

Effect of Nonstoichiometry on Reaction Crystallization of Calcium Carbonate in a Couette–Taylor Reactor

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ABSTRACT: The effect of stoichiometric reaction conditions on CaCO_3 crystallization was investigated using a $\text{Ca}(\text{OH})_2\text{--H}_2\text{CO}_3$ reaction system in which the influence of ionic byproducts on the crystallization was effectively excluded. The largest rhombohedron-like crystals were produced under stoichiometric reaction conditions (pH 7.8), which corresponded closely to the isoelectric point (pH $\approx$ 8.2). When increasing the excess of the Ca^{2+} species, the individual crystal size was rapidly reduced and the crystal shape gradually became a spindle and then a needle. Meanwhile, with an excess of CO_3^{2-} , rhombohedron-like crystals were predominantly formed, although the individual crystal size decreased responsively when increasing the excess species concentration. Accordingly, on the basis of the experimental results, the modifications in the crystal shape and size apparently stemmed from the excess species and involved molecular growth on the crystal faces via preferential adsorption. Plus, the agglomeration of individual crystals was promoted when increasing the excess concentration as a result of enhancing the collision efficiency of the crystals.

1. Introduction

Calcium carbonate crystals are generally used as fillers in the textile and rubber industry, which requires crystals with a fine size and uniform morphology.¹ The crystallization of calcium carbonate can be conducted by either liquid–liquid (L–L) or gas–liquid (G–L) reactions. A G–L [$\text{CO}_2\text{--Ca}(\text{OH})_2$] reaction system would seem to be preferable, as the reaction produces water as the byproduct, thereby eliminating any byproduct influence on the crystallization.^{2,3} However, a G–L reaction system also has certain limitations due to the difficulty involved in controlling the reaction conditions and complications related to analyzing the crystallization processes in combination with the mass transfer and reaction occurring during the G–L interface process. For example, the gas hold-up volume and residence time are hard to control and uniform mixing in the reactor is difficult to achieve. Plus, it is difficult to estimate stoichiometric reaction conditions for crystallization.

In contrast, an L–L reaction system provides certain advantages as regards control of the reaction conditions and adjusting the crystallization conditions, such as the temperature, pH, solution mixing, and holding time (residence time), etc. Therefore, these systems are more frequently adopted for calcium carbonate crystallization,^{4–8} even though the production of ionic byproducts, such as sodium chloride, potassium chloride, and ammonium chloride, is inevitable when cationic reagents [CaCl_2 , $\text{Ca}(\text{NO}_3)_2$] and anionic reagents [Na_2CO_3 , K_2CO_3 , $(\text{NH}_4)_2\text{CO}_3$] are used for the reaction. Such ionic byproducts can have an influence on the crystallization processes, like an electrolytic additive; yet, it is hard to

distinguish the modified crystallization from the crystallization resulting from the apparent reaction conditions.

Although the effect of the crystallization conditions, such as the concentration, pH, temperature, and mixing, has already been well-investigated in L–L reaction systems, there have been relatively few studies on the effect of nonstoichiometric conditions on calcium carbonate crystallization.^{1,9} Plus, none of these previous studies has carefully considered the potential involvement of byproducts in the crystallization. Accordingly, the purpose of the present study was to investigate the effect of nonstoichiometric reaction conditions on CaCO_3 crystallization in terms of the size, morphology, and agglomeration of crystals using a $\text{Ca}(\text{OH})_2\text{--H}_2\text{CO}_3$ reaction based on combining the advantages of an L–L reaction system as regards controlling the reaction conditions and a G–L reaction system as regards excluding any byproduct effect. The experiment was carried out in a continuous Couette–Taylor reactor that maintained a strong turbulent vortex to minimize any local fluctuation in the crystallization conditions.

