaCO_3$), were carried out in a fluidized-bed crystallizer under the influence of magnetic field. In the growth process, the solution properties, including relative supersaturation (σ), pH, ionic strength (I), and Ca^{2+} to $CO_3{}^{2-}$ activity ratio (R), were maintained almost constant in the growth process using an auto-titrator. Different types and intensities of magnetic field, including a permanent magnet (PM) and a commercial magnetic water treatment device (MWTD) with an effective intensity of 212.6 and 1800.0 G, respectively, were tested. The aragonite seed crystals did not grow without magnetization at room temperature, but did grow under the influence of the magnetic field. The magnetic field with a higher intensity developed its effect in a shorter time. Aragonite crystals grew faster in a lower pH environment, in which the growth of calcite was almost stopped in the presence of an MWTD. In addition, high levels of supersaturation and activity ratios far from unity favored aragonite growth. Finally, a possible mechanism was proposed to explain the effects of the magnetic field on the crystal growth of aragonite and calcite.

1. Introduction

The formation of calcite scale caused by the crystallization of $CaCO_3$ is a common and costly problem in the industries using cooling water. To solve such a problem, many physical and chemical techniques have been adopted, including various treatments using acid, additives, ion-exchange, and magnetic fields [1]. Among them, magnetic water treatment has been around for a hundred years due to its convenience and inexpensiveness. However, its effect is controversial and its working mechanism remains unclear [2]. In general, the anti-scale effects can be judged from the two steps of solid formation, *i.e.*, nucleation and crystal growth. For a fresh surface, the first deposition of scale was caused by nucleation, and the succeeding deposition of scale was due to crystal growth. In this view, the crystallization of $CaCO_3$ is a key point in understanding the scaling problem and the magnetic anti-scale effect.

In the previous studies in our laboratory, the constant-composition method, which was originally designed by Tomson and Nancollas [3], was first used to investigate the magnetic effect on $CaCO_3$ crystallization [4]. The calcite growth rate was measured in the presence of the magnetic field over a wide range of operating conditions. In most cases, the growth rate of calcite was suppressed by magnetizing the solution. The magnetic field with higher intensity was more effective for reducing the calcite growth rate. In the other study [5], when the magnetic field was applied directly on the region where calcite seed crystals suspended in the solution, the suppression effect was more significant. It was conjectured that under the influence of the magnetic field, the clusters in the supersaturated solution and on the crystal/solution interface changing their structure to one that was unfavorable for adsorption and incorporation into the crystal lattice of calcite seed. On the other hand, aragonite nucleated from supersaturated solutions under the influence of a magnetic field has been reported in the literature using various magnetization modes. Higashitani et al. [6] examined the morphology of $CaCO_3$ crystals formed by mixing $CaCl_2$ and Na_2CO_3 solutions that were exposed to magnetic fields quiescently and separately before mixing and concluded that the formation of aragonite was accelerated by the magnetic exposure. Kobe et al. [7] let the solution of $CaCO_3$–$Ca(HCO_3)_2$–H_2O flow through a magnetic field between 0.4 and 1.5 T to induce $CaCO_3$ nucleation and found that the percentage of aragonite in the product increased with increasing intensity of the magnetic field. Their results concerning the effect of magnetic field on the acceleration of aragonite formation have been checked in our laboratory. Tai et al. [5] investigated the morphology of the $CaCO_3$ precipitates by applying the magnetic field before the nucleation occurs, *i.e.*, to magnetize the supersaturated $CaCO_3$ solution using permanent magnets, and found that the magnetization increased the aragonite percentage of the precipitates.

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Nomenclature

$[Ca^{2+}]_a$	Ca^{2+} concentration of the titrated solution ($kmol/m^3$)
$[Ca^{2+}]_o$	Ca^{2+} concentration of the original solution ($kmol/m^3$)
G	linear crystal growth rate (m/s)
I	ionic strength ($kmol/m^3$)
L	characteristic length of the crystal seeds (m)
M	molecular weight of $CaCO_3$ (kg/kmol)
R	Ca^{2+} to ${CO_3}^{2-}$ ionic activity ratio, dimensionless
t	time (s)
V_a	the volume of the added solution (m^3)
W	total mass of the crystal seeds (kg)

Greek letters

σ	relative supersaturation, dimensionless
σ_{cal}	relative supersaturation with respect to calcite, dimensionless
σ_{ara}	relative supersaturation with respect to aragonite, dimensionless

Up to the present time, most of the studies related to the subject of magnetic effects on $CaCO_3$ crystallization focused on the calcite nucleation and growth and on the aragonite nucleation; however, the growth of aragonite influenced by a magnetic field has never been discussed. Judging from the magnetic effects reported in the literature about the magnetic field accelerating the aragonite formation and retard the calcite nucleation and growth, it is interesting to see whether the magnetic field will influence the aragonite growth. In this study, the crystal growth of aragonite in a fluidized bed was investigated using a constant-composition method [4,5], which can keep the pH and concentration of Ca^{2+} and ${CO_3}^{2-}$ ions constant during the growth process. A commercial magnetic water treatment device (MWTD), Descal-A-Matic DC-3, and a pair of permanent magnets (PM), MagneGen Model 100, with effective intensities of 1800.0 and 212.6 G, respectively, were used as the magnetic source. In the preliminary test, the aragonite seeds did grow in the presence of either magnetic field. On the other hand, there was no sign of growth without magnetization. The change of surface structure of the seeds before and after growth was examined under a scanning electronic microscope (SEM, JEOL JSM-5600). Then, the effects of solution properties, such as pH, supersaturation, and ionic activity ratio on the crystal growth rate were investigated. In addition to the growth experiment, nucleation experiments were performed under the influence of the magnetic field, emphasizing on the induction period and polymorphism. Finally, a possible mechanism was proposed for the explanation of the results related to the crystal growth of aragonite and calcite in the presence of the magnetic filed.

