Effects of magnetic field on the crystallization of CaCO₃ using permanent magnets

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ABSTRACT

Permanent magnets of different intensities were used to investigate the effect of a magnetic field on the crystal growth of calcite suspended in a fluidized bed. The magnets were fixed on the suspended bed where the crystal grew. The growth rates of calcite were measured at various levels of supersaturation (σ), pH, and ionic strength (I) using the constant-composition technique. The calcite growth rates in the presence of the magnetic field were lower than those in the absence of the magnetic field, and higher magnetic intensity yielded a lower growth rate. The effect of a magnetic field on CaCO₃ polymorphism was also studied. The percentage of polymorphs was dependent on the magnetization time. Aragonite was the predominant polymorphic form in the precipitate mixture, which was induced spontaneously by changing the solution pH after the supersaturated solution had been magnetized for 48 h.

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1. Introduction

The formation of scales inside cooling water pipes and boiler walls is a common and costly problem for many industrial processes. Although several methods have been used for scale prevention, they usually cause some other problems, such as high cost of added chemicals, process water being polluted by additives, waste of water by purging, and low efficiency. Among these methods, a more economical and convenient method is the magnetic treatment. However, although many investigators have indicated that the magnetic field would suppress (Dalas and Koutsoukos, 1989; Parsons et al., 1997), accelerate (Higashitani et al., 1993; Barrett and Parsons, 1998), or have no effect (Duffy, 1977; Hasson and Bramson, 1985) on the CaCO₃ growth, the effect of a magnetic field on CaCO₃ polymorphism was undoubted.

Although many investigators have indicated that the magnetic effect is dependent on the nature and condition of solution, such as supersaturation, pH, and ionic strength, most of them have not controlled the solution properties in their studies, except for a few cases using a pH-stat technique (Dalas and Koutsoukos, 1989; Parsons et al., 1997). An additional drawback of some reported studies was measuring the deposit rate of scales on the pipe wall, which took a long time to collect any data, probably several weeks or months (Kobe et al., 2001). Recently, Tai et al. (2008) investigated the effect of a magnetic field on the calcite growth rate in a constant-composition environment. Using a commercial magnetic water treatment device (MWTD) with a magnetic intensity of 0.18 T, the crystal growth rate was measured in a fluidized bed using calcite seeds. Although the growth rate data obtained in such a manner is somewhat different from the deposit rate of CaCO₃ scale grown on the pipe wall, the trend of growth phenomena should be qualitatively similar. There are two advantages of using the constant-composition technique for simulating the scale deposition, i.e., an experimental run can be completed within a few hours and the interaction between the magnetic field and one of the solution properties, including pH, supersaturation, ionic strength, ionic activity ratio, or superficial velocity can be observed by keeping other solution variables constant. Interesting results have been obtained using this type of study. The calcite growth rate was greatly suppressed by applying a magnetic field at low pH and supersaturation. On the other hand, the crystal growth rate seemed to increase when the solution pH was above 10.0 and the relative supersaturation was higher than 1.4. A more surprising result was that the suppression effect was observed in a wide range of species activity ratio ($R = a_{Ca^{2+}}/a_{CO_3^{2-}}$) from 0.25 to 8.5, except at the ratios near unity. Thus, the magnetic effect on calcite growth, either suppression or promotion, was evident.
In the studies of positive magnetic effect, all the authors agreed that the strength of the magnetic field should be higher than a certain value to become effective. In our laboratory, the effect of a magnetic field on calcite growth was noticeable using a commercial MWTD with an intensity of 0.18 T (Tai et al., 2008). It was interesting to compare the effectiveness of lower intensity; however, the commercial MWTD, Descal–A–Matic DC-3, used in our laboratory was the model of the lowest intensity and capacity that we were able to acquire. After this, we tried to use permanent magnets to replace the commercial device. Two magnets of different intensities, MagneGen Model 1000 and 100, were chosen in this study. At first, the operation mode was similar to that in the previous study using a commercial MWTD, i.e., the magnetic field was used to magnetize the solution. However, the calcite growth rate remained the same for a magnetization time of 3 h by using the magnet of higher intensity. Then, the operation mode was changed by moving the magnet to the fluidized bed, where the seed crystals suspended and grew. This meant that the magnetic field magnetized the solution and seed crystals simultaneously. This mode of operation worked well and the growth phenomena at various levels of supersaturation (σ) pH, and ionic strength (I) were investigated in the presence of magnet fixed on the suspension bed.