2. Experimental Section

2.1. Couette–Taylor Reactor. The Couette–Taylor reactor consisted of an outer cylinder made of PMMA and an inner cylinder made of stainless steel. The reactor was placed horizontally to minimize the effect of hydraulic pressure on the fluidic motion. To induce a Taylor vortex, the inner cylinder was rotated by a DC motor equipped with a speed controller. Sample ports were positioned on the top side of the outer cylinder. The two aqueous reactants were injected into the reactor through two ports located opposite the inlet of the reactor. The reactor design is summarized in detail in Figure 1. The turbulent vortex intensity in the Couette–Taylor reactor was estimated via the Taylor number (Ta) defined as $\text{Ta} = (d/R_1)^{1/2}(\omega_1 R_1 d/\nu)$, where d , R_1 , ω_1 , and ν are the gap size between the two cylinders, radius, rotating speed of the inner cylinder, and kinematic viscosity of the solution, respec-

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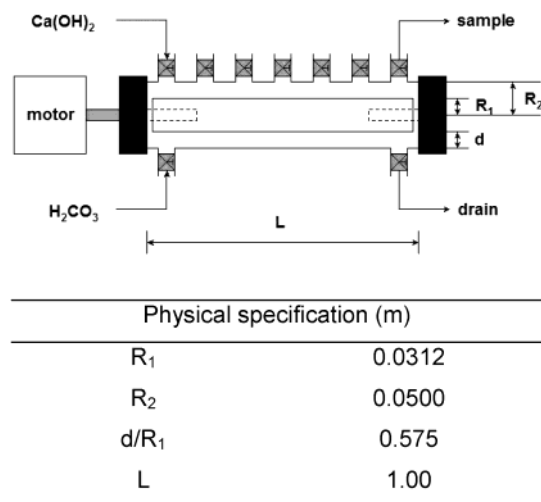


Figure 1. Schematic diagram of the Couette–Taylor reactor.

tively.^{10,11} In addition, the axial Reynolds number (Re_z) was calculated using the definition $\{Re\}_z = (d/\nu)[Q/\pi(R_2^2 - R_1^2)]$, where Q and R_2 are the volumetric flow rate of the reactants and radius of the outer cylinder, respectively. On the basis of the above definitions, Ta was calculated as 35 500 and Re_z as 20.0 under the operating conditions used in the present study. As such, this indicates that the fluidic motion belonging to a turbulent region produced strong radial and weak axial mixing in the reactor, like a plug flow.

2.2. Experimental Procedure. The calcium carbonate was crystallized by the reaction between aqueous H_2CO_3 and $Ca(OH)_2$ solutions in the reactor. The feed solution was prepared with $Ca(OH)_2$ (99%) purchased from Shinyo Chem. Co. (Japan) without further purification and filtered to eliminate any solid impurities, while the H_2CO_3 solution was prepared by absorbing CO_2 gas (99%) into deionized water (20 L) until reaching an equilibrium at 25 ± 0.1 °C. The absorption of CO_2 by the water was monitored using a pH meter (Orion Research, 720A, U.S.A.), and an absorption equilibrium was consistently attained within 1 h. An aerator was also used for effective CO_2 absorption. The temperature of the solutions was maintained at 25 ± 0.1 °C using a temperature circulation bath.

The reactor was initially filled with deionized water while rotating the inner cylinder to fully develop a turbulent vortex motion, and then, the crystallization of calcium carbonate was initiated by injecting the two reactants into the reactor using a peristaltic pump (Cole-Parmer Instruments, Masterflex P-77921-20, U.S.A.). The rotating speed and mean residence time in the reactor were fixed at 800 rpm and 10 min, respectively. The crystallization process was monitored using pH and Ca^{2+} ionic meters (Orion Research, Ion plus 9720BN) at the outlet stream and usually reached a steady state within 10 times of the mean residence time. In the present experiment, more than 15 times of the mean residence time was always allowed to ensure a steady state of crystallization in the reactor.