2. Experimental

2.1. Magnetic devices

Two kinds of magnetic devices utilized in this study, *i.e.*, Descal-A-Matic DC-3 and MagneGen Model 100, are illustrated in Fig. 1. The Descal-A-Matic DC-3 is a commercial magnetic water treatment device (MWTD), and its detailed construction from the side view is shown in Fig. 1(a). Three permanent magnets were placed in the device with identical poles facing each other. The supersaturated solution was pumped through the annular space in the device for magnetization. The effective field intensity in the device measured by a Gauss meter (Bell, Model 6010) was 1800.0 G. The other device, MagneGen Model 100, is a pair of permanent magnets (PM) with a nominal field intensity of 1265.6 G. The specification of the PM is shown in Fig. 1(b). When it is fixed on the Plexiglas wall of a fluidized bed, it offers an effective intensity of 212.6 G measured within the fluidized bed. Note that both magnetic devices produce an orthogonally applied field to the flow direction of the supersaturated solution, which are classified as class III of magnetic devices [8], and have a better anti-scale performance, as pointed out by Baker and Judd [2].

2.2. Preparation of aragonite seed crystals

Natural aragonite from Morocco was used as seed crystals in this study. After being crushed and ground into small particles mechanically, it was analyzed by the X-ray diffractometer, as shown in Fig. 2, which shows pure aragonite as compared with JCPDS card

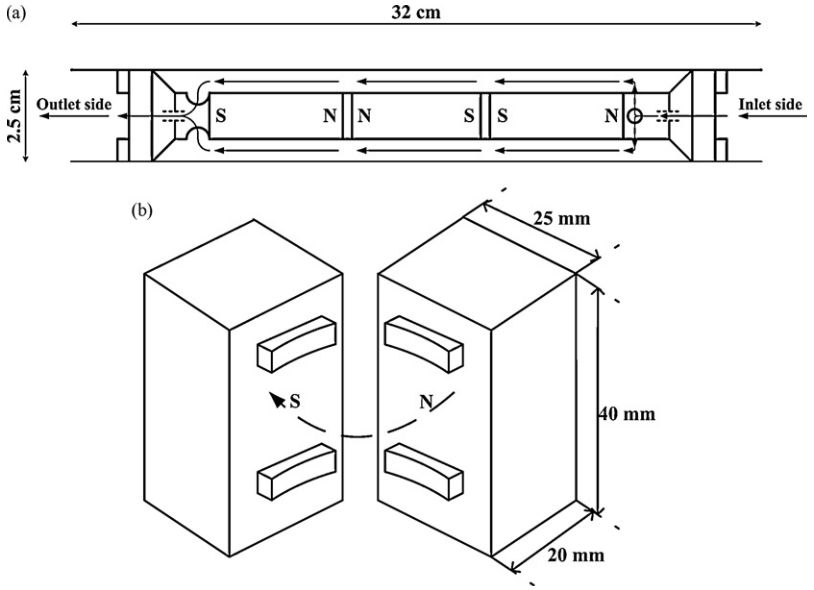

Fig. 1. The detailed structure of the magnetic devices. (a) Descal-A-Matic DC-3, where the arrow indicates the solution flow direction. (b) MagneGen Model 100, where the arrow indicates the orientation of the magnetic field.

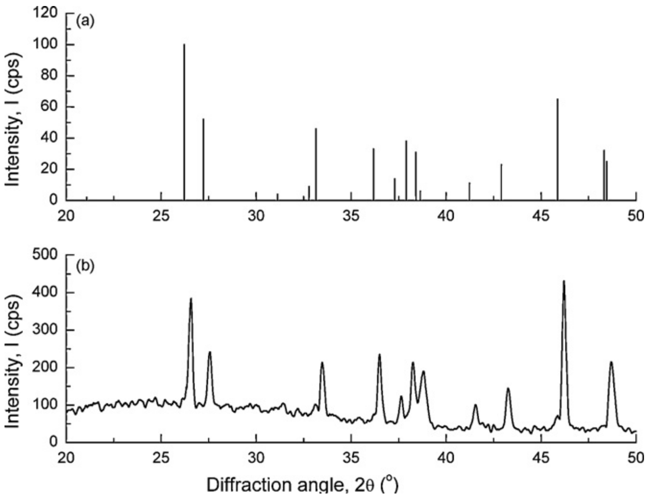

Fig. 2. The XRD patterns of (a) aragonite from JCPDS card and (b) natural aragonite from Morocco.

[9], *i.e.*, the orthorhombic system. The ground aragonite particles were sieved to give an average size of 774 μm as seeds, using the 16 and 24 mesh sieves. The seeds were rinsed with ethyl alcohol and deionized water. Before the growth experiment, the fresh aragonite seeds were cured in the presence of the commercial magnetic device for about 5 h and repeated, if necessary, to make sure that the seed crystals had similar surfaces to start with, *i.e.*, the seed surface was uniformly covered with acicular aragonite. The solution conditions for curing were chosen as: pH 9.0, I (ionic strength) = 0.018 M, $\sigma_{\text{ara}} = 0.73$ ($\sigma_{\text{cal}} = 1.0$), $R\,(a_{\text{Ca}^{2+}}/a_{\text{CO}_3{}^{2-}}) = 5.54$, and $T = 298.15$ K. The surface structure of seed crystals will be shown later.

2.3. Experimental procedures for crystal growth

The experimental apparatus used in this study, similar to that used by Tai et al. [4,5], but with a magnetic device, Descal-A-Matic DC-3 or MagneGen Model 100 incorporated into the system, as shown in Fig. 3. For some experimental runs, the MagneGen Model 100 was placed on the suspension bed where the seed crystals grow as in the previous study [5]. A supersaturated solution prepared by following the procedures stated in the previous study [4,5] was pumped from the storage tank to the fluidized bed via the magnetic device. The fluidized bed, in which the aragonite crystals grew, was a Plexiglas column with a distributor at the bottom to give an even flow. Then, the solution overflowed back to the storage tank. The aragonite seeds with an average size of 774 μm and a total weight of 25 g were poured into the fluidized bed to begin an experimental run when the temperature, pH, and Ca^{2+} electric potential became steady. The crystal growth process caused a decrease in the solution concentration and pH. The constant-composition system, which consists of two auto-titrators for adding reactants and NaOH solution separately, maintained the system at the steady state. During an experimental run, the Na^+ and Cl^- ions would accumulate to increase the ionic strength of the solution. However, the change in growth rate was negligible due to an increment of ionic strength within 5%. The volume of the titration solution was recorded automatically to give the titration curve. The slope of the titration curve was used to evaluate the crystal growth rate according to the following equation, which was derived by Tai et al. [10]:

$$G = \frac{LM}{3W}([\text{Ca}^{2+}]_a - [\text{Ca}^{2+}]_o)\frac{dV_a}{dt} \tag{1}$$

where W is the total mass of the crystal seeds, L is the characteristic length of the crystal seeds, M is the molecular weight of CaCO_3, V_a is the volume of titrated solution, t is the experimental time, and $[\text{Ca}^{2+}]_o$ and $[\text{Ca}^{2+}]_a$ are the Ca^{2+} concentration of the original solution and added solution, respectively. After an experimental run, the seed crystals were removed, washed with deionized water and ethyl alcohol, then air-dried for the next experiment.