2. Experimental section

2.1. Apparatus and procedures for crystal growth

The experimental apparatus and procedures using a permanent magnet are similar to that reported by Tai et al. (2008) using a commercial MWTD. The schematic diagram of the crystallization system is shown in Fig. 1, which consists of a Plexiglas column used as the fluidized-bed crystallizer where the seed crystals grew, a storage tank where the solution composition and pH were adjusted, and a constant-composition control system which consisted of two autotitrators for adding reactant solution and NaOH solution to keep the solution at constant composition and pH, respectively. The system was modified in two aspects, i.e., the location for the magnetic field and the construction of the fluidized bed. In the original design, an MWTD was installed in line before the fluidized bed; however, the permanent magnet was fixed on the fluidized bed. To fix the magnet, a piece of steel pipe with its inside wall coated by Teflon to prevent the dissolution of iron was inserted into the lower part of the Plexiglas column as shown in Fig. 2. During the operation of the growth experiment, the bed of seed crystals was expanded to a height that was slightly over the top of the magnet. In the study of the column material effect, the permanent magnet was fixed outside the Plexiglas column using adhesive tape. In both cases, the magnetic field was oriented approximately orthogonal to the direction of flow. Such an orientation was considered to be most effective for the magnetic field (Baker and Judd, 1996). Two permanent magnets of different intensities were chosen in this study, i.e., MagneGen Model 1000 and Model 100, which were manufactured by a local company in Taiwan. The intensities of the magnets were measured by a Gauss meter (Model 6010, Bell), which would record the maximum intensity during the course of measurement. The average maximum intensities of five measurements are listed in Table 1. Without fixing to any pipe, the measured nominal intensities of Model 1000 and Model 100 were 3388.0 and 1265.6 Gauss, respectively. However, the magnetic intensity in the pipes dropped sharply, and the intensity was lower in the steel pipe. The intensity in the steel pipe was as low as 74.0 Gauss for Model 100 because the inside surface of steel pipe was coated with Teflon. It should be noted that the whole section of the steel pipe was magnetized when a magnet was fixed on it; however, the magnetic force was confined to the region covered by the magnet when a Plexiglas pipe was used.

The experimental procedure is described briefly as follows. The typical condition for crystal growth was set as pH = 8.5, I (ionic strength) = 0.018 M, σ (supersaturation) = 1.0, R (activity ratio) = 5.54, \( v \) (superficial velocity) = 0.047 m/s, and \( T \) (temperature) = 25 °C. In the later sessions, only the discussed variable was varied over a range while the other variables kept the same. The supersaturated solution of specified conditions was prepared by mixing a certain amount of Na₂CO₃ and CaCl₂ with deionized water. After the pH value was adjusted using NaOH solution (Tai et al., 1999, 2008), the solution was then pumped from the storage tank to the fluidized bed. Passing the fluidized bed, the solution would flow over back into the storage tank. When the flow rate and pH of solution became steady, calcite seed crystals of 25 g were charged into the fluidized bed and the seed crystals started to grow. Usually, it took 40–50 min for the flow rate and pH value to become steady. Once the seed crystals started to grow, a drop in Ca²⁺ concentration or pH value would trigger the autotitrators to replenish the reactants (0.1 M Na₂CO₃ and CaCl₂ solutions) simultaneously, or NaOH solution into the storage tank to maintain constant composition. The titration curve, which showed the volume of CaCl₂ solution added to the system, was recorded automatically and was used to estimate the linear growth rate of CaCO₃. A representative titration curve obtained in the presence of a magnetic field is shown in Fig. 3, in which the titration curve was shown as almost a straight line, meaning that the crystal growth rate did not change during the growth period. As far as the impurity effect was concerned, the Fe²⁺, Fe³⁺, and Cu²⁺ would reduce the calcite growth rate (Takasaki et al., 1994; Herzog et al., 1989; Parsieglia and Katz, 2000). Thus, the concentrations of these ions were checked by induced coupled plasma (ICP) analysis (Optima 3100, Perkin-Elmer) after every run of the experiment to make sure that they were at an undetectable level.