2.3. Analysis. Suspension samples were taken from the outlet stream in a steady state and immediately diluted in a saturated solution to quench the crystallization in the suspension. Thereafter, the solid crystals in the sample suspension were filtered out using a cellulose membrane filter with 0.2 μm diameter pores (Advantec MFS Inc., A020A047A, U.S.A.). The filtered crystals were dried in a desiccator at room temperature for 24 h, and then, the size and morphology of the individual crystals were analyzed using a scanning electron microscope (SEM; Leica, Stereoscan 440, Germany). On the basis of the Heywood diameter definition, the mean size of the individual crystals was determined from SEM images of 50–100 crystals, as previously suggested by Jung et al.³ In addition, the agglomerates of crystals in the product suspension were measured as regards their size and distribution using a particle size analyzer (PSA; Malvern Instruments,

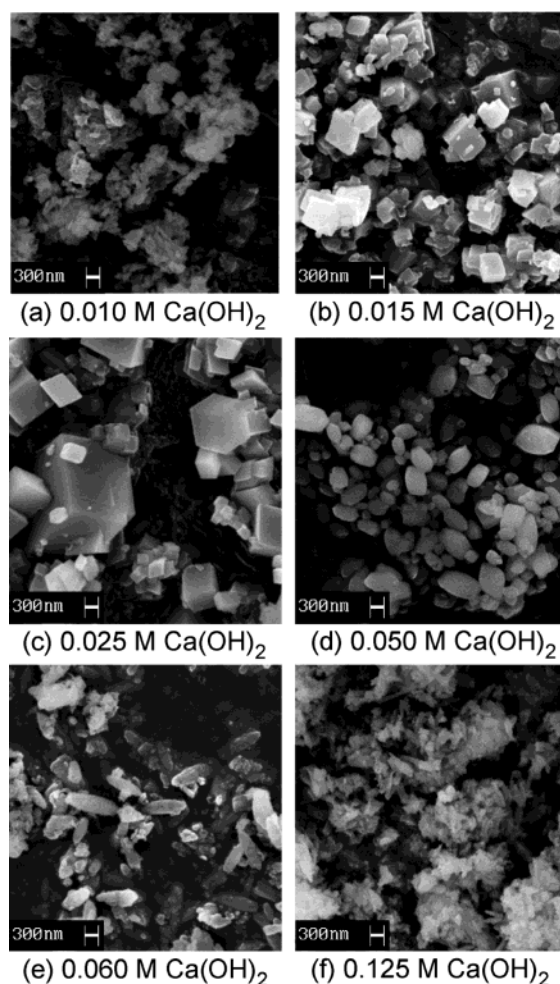


Figure 2. Typical SEM images of $CaCO_3$ produced by crystallization at various stoichiometric conditions for reaction.

Mastersizer 2000, U.K.). To redisperse those crystals weakly adhered to the agglomerates, an ultrasonic treatment was applied to the suspension. Usually, the redispersion of the weakly adhered crystals was achieved with 50 W of sonic power within 10 min. Also, an X-ray diffractometer (XRD; MAC Science, M18XHF-SRA, Cu $K\alpha$ line, Japan) was used to examine the crystal structure of the samples.

3. Results and Discussion

3.1. Morphology and Size of Crystals. In a saturated aqueous solution, H_2CO_3 is partially dissociated into carbonate ions of HCO_3^- and CO_3^{2-} . Therefore, the pH value of the saturated solution as well as the equilibrium constants of dissociation⁴ are required to estimate the total H_2CO_3 absorbed in the solution ($[H_2CO_3] = C_{A0}$), which is equal to a summation of the undissociated H_2CO_3 ($[H_2CO_3]_{undis}$) and dissociated carbonate ion ($[HCO_3^-]$ and $[CO_3^{2-}]$) concentrations. In the present study, a pH of 3.98 for the saturated solution revealed that the total H_2CO_3 was about 0.025 M, and among the species in the solution, $[H_2CO_3]_{undis}$ ($=2.47 \times 10^{-2}$ M) was dominant over $[HCO_3^-]$ ($=1.05 \times 10^{-4}$ M) and $[CO_3^{2-}]$ ($=4.69 \times 10^{-11}$ M).