Several tips provided below were essential for acquiring reliable growth rate data. The Ca^{2+} concentration should be checked immediately after every experimental run to make sure that the constant-composition system was maintained; an inductively coupled plasma spectrometer (ICP, Optima-3000XL) was used here. In

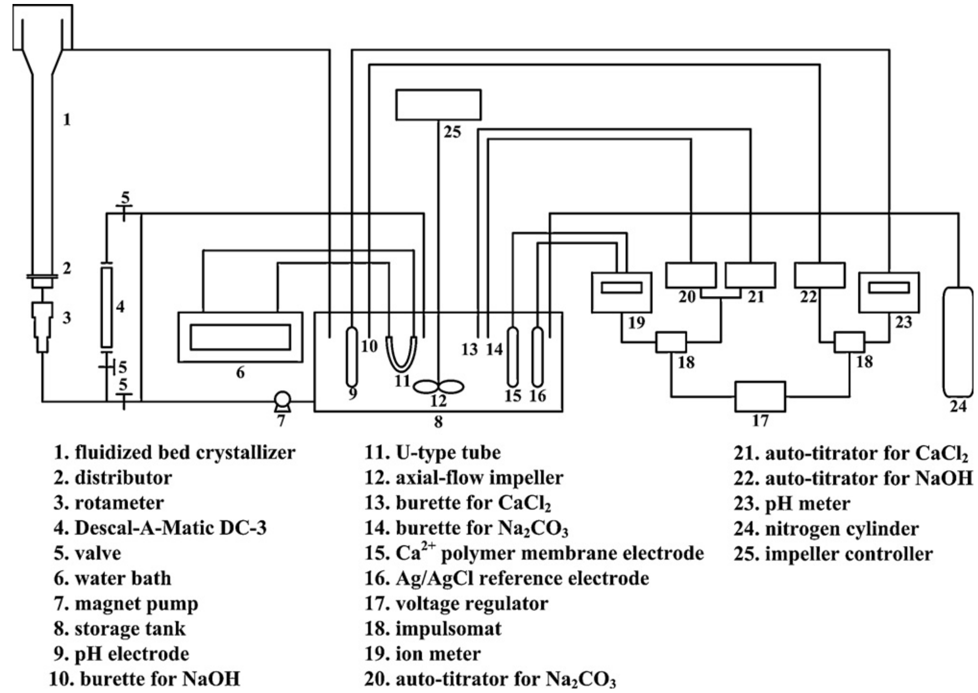

Fig. 3. Diagram of constant composition crystallization system with magnetic treatment device, Descal-A-Matic DC-3.

addition, the concentration of iron ion (~0.6 ppm), which would reduce the calcite growth rate [11,12], was also checked occasionally to make sure that no iron ions were dissolved from the magnetic device. The analytical sensitivity of the ICP regards to concentration of iron was ~0.1 ppm, and it was appropriate to check if the iron concentration was lower than the threshold value via the ICP. To obtain a reliable titration curve, a voltage regulator was installed in the experimental system in order to reduce noise caused by unstable power supply, and nitrogen gas was provided as blanket to prevent the absorption of CO_2 from air.

2.4. Calculation of supersaturation for calcite and aragonite

According to the definition of Nielsen and Toft [13], the relative supersaturation of $CaCO_3$ was expressed as the following equation:

$$\sigma_{\mathrm{CaCO_3}} = \sqrt{\frac{a_{\mathrm{Ca^{2+}}} a_{\mathrm{CO_3}^{2-}}}{K_{\mathrm{sp,CaCO_3}}}} - 1 \qquad (2)$$

Calcium carbonate has several polymorphs with different solubilities. The solubility of aragonite is higher than that of calcite over a wide range of temperatures [14]. The solubility product at 298.15 K is about 4.5×10^{-9} and 6.0×10^{-9} M^2 for calcite and aragonite [15], respectively. Therefore, the relative supersaturation calculated with respect to calcite or aragonite in the same solution is different. Taking a typical solution condition, as stated by Tai et al. [4], for example, a 6 L supersaturated solution, prepared by adding 36.13 mL of 0.1 M $CaCl_2$ solution and 95.60 mL of 0.1 M Na_2CO_3 solution to deionized water, possesses a relative supersaturation of 1.0 with respect to calcite (σ_{cal}) and 0.73 with respect to aragonite (σ_{ara}), which is lower than σ_{cal} due to the higher solubility of aragonite.

2.5. Experimental procedures for nucleation

Nucleation experiments were designed for observing the magnetic effects on the induction time and polymorphism of $CaCO_3$ precipitates. Solutions with relative supersaturation (σ_{cal}) in the range between 3.0 and 5.0, and with fixed pH at 9.0, I at 0.018 M, and R at 5.54, were prepared and circulated in the system without seeding in the presence/absence of the MWTD (Descal-A-Matic DC-3). The onset of primary nucleation, usually taking a few hours, was detected when the auto-titrator replenished the reactant at a rate that was much faster than that of a crystal growth run. Here, three specific times, *i.e.*, total-circulation time, induction time, and post-circulation time, were defined as follows. The total-circulation time was the period starting from the moment when the solution was prepared by mixing the two reactant solutions to the moment when the slurry was taken out of the crystallizer for filtration. The induction time and the post-circulation time together made up to the total-circulation time, and the cut-off point was the moment when the auto-titrator started to replenish the reactants, *i.e.*, when the $CaCO_3$ started to precipitate. The precipitates collected were then filtered, washed with deionized water and ethyl alcohol, and air-dried before being analyzed by an X-ray diffractometer (Mac Science, MXP-3TXJ-7266) for polymorphism.