2.2. Determination of supersaturation and crystal growth rate

The relative supersaturation, \( \sigma \), defined by Nielsen and Toft (1984) was adopted as the driving force for crystal growth.

\[
\sigma = \left( \frac{K_{\text{sp}}}{K_{\text{eq}}} \right)^{1/2} - 1 \tag{1}
\]

A computer program, which contains mass-action equation, mass-balance equation, and the modified Debye–Hückel equation for estimating the activity coefficients, was used to calculate the relative supersaturation, once the total carbonate and calcium concentration and pH were known (Nancollas, 1966; Tai et al., 1993).

The crystal growth rate of calcite was estimated by the following equation developed by Tai et al. (1999) for the constant-composition operation.

\[
G = \frac{L M}{W} \left( [\text{Ca}^{2+}]_0 - [\text{Ca}^{2+}]_t \right) \frac{dV_t}{dt} \tag{2}
\]

When the titration curve, \( V_t \) vs. \( t \), is available, the crystal growth rate can be calculated by using the slope of the curve, \( dV_t/dt \), which should be a constant. If the slope of the curve does not remain constant, meaning that the extent of magnetic influence keeps changing, no meaningful data can be obtained.

2.3. Nucleation experiment

The nucleation experiment was designed for observing the magnetic effects on the polymorphism of CaCO₃ precipitates. A solution of low supersaturation, \( \sigma = 2.23 \) at pH = 9.0, was prepared and circulated in the system without adding seed crystals. The MagneGen Model 100 magnet fixed on the Plexiglas column was used as magnetic source to magnetize the circulating solution. After a certain
period of magnetization time, ranging from 24 to 48 h, a concentrated NaOH solution was added to raise the pH from 9.0 to 12.5. The solubility of CaCO₃ was a function of pH (Plummer and Busenburg, 1983), and primary nucleation was induced due to the solubility change. The precipitates were filtered immediately, then washed by ethyl alcohol and deionized water and air dried. Finally,
Table 1
Intensities of magnetic field used in this experiment

<table>
<thead>
<tr>
<th>Magnet type</th>
<th>Magnetic field intensity (Gauss)</th>
<th>Measured in Plexiglas pipe</th>
<th>Measured in steel pipe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model 1000</td>
<td>3388.0 ± 305.0</td>
<td>1024.0 ± 41.5</td>
<td>356.0 ± 15.0</td>
</tr>
<tr>
<td>Model 100</td>
<td>1265.6 ± 30.0</td>
<td>212.6 ± 2.9</td>
<td>74.0 ± 3.0</td>
</tr>
</tbody>
</table>

Fig. 3. A representative titration curve for $B = 356.0$ Gauss, pH = 8.5, $I = 0.018$ M, $\sigma = 1.2$, $R = 5.54$, $L = 774$ μm, $v = 0.047$ m/s, $T = 25^\circ$C.

Fig. 4. Growth rate of calcite as a function of relative supersaturation for pH = 8.5, $I = 0.018$ M, $R = 5.54$, $L = 774$ μm, $v = 0.047$ m/s, $T = 25^\circ$C: (○) without magnetic treatment, (•) magnetized for 3h prior to growth ($B = 356.0$ Gauss).

3. Results and discussion

3.1. Preliminary test on magnetic effect

In the early stage of this research, the experimental mode was similar to that using the commercial MWTD, i.e., the magnet was used to magnetize the solution (Tai et al., 2008). The results of calcite growth at various levels of supersaturation using the Model 1000 magnet to magnetize the supersaturated solution for 3h prior to growth of seed crystals are shown in Fig. 4, in which the calcite growth rates without magnetic treatment are also presented. The calcite growth rate increased with an increase in supersaturation for either case, and there was almost no difference between these two sets of data. These results meant that the magnetic force induced by Model 1000 magnet did not work after magnetizing the solution for 3h.