When the $Ca(OH)_2$ concentration (C_{B0}) is varied from 7.0×10^{-3} to 1.25×10^{-1} M with a fixed $[H_2CO_3]$ of 2.5×10^{-2} M, the typical morphological change in the crystals is displayed in Figure 2. Below a 0.01 M $Ca(OH)_2$ concentration, the individual crystals were hun-

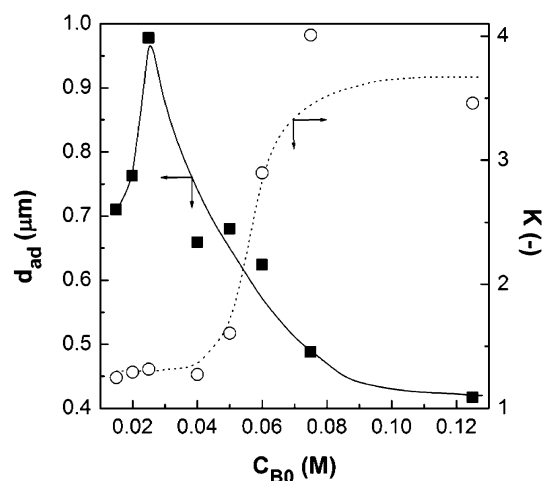


Figure 3. Aspect ratio (K) and mean size of individual crystals (d_{ad}) relative to various stoichiometric conditions for reaction.

dreds of nanometers in size and their morphology was not well-configured; however, when the Ca(OH)_2 concentration was increased, the individual crystals became clearly rhombohedron-shaped. The clearest and largest individual rhombohedron-shaped crystals were obtained under stoichiometric reaction conditions corresponding to 0.025 M. Beyond this concentration of Ca(OH)_2 , the morphology of the individual crystals became first spindle-shaped and then needle-shaped when further increasing the Ca(OH)_2 concentration. As such, corner-cut rhombohedron-like crystals were produced at 0.04 M, meaning the formation of new faces at the edges and corners of the crystals, and the new faces were even better developed at 0.05 M. Then, a higher concentration of Ca(OH)_2 brought about spindle-shaped crystals, and needlelike crystals appeared within a range of 0.075–0.125 M.

The individual crystal size (d_{ad}) significantly changed relative to the Ca(OH)_2 concentration, as shown in Figure 3. The mean size of the individual crystals was maximized under the stoichiometric reaction conditions of 0.025 M and then rapidly reduced when the Ca(OH)_2 concentration was either increased or decreased from the maximized concentration. In addition, the shape factor of the individual crystals, defined as the ratio of the particle size on the major axis to the size on the minor axis,³ quantitatively indicated a morphological shift from cubic-shaped to needle-shaped crystals when increasing the Ca(OH)_2 concentration above 0.025 M. However, a decrease in the Ca(OH)_2 concentration below 0.025 M did not bring about a variation in the shape factor of the individual crystals. Therefore, it would appear that the crystal morphology and size were closely dependent on the reactant concentration ratio of Ca(OH)_2 to H_2CO_3 . Similar results have also been reported for calcium carbonate crystallization using a G–L reaction system.³

The pH of the suspension varied with the reactant concentration, as shown in Figure 4. Under stoichiometric reaction conditions, the pH was measured as 7.8. On the basis of the surface charge of the crystals, the stoichiometric conditions provided equal amounts of cations and anions in the solution, for which the pH was closer to isoelectric point conditions (pH 8.2) than neutral conditions (pH 7.0).^{12,13} When the Ca(OH)_2