3. Results and discussion

3.1. Surface structure of seed crystals

The SEM photographs of aragonite crystal surface at different stages of growth process are shown in Fig. 4. The surface of the crushed natural aragonite is flat with some crystal dust adhering to the surface as shown in Fig. 4(a). After the curing process, the surface of aragonite seeds was covered with acicular particles of micron size, shown in Fig. 4(b), which is the most common structure

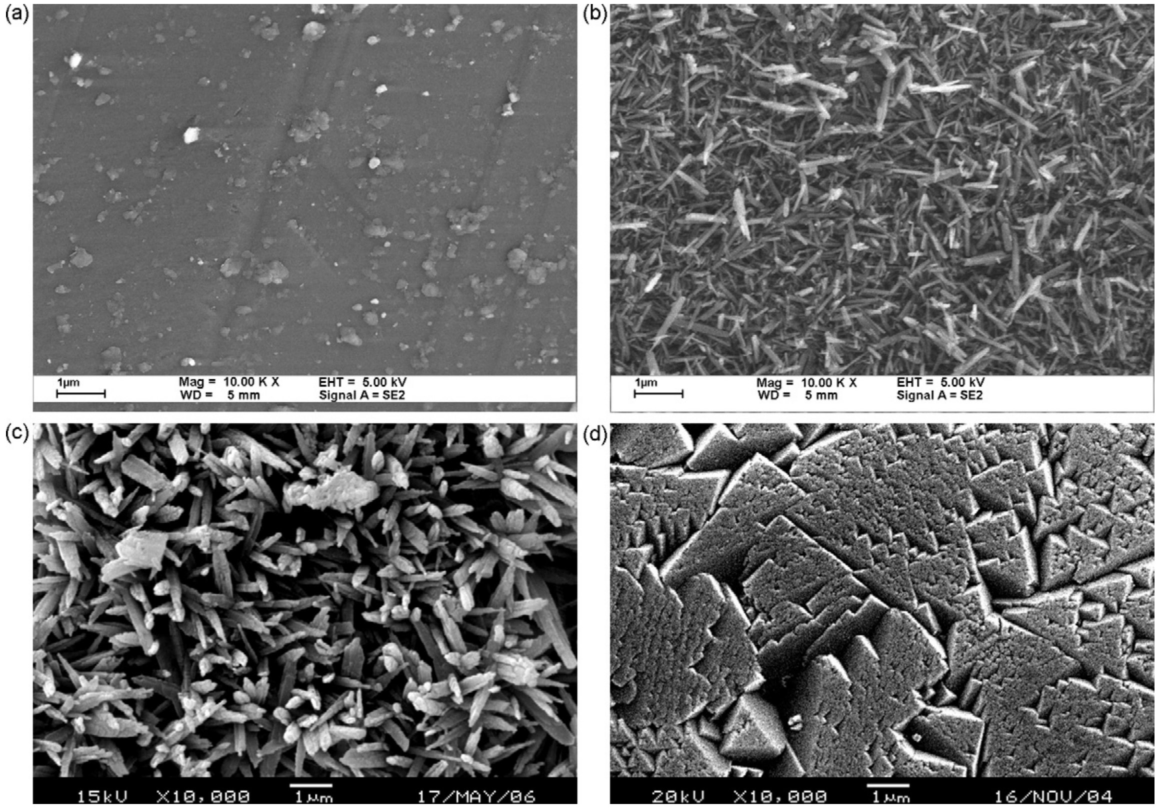

Fig. 4. The surface structure of $CaCO_3$ crystal seeds: (a) crushed natural aragonite before curing (b) aragonite seeds after curing (c) aragonite seeds after a long period of growth and (d) calcite seeds after growth.

Table 1
Effects of magnetic intensity and premagnetization time on aragonite growth rate at pH 9.0, $I = 0.018$ M, $\sigma_{\text{ara}} = 0.73$, $R = 5.54$, and $T = 298.15$ K.

Type of the magnetic field	Effective intensity (G)	Premagnetization time (h)	Growth rate (10^{-10} m/s)
MWTD	1800	1.5	0.918
		10	0.958
		20	0.975
Permanent magnet	212.6	1.5	0.521
		20	0.802
		30	0.838

of aragonite [16]. After a long period of growing time, the seed surface was covered with larger and wider acicular particles, as shown in Fig. 4(c). Thus, the growth rate measured in this experiment was the growth rate of the acicular crystals adhering to the surface of seed crystals. For comparison, the surface of the calcite seed used after slow growth in the presence of the magnetic field is also included here [4]. After slow growth, the calcite surface was covered with platelet crystals, as shown in Fig. 4(d), which was quite different from the acicular particles covered on the surface of aragonite seeds. It should be noted that the natural aragonite did not grow in the absence of the magnetic field and the surface remained unchanged. From the SEM observation, we may conclude that it is difficult for aragonite to grow on calcite seeds, and vice-versa.

3.2. Effects of magnetic intensity and premagnetization time

In the previous experiment conducted in our laboratory [4,5] for the study of the effects of magnetic field on calcite growth and nucleation, we found that the magnetic field of high intensity was more effective and the solution should be premagnetized for a certain period of time using a permanent magnet. Thus, the effects of magnetic intensity and premagnetization time were investigated first in this study. Recall that the MWTD (magnetic water treatment device) and PM (permanent magnet) have the effective intensity of 1800.0 and 212.6 G, respectively. Three premagnetization times, *i.e.*, 1.5, 10, and 20 h were chosen for the preliminary study. The operating conditions used here were similar to those in the study of magnetic field on calcite growth. The aragonite seeds did grow under the influence of the magnetic field, and the growth rates were higher using the MWTD as shown in Table 1. In addition, the growth rate increased with an increase in premagnetization time. For example, the aragonite growth rate increased 54% when the premagnetization time changed from 1.5 to 20 h for the case of a permanent magnet acting on the solution. For a further increase in the premagnetization time to 30 h, the growth rate did not increase much, only by 4%. For the case of MWTD, the growth rate differed by 6.2% between the premagnetization times of 1.5 h and 20 h. It seems that a magnetic field of low intensity needs a longer time to reach a steady state. In viewing the aragonite growth rates at different intensities and premagnetization times, it is reasonable to presume that the aragonite growth rate has reached a constant at the premagnetization time of 20 h using the MWTD because the increase in growth rate was less than 2% when the premagnetization time changed from 10 to 20 h. Thus we applied the MWTD by setting the premagnetization time at 20 h for the study of the effects of solution properties, such as pH, supersaturation, and activity ratio of $Ca^{2+}/CO_3{}^{2-}$, under the influence of the magnetic field in the following experiments.