Tai et al. (2008) investigated the effect of magnetic field on the calcite growth rate using a commercial magnetic device with an intensity of 1800 Gauss, which was much higher than the highest intensity of 1024.0 Gauss used in this study. They found that the calcite growth rate was reduced immediately after the supersaturated solution passed through the magnetic device. As the magnetic effect did not show up in 3h using the permanent magnet, we decided to change the operation mode. The magnet was moved to the position outside the suspended bed of seed crystals instead of the inlet pipe to the suspended bed. In this way, the seed crystals and solution were magnetized simultaneously. Recall that 40–50 min was needed for the flow rate and pH value to become steady before the seed crystals were charged into the fluidized bed. This means that the solution was magnetized for 40–50 min prior to growth. The magnetic effect appeared immediately after the fluidized-bed crystallizer was loaded with seed crystals and the slope of titration curve stayed constant in the growth period. Experiments were then continued for studying the magnetic effects systematically using the permanent magnet.

3.2. Effects of magnetic intensity at various supersaturations

To compare the effectiveness of the magnetic field, the experiments were conducted at different magnetic intensities, i.e., without magnetic treatment or magnetized by Model 100 magnet and Model 1000 magnet fixed on steel pipe. The growth rates at various levels of supersaturation are plotted in Fig. 5. For the three cases, the calcite growth rate increased with an increase in supersaturation. The magnetic force decreased the calcite growth rate: the higher the magnetic intensity, the lower the growth rate. It is also shown in Fig. 5 that the retarded effect of a magnetic field on calcite growth was less significant in the higher supersaturation range. For instance, for the Model 100 magnet the calcite growth rate was not affected when $\sigma$ was higher than 1.3; for the Model 1000 magnet the growth rate was reduced by an order of magnitude at $\sigma = 0.5$ and by 37% at $\sigma = 1.5$. Similar results were reported by Tai et al. (2008) by using a commercial MWTD to magnetize the solution. However, they found that the calcite growth rate of treated system exceeded that of an untreated system for $\sigma$ higher than 1.4. The actual mechanism of the magnetic effect is not clear at the present time. We believe that the different growth behavior was due to the difference in magnetic intensity and operation mode.
growth rate was reduced by an order of magnitude at pH = 8.5 and did not increase much at higher pHs. As far as the effect of ionic strength was concerned, the growth rates increased with increasing ionic strength then tended to remain constant at higher levels for both cases. A slight difference is that the growth rate curve leveled off at a higher ionic strength for the case with magnetization.

The effects of pH and ionic strength on the calcite growth rate have been reported by Tai et al. (2008) using a commercial magnetic device to magnetize the supersaturated solution. They found that the growth rates were reduced by an order of magnitude at lower pH and increased after the pH exceeded 10.0 in the presence of magnetic field. The pH effect in this study is similar to the results in Tai et al. (2008) at lower pH, but is different at higher pH. In this experiment, the calcite growth rates of the magnetized system were still far below than that of the untreated system, as shown in Fig. 6. As far as the ionic strength is concerned, similar results were obtained for the system without magnetization in the two studies, and, as it should be, even the level-off point for the growth rate curves is about the same. However, the growth phenomena were quite different in the case of the magnetized system. The calcite growth stayed constant and was almost stopped by the magnetic force in the whole range of ionic strength as reported by Tai et al. (2008), but the crystal growth rate increased almost by an order of magnitude in the same range of ionic strength in this study ranging from 0.005 to 0.027 M, as shown in Fig. 7. Recall that the intensity of the magnetic field and operation mode were different in the two studies.