3.3. Effects of magnetization position

In the previous study, we found that the position for fixing the permanent magnet made a great difference in the magnetic effect on the calcite growth rate [5]; *i.e.*, placing the magnet around pipe in front of the fluidized bed or on the suspension bed of growing crystals. The latter was more effective than the former on reducing the calcite growth rate. In this study, the position for fixing the magnet of MagneGen Model 100 was tested again for the aragonite growth. The titration curves obtained from the auto-titrator were used to demonstrate the effects of magnetization position. Recall that the growth rate was evaluated from the slope of the titration curve until it became a straight line, meaning that the growth rate became steady. The titration curves for the two magnetization positions are plotted in Fig. 5. Curve 1 stands for the case of placing the magnet in front of the fluidized bed and curve 2 for the case on the suspension bed. These two curves look different. The titration time for the curve to become straight was about 2000 s for curve 2, yet the slope of curve 1 was very small at first then changed gradually to become steady and approach that of curve 2 after 6000 s. The titration curves indicate that the magnet placed in front of the fluidized bed, *i.e.*, when the magnet magnetized only the supersaturated solution, needed more time to develop its full effect than the case of placing the magnet on the suspension bed to magnetize the solution and seed crystals simultaneously. Thus, in the latter mode of operation, both the solution and the crystal surface seemed to be influenced by the magnetic field. In the long run, there would be no difference between the two cases. As far as the effectiveness of the fixing position is concerned, the aragonite growth behaves similarly to that of calcite growth; however, the magnet has an adverse effect on the two growth rates.

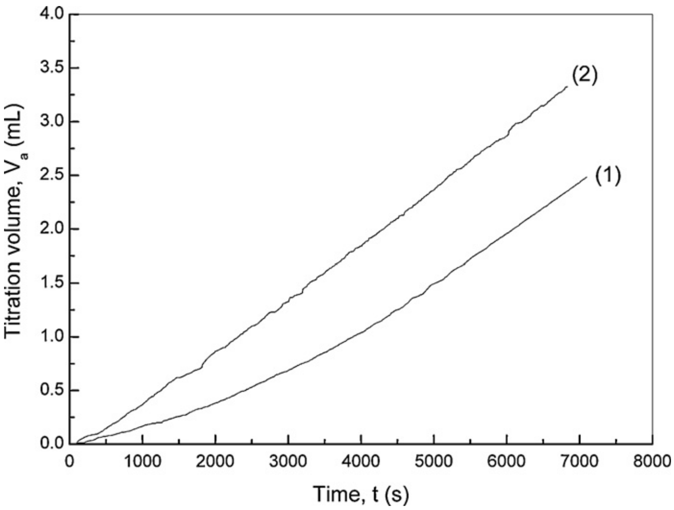

Fig. 5. Titration curves recorded by the auto-titrator under condition of pH 9.0, $I = 0.018$ M, $\sigma_{\text{ara}} = 0.73$, $R = 5.54$, and $T = 298.15$ K, at different magnetization positions.

3.4. Effects of solution variables

The aragonite growth rates were measured at various supersaturations for two levels of pH, *i.e.*, 8.5 and 9.0, under the influence of magnetic field using the MWTD. The supersaturated solution was premagnetized by the Descal-A-Matic DC-3 device for 20 h, and the results are shown in Fig. 6. The aragonite growth rates were higher for the lower pH, and increased with an increase in supersaturation except for the supersaturation below 1.25 of pH 9.0. The trend of pH effect for aragonite is opposite to that of calcite [4], and the supersaturation effect is similar for the two polymorphs. However, the level-off of growth rate at supersaturation below 1.25 for pH 9.0 was a peculiar growth behavior. The growth rate data have been checked for $\sigma_{\text{ara}} = 0.91$ and 1.25 with no difference. One thing worth mentioning here is that the growth rate responding to the pH

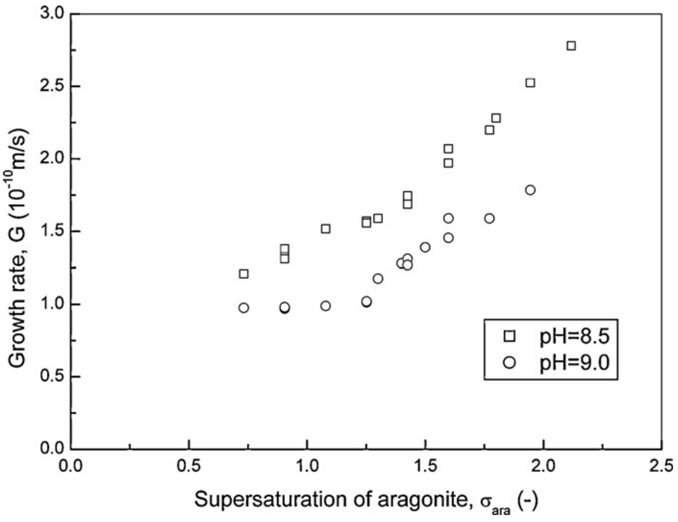

Fig. 6. Relationship between aragonite growth rate and relative supersaturation in supersaturated solution premagnetized by Descal-A-Matic DC-3 for 20 h, with solution properties: $I = 0.018$ M, $R = 5.54$, $T = 298.15$ K. (□) Aragonite growth rate under pH 8.5 and (○) aragonite growth rate under pH 9.0.

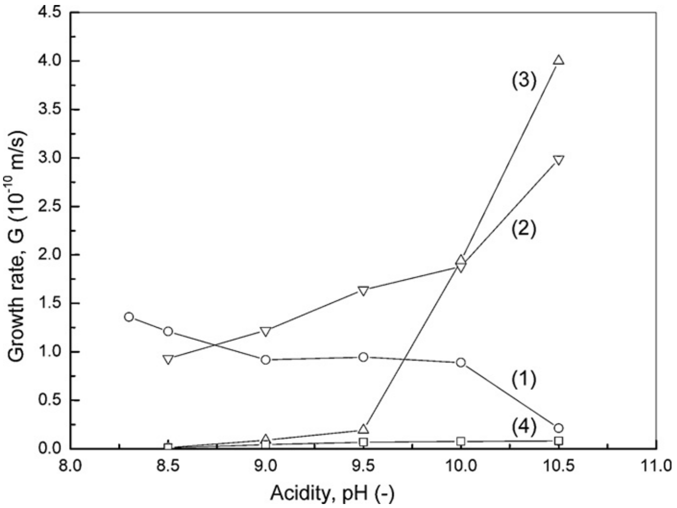

Fig. 8. Comparison of aragonite and calcite growth rates under different pH in the presence/absence of the magnetic field. (○) Aragonite seeds in the presence of the Descal-A-Matic DC-3 with 20 h premagnetization, (▽) calcite seeds in the absence of the Descal-A-Matic DC-3 [4], (△) calcite seeds in the presence of the Descal-A-Matic DC-3 but without premagnetization [4], and (□): calcite seeds in the presence of the Descal-A-Matic DC-3 and with 20 h premagnetization.

change is similar to nucleation, *i.e.*, the lower pH favors the aragonite formation [16] and growth (this study), while higher pH favors the calcite formation [16] and growth [4,5].

In the previous paper published by our laboratory, the calcite growth rates exhibit a maximum at $R\ (a_{\mathrm{Ca}^{2+}}/a_{\mathrm{CO_3}^{2-}}) = 5.54$ being 1.0 with or without magnetization of the supersaturated solution [4]. In this study, the aragonite growth rates measured at the same solution composition as the calcite growth showed an opposite trend to that of calcite growth rate, *i.e.*, a minimum occurring at $R = 1.0$. The growth rate data of calcite and aragonite at various values of R are presented in Fig. 7. It is interesting to note that the aragonite seeds did grow but the growth rate was very low at $R = 1.0$, approximately 0.255×10^{-10} m/s, as compared with that obtained at $R = 5.54$. On the other hand, the calcite growth rates reached a maximum at $R = 1.0$ in the absence of the magnetic field, and remained the same at $R = 1.0$ in the presence of the magnetic field. When the R values were far from $R = 1.0$, the calcite growth rates were reduced by an order under the influence of the magnetic field. This kind of $CaCO_3$ growth behavior has never been reported in the literature; however, the crystal growth rates of some sparingly soluble salts were also influenced by the activity ratio of reactants. For example, Stubičar et al. [17] studied the PbF_2 crystallization system and observed that the effective order of crystal growth changed when the activity ratio $(a_{\mathrm{Pb}^{2+}}/a_{\mathrm{F}^-})$ crossed 1.0. When the ratio was larger than 1, the effective order of crystallization was determined as 1.55. With the ratio decreasing to values lower than 1, the kinetic order dramatically shifted to 4.0. The shift of kinetic order was attributed to the growth of different crystal phases under different activity ratios. As to the nucleation experiment of $CaCO_3$, Tai and Chen [16] concluded that aragonite was hardly obtained under the condition of $R = 1.0$, which also gave us a clue to the relation between the polymorphism and the crystal growth rate.

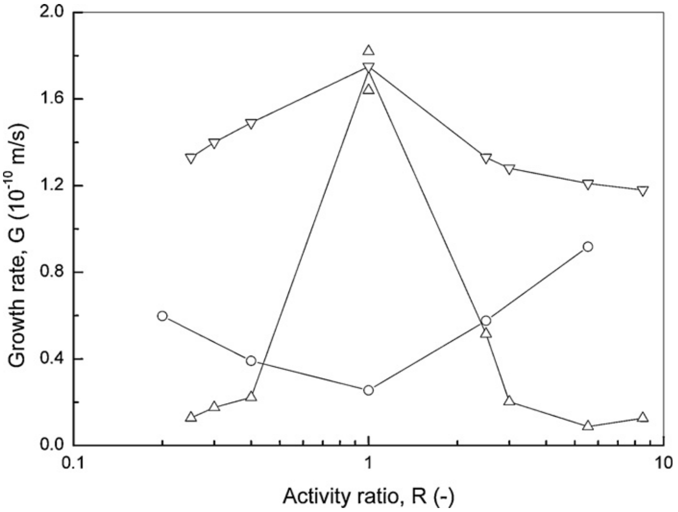

Fig. 7. Comparison of aragonite and calcite growth rates under different activity ratios in the presence/absence of the MWTD. Experimental conditions: pH 9.0, $I = 0.018$ M, $\sigma_{\mathrm{cal}} = 1.0$ ($\sigma_{\mathrm{ara}} = 0.73$), and $T = 298.15$ K. (○) Aragonite seeds in the presence of the Descal-A-Matic DC-3, (▽) calcite seeds in the absence the Descal-A-Matic DC-3 [4] and (△) calcite seeds in the presence of the Descal-A-Matic DC-3 [4].