3.4. Effect of bed material

Gabrielli et al. (2001) investigated the effects of a magnetic field on scale prevention using a home-made magnetic device fixed on the pipe. They used different pipe materials and found that stainless steel was more effective than PVC. In this experiment, growth rate results were compared between two cases when the Model 1000 magnet was fixed on the steel and Plexiglas pipes, respectively. The results at various levels of supersaturation are presented in Fig. 8. The calcite growth rate was lower when the Plexiglas pipe was used, meaning that Plexiglas was more effective in suppressing the calcite growth. However, the difference was not really great; the greatest difference being 35% at σ = 1.5. The result was not consistent with that reported by Gabrielli et al. (2001). The conflicting results were attributed to the coating of Teflon on the inside surface of steel pipe.
Referring to Table 1, the magnetic intensity measured in the steel pipe was 356.0 Gauss, which was lower than 1024.0 Gauss in the Plexiglas column. It seemed reasonable that a higher intensity field would be more effective. Therefore, there is no conclusion on the effect of the bed material.

### 3.5. Memory effect of magnetic field

In the preliminary test of magnetic field using the Model 1000 magnet, the magnetic effect was not observed in 3 h, so we continued the experiment by extending the magnetization time. The magnetic effect appeared at 4 h. When the solution was magnetized for 5 h prior to growth, the seed crystals almost did not grow at all in the first hour, as indicated by the titration curve shown in Fig. 9. Then, the growth rate of seed crystals increased gradually, as judged from the increase in the slope of titration curve. The growth rates estimated from the titration curve for different periods of time are presented in Table 2. The growth rate increased from 0 to 0.698 \times 10^{-10}\, \text{m/s}, which approached to that without magnetization. It meant that the calcite growth rate was fully recovered in the period between 14200 and 17700 s, i.e., about 4–5 h. This growth behavior is similar to the “magnetic memory” reported by a number of investigators, which means that the antiscaling properties of the treated water will retain for some time following magnetic treatment (Baker and Judd, 1996).

### 3.6. Effect of magnetic field on the polymorphs of CaCO₃

The influence of aging time on the polymorphs of CaCO₃ has been investigated in the presence of magnetic field (Kobe et al., 2002). The percentage of aragonite increased with aging time when the magnetic field was applied. The magnetic effect which we discussed here excluded the aging effect. Recall that in this experiment the precipitate was induced by changing pH of supersaturated solution, which had been magnetized for a period of time, and was filtered right after the nucleation occurred. The results are shown in Table 3. Runs 11 and 12 compared the percentage of polymorphs produced without and with magnetization, respectively, after a circulation time of 24 h. In the case without magnetization, the product was almost all calcite, which was precipitated at a pH of 12.5. This result was consistent with that reported by Tai and Chen (1998) who found that calcite was the predominant form of CaCO₃ precipitated at a pH greater than 12.0 using a constant-composition method. When the solution was magnetized for 24 h before nucleation, aragonite appeared in an appreciable percentage, which was greater than 50%. If the magnetization time was extended to 48 h, the predominant polymorphic form was aragonite and the calcite disappeared. In this study, the CaCO₃ crystals were induced spontaneously, by changing pH, so the clusters existing in the supersaturated solution did not have time to change their form in the nucleation process, i.e., the clusters possessed distinct form with and without magnetization, and, as a result, different polymorphs of CaCO₃ crystals were produced.

### 3.7. A possible mechanism of magnetic effect on calcite growth

Before we propose a possible mechanism of the magnetic effect on the calcite growth in this study, we would first like to summarize the unique features of this experiment. As far as the operation mode is concerned, the magnetic field was applied on the solution and seed crystals simultaneously, instead of the solution only. The intensities of the magnets used here were rather low, i.e., 356.0 and 74.0 Gauss, respectively, but they were effective for suppressing the calcite growth rates. The lowest intensity of the magnetic field to affect the calcite growth rate reported in previous literature was about 1000 Gauss when the solution was subjected to magnetization for 2 h (Chibowski et al., 2003).