3.5. Comparison of pH effects between aragonite and calcite growth

The aragonite growth rates were measured at various levels of pH in the supersaturated solution with the same composition as that for calcite growth with and without magnetization [4], and the results of aragonite and calcite are compared in Fig. 8. The operating conditions kept constant were $I = 0.018$ M, $\sigma_{\mathrm{cal}} = 1.0$ ($\sigma_{\mathrm{ara}} = 0.73$), $R = 5.54$, and $T = 25\,^{\circ}\mathrm{C}$. The growth rate of aragonite in the presence of the magnetic field and with 20 h premagnetization (curve 1) decreased with an increase in pH ranging between 8.3 and 10.0. The trend in growth rate responding to pH for aragonite under the influence of the magnetic field was opposite that of calcite (curve 2) in the absence of the magnetic field. As far as the crystal growth of calcite in the presence of the magnetic field is concerned, two sets of growth rate data measured at different premagnetization times were plotted, *i.e.*, curve 3 without premagnetization [4] and curve 4 with premagnetization time of 20 h just like curve 1 for aragonite growth. Without premagnetization, the calcite grew very slowly and increased slightly with increasing pH when the pH was smaller than 9.5, and the calcite growth rate increased tremendously at higher levels of pH. When the supersaturated solution was premagnetized for 20 h, the calcite growth rate maintained the low level in the whole range of pH. Obviously, the magnetic

Table 2
Magnetic effect on induction period and polymorph of $CaCO_3$ at various levels of relative supersaturation, with other solution variables kept constant: pH 9.0, $I = 0.018$ M, $R = 5.54$, $T = 25\,°C$, and $v = 0.0472$ m/s.

Run no.	σ	Magnetization by Descal-A-Matic DC-3	Total-circulation time (min)	Induction time (min)	Post-circulation time (min)	Percentage of polymorphism (wt.%)		
						Aragonite	Calcite	Vaterite
1	5.0	No	15	7	8	2.2	3.2	94.6
2		Yes	15	7	8	7.2	3.8	89.0
3		Yes	450	7	443	83.7	16.3	0
4	4.0	No	135	21	114	0	2.5	97.5
5		Yes	300	150	150	88.5	11.5	0
6	3.0	No	70	29	41	2.3	1.7	96.0
7		Yes	385	198	187	69.0	20.5	10.5

field needs some time to develop its effect on the crystal growth of calcite (Fig. 8) and aragonite (Table 1), especially at high levels of pH, which favor the formation of calcite. Later in this report, we will propose a mechanism to explain the magnetic effect.

3.6. *Magnetic effects on induction time and polymorphism of $CaCO_3$*

The magnetic effects on the induction time and crystal polymorphism of $CaCO_3$ have been observed from the nucleation experiments conducted at three levels of relative supersaturation, and the results are listed in Table 2. The induction time was shortened by increasing the degree of relative supersaturation in the absence of magnetic field as we compared the results of Runs 1, 4, and 6. The induction time increased from 7 to 29 min as the relative supersaturation (σ_{cal}) decreased from 5.0 to 3.0. Similar results have been reported by Söhnel [18] and Tai and Chien [19]. In the presence of Descal-A-Matic DC-3, the induction time was extended for the lower supersaturation but not for the highest relative supersaturation of 5.0. The degree of extension decreased with increasing supersaturation. For example, the induction time was extended from 29 to 198 min for $\sigma_{cal} = 3.0$, and the magnetic effect was not observed at $\sigma_{cal} = 5.0$ as we compared the induction time of Runs 1 and 2. It is understandable that the solution was quite unstable and ready to nucleate at high supersaturation, giving the magnetic field no time to develop its effect. Higashitani et al. [6], Barrett and Parsons [20], Chibowski et al. [21], and Gabrielli et al. [22] also reported that the magnetic field would delay the nucleation of $CaCO_3$. However, the magnetization techniques employed were not exactly the same as those used in this study: Higashitani et al. [6] and Barrett and Parsons [20] magnetized the $CaCl_2$ and Na_2CO_3 solution individually prior to mixing, Chibowski et al. [21] magnetized the solution with two S–S poles, and Gabrielli et al. [22] treated hard water instead of the solution made up from deionized water.

The percentage of each polymorph in the precipitate, calculated by direct linear analysis [16,23], is listed in the last column of Table 2, and the XRD patterns of some runs, *i.e.*, Runs 1, 2, and 3, are shown in Fig. 9 as examples. The XRD patterns of Runs 1 and 2 were almost the same because there was not much difference in composition. For Run 3, with 83.7% aragonite, the XRD pattern showed the characteristic peaks of aragonite. The major constituent of the precipitated $CaCO_3$ for the case of σ between 3.0 and 5.0 was vaterite in the absence of the magnetic field. The result was similar to that reported by Tai and Chen [16], in which the constant-composition technique was adopted for nucleation experiments. They identified the favorable operating conditions for vaterite in a pH range between 9 and 9.5 at room temperature and $\sigma_{cal} = 5.5$. In the presence of the magnetic field, vaterite transformed to aragonite and some calcite after circulation for all supersaturations and the portion of aragonite increased with an increase in post-circulation time because the weight percentage of aragonite was 2.2 for Run 1 (without magnetization), 7.2 for Run 2 (with magnetization and post-circulation time of 8 min), and 83.7 for Run 3 (with magnetization and post-circulation time of 443 min).

Similar results focused on $CaCO_3$ polymorphism have been reported in the literature. In the absence of the magnetic field, Wray and Daniels [24] conducted $CaCO_3$ precipitation experiments over a wide range of temperatures and aging times, and concluded that vaterite was the major product at the beginning under room temperature. On the other hand, the experiments of Higashitani et al. [6] and Kobe et al. [7] were carried out in the presence of the magnetic field to observe the $CaCO_3$ polymorphism. Higashitani et al. [6] mixed $CaCl_2$ and Na_2CO_3 solutions after magnetizing individually, and observed that aragonite appeared in the product precipitated from the magnetized solution; from the unmagnetized solution, only pure calcite was acquired. Kobe et al. [7] applied a magnetic field with intensity that varied from 4000 to 12,200 G to treat a recirculating $CaCO_3$–$Ca(HCO_3)_2$–H_2O equilibrium system for 8 h. The composition of the $CaCO_3$ precipitate was in a ratio of calcite:aragonite:vaterite = 80.0:10.4:9.6 for the 4000 G field, and 28.9:70.6:0.5 for the 12,200 G field. They concluded that the portion of aragonite increased with the intensity of magnetic field.

3.7. *Proposed mechanism of the magnetic effects*

Before we bring up the mechanism of the magnetic effect, let us review the polymorphs of $CaCO_3$ and their structure. The common polymorphs of $CaCO_3$ are calcite, vaterite, and aragonite, in which

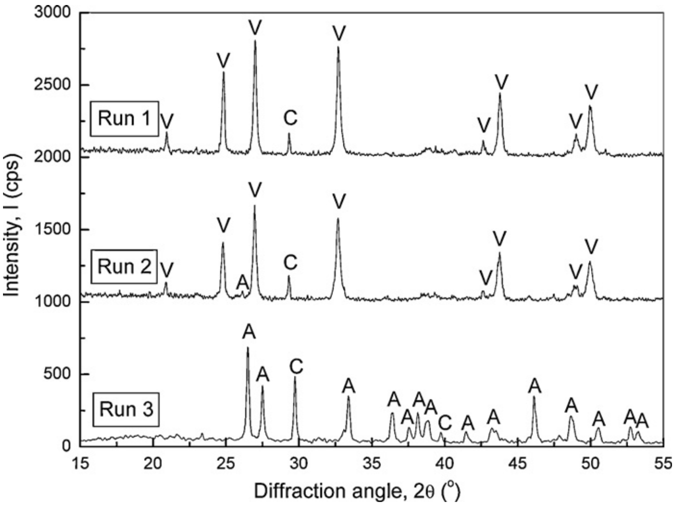

Fig. 9. X-ray diffraction patterns of Runs 1, 2, and 3. V, vaterite; A, aragonite; C, calcite.

the first two belong to the hexagonal system, and the last to the orthogonal system. It is well understood that calcite is the most stable form at room temperature and the crystal surfaces are difficult for other polymorph to deposit [4]. The mechanism to be proposed here is related to the formation of different $CaCO_3$ clusters existing in the supersaturated solution. The clustering of solute in a supersaturated solution has long been recognized including organic [25] and inorganic salts [26].

In viewing the effects of the magnetic field on the nucleation and crystal growth of $CaCO_3$ polymorphs, *i.e.*, calcite and aragonite, a possible mechanism is proposed here to explain the magnetic effects. The observed phenomena of the magnetic effects are as follows. Under the influence of the magnetic field, more aragonite would precipitate or the initially precipitated vaterite would transform to aragonite rather than to calcite [5–7]. As far as the growth behavior is concerned, the most striking phenomena are that the calcite almost stops growing [4] and the aragonite starts to grow at room temperature as reported in this communication after the supersaturated solution has been magnetized for a certain period of time. It is intuitive to suggest that $CaCO_3$ clusters of different structure form in the absence and in the presence of the magnetic field. At room temperature, the clusters with a structure similar to calcite existing in the solution without magnetization would be able to adsorb onto the calcite surface then incorporate into the crystal lattice. When the supersaturated solution is subjected to magnetization, the clusters would transform into something that has an affinity for aragonite but not for calcite. The Lorentz force induced by the magnetic field must be responsible for the transformation of clusters, probably through a solution-mediated process. The transformation rate is a function of magnetic intensity, magnetization time, solution supersaturation, pH, and perhaps temperature, which has not been investigated in this study and will be studied in the future.

The growth behavior of calcite and aragonite under the influence of the magnetic field can be explained by the proposed mechanism. First, let us look at the effect of the magnetic intensity. Tai et al. [4] reported that the calcite growth rate was reduced immediately after the supersaturated solution passed through the MWTD with an intensity of 1800 G, shown in Fig. 7 for lower supersaturation, whereas the growth rate remained the same at the same solution composition after the solution was magnetized for 3 h by a permanent magnet with a lower effective intensity of 1024.0 G [5], which was less effective than the MWTD. The type and intensity of the magnetic field made a difference because the high intensity accelerated the transformation of clusters. Table 1 also shows a similar intensity effect, in which the magnetization time also showed its influence on the aragonite growth rate for both magnetic fields. The magnetic field of lower intensity needed a longer time to reach the steady growth rate in line with the kinetics of cluster transformation. The effect of magnetization time is more clearly shown in Fig. 8, in which curve 3 was the growth rate without premagnetization, whereas curve 4 was that evaluated after 20 h of premagnetization. For pH higher than 9.5, the difference was tremendous, presuming that the transformation of clusters was slower at a higher pH. As to the effect of position of fixing the permanent magnet, the possible mechanism has been proposed in a previous report [5] based on the cluster transformation taking place in the adsorption layer. When the magnetic field was applied to the suspension bed of crystals, it not only transformed the clusters in the solution but also on the crystal surface. Finally, if we assume the condition of $R = 1.0$ as being most favorable for the formation of calcite clusters, even in the presence of the magnetic field, the maximum and minimum growth rate for calcite and aragonite, respectively, as shown in Fig. 7, are explained. The mechanism of R effects needs to be further explored.

4. Conclusion

The magnetic effect on crystallization of $CaCO_3$ was investigated by conducting aragonite growth and nucleation experiments in the absence and in the presence of two types of magnetic fields, *i.e.*, the Descal-A-Matic DC-3 and the MagneGen Model 100. Under normal conditions, the aragonite seed crystals can hardly grow. When the magnetic field was applied, the aragonite did grow. The aragonite growth rate increased to a constant value after a certain period of magnetization time. The premagnetization time to reach a steady growth rate was shortened by applying a magnetic field of higher intensity or by applying the magnetic field on the aragonite seed crystals. As the solution properties were concerned, low pH, high level of supersaturation, and activity ratio far from unity were favorable environment for aragonite growth, whereas high pH and activity ratio near unity favored calcite growth. According to the nucleation experiments, vaterite was the major product precipitated at the initial stage; it would transform to aragonite with time in the presence of the magnetic field, instead of calcite. According to the experimental fact that the conditions favor aragonite growth can also favor aragonite formation, a possible working mechanism of the magnetic field was proposed on the basis of cluster transformation. The magnetic field may gradually convert the $CaCO_3$ clusters in the supersaturated solution from a calcite-like form to an aragonite-like form, causing an acceleration of aragonite growth and a suppression of calcite growth. The mechanism drawn from this study might be a clue to understand the anti-scale performance of the magnetic water treatment device, *i.e.*, a magnetic field is likely to work better in the environment with low pH and low degree of supersaturation, in which the calcite growth might be completely stopped under the influence of a magnetic field with a specified intensity. Although a mechanism of magnetic effect, which is related to the transformation of $CaCO_3$ clusters with different form, is proposed here, there is lacking of instrument to identify the cluster form existing in a supersaturated solution.

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