From the results of the nucleation experiments in this study, we postulated that different forms of CaCO₃ cluster exist in the supersaturated solution after the magnetic field was applied for a period of time. Thus, the calcite growth rate was reduced by magnetizing the supersaturated solution because the clusters unfavorable for calcite were not adsorbed by the crystal surface. When the solution and seed crystals were magnetized simultaneously, as in the case of...
this study, the magnetic effect was more significant. This can be explained by the theory proposed by Clontz and McCabe (1971) and Tai et al. (1992) regarding the source of secondary nuclei. It was suggested that the source of nuclei in secondary nucleation was an adsorption layer comprised solute clusters on the surface of growing seed crystals. These clusters lined up in the adsorption layer accompanying incorporation into the growing crystal. It was possible that the structure of the adsorbed clusters was altered by the magnetic force just like the clusters in the solution. Then, they desorbed from the crystal/solution interface after they became the unfavorable form for calcite growth. Thus, the growth rate of the seed crystals was further reduced. However, there is no instrument available for detecting the structure of clusters either in the solution or adsorbed on crystal surface to make a good judgment on the magnetic effect.

4. Conclusion

The effect of a magnetic field on calcite crystal growth was studied by fixing permanent magnets, MagneGen Model 1000 or 100, outside the fluidized bed where the seed crystals grew, using the constant-composition technique. The calcite growth rates were measured at various levels of supersaturation, pH, and ionic strength. In the presence of a magnetic field, the growth rates of calcite were reduced and the suppression percentage was higher for the magnet of higher intensity. The percentage of suppression was higher at low levels of supersaturation, pH, and ionic strength, especially at low supersaturation. When the relative supersaturation, \( \sigma \), was 0.5, the calcite growth rate was reduced by an order of magnitude in the presence of Model 1000 magnet. In cases where the magnets were used to magnetize the solution only, the magnetic field was ineffective for several hours. As far as the magnetic effect on the polymorphic form of CaCO\(_3\) was concerned, the magnetization of solution would favor the formation of aragonite. In view of the experimental results of this growth and nucleation study, a mechanism regarding the structure alternation of CaCO\(_3\) clusters was proposed to explain the effect of magnetic field on the calcite growth rate.

### Notation

- \( a_i \): activity of \( i \) species, kmol/m\(^3\)
- \( B \): intensity of magnetic field, Gauss
- \( [\text{Ca}^{2+}]_0 \): Ca\(^{2+}\) concentration of the added solution, kmol/m\(^3\)
- \( [\text{Ca}^{2+}]_i \): Ca\(^{2+}\) concentration of the original solution, kmol/m\(^3\)
- \( C_i \): concentration of \( i \) species, kmol/m\(^3\)
- \( G \): linear growth rate, m/s
- \( I \): ionic strength, kmol/m\(^2\)
- \( K_{\text{ip}} \): ionic product
- \( K_{\text{sp}} \): solubility product
- \( L \): mean crystal size, m
- \( M \): molecular weight, kg/kmol
- \( R \): Ca\(^{2+}\) to CO\(_2\)\(^{−}\) activity ratio, dimensionless
- \( t \): time, s
- \( T \): temperature, °C
- \( v \): superficial velocity, m/s
- \( V_a \): volume of the added solution, ml
- \( W \): weight of seed crystals, kg
- \( z_i \): valence of \( i \) species, dimensionless
- \( \sigma \): relative supersaturation, dimensionless

### Greek letter

- \( \gamma \): surface tension, N/m

### Table 3

<table>
<thead>
<tr>
<th>Run no.</th>
<th>Magnetization by Model 100</th>
<th>Circulation time (h)</th>
<th>Percentage of polymorphs (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>11</td>
<td>No</td>
<td>24</td>
<td>Aragonite: 100</td>
</tr>
<tr>
<td>12</td>
<td>Yes</td>
<td>24</td>
<td>Calcite: 42.2</td>
</tr>
<tr>
<td>13</td>
<td>Yes</td>
<td>48</td>
<td>Vaterite: –</td>
</tr>
</tbody>
</table>

Initial solution conditions: pH = 9.0, \( f = 0.018 \) M, \( \sigma = 2.23, R = 5.54 \), and \( T = 25 \) °C.