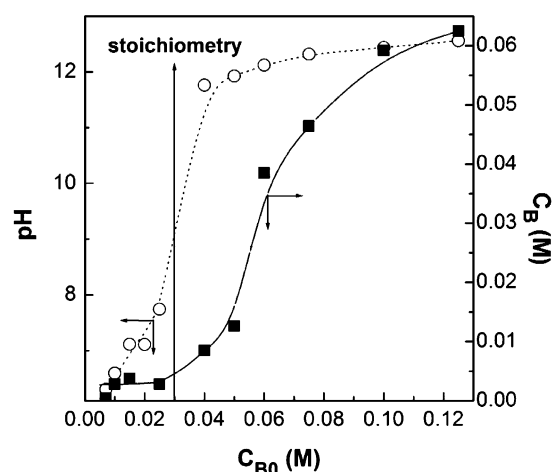


Figure 4. pH and Ca^{2+} ionic concentration (C_B) relative to various stoichiometric conditions for reaction.

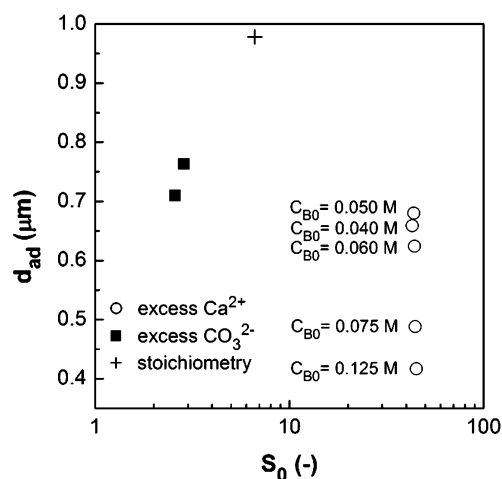


Figure 5. Mean size of individual crystals (d_{ad}) relative to initial supersaturation (S_0).

concentration was increased beyond 0.025 M, Ca(OH)_2 became the excess species and the solution pH sharply increased to around 12.5, which almost corresponded to the pH of the Ca(OH)_2 reactant solution. Conversely, when the Ca(OH)_2 reactant concentration was decreased below 0.025 M, H_2CO_3 became the excess species and the solution pH decreased.

The contribution of initial supersaturation (S_0) on the crystal size was evaluated as shown in Figure 5. Here, the initial supersaturation was estimated using the method suggested by Ogino et al.⁴ and the pH value was measured in the present study. Below $S_0 = 6.63$ where CO_3^{2-} was in excess, the individual crystal size increased as S_0 increased, which corresponded to a decrease of excess ion concentration. Above $S_0 = 6.63$ where Ca^{2+} was in excess, the crystal size was slightly reduced although S_0 increased from 6.63 to 42.9 by increasing the excess ion concentration. However, although S_0 slightly increased from 42.9 to 45 by increasing the excess species concentration from 0.04 to 0.125 M, a significant reduction of crystal size was caused. Therefore, in the present crystallization, the change in the crystal morphology and size with a variation in the reactant concentration was predominantly related to the excess reactant species in the crystallization process.

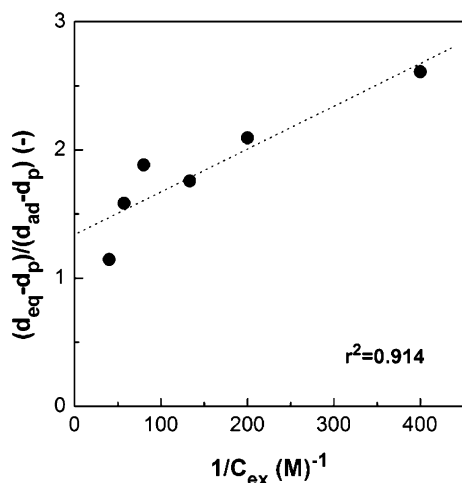


Figure 6. Correlation of mean size of individual crystals (d_{ad}) with excess ion concentration (C_{ex}) based on the Bliznakov and Kirkova equation (eq 1).

To determine the influence of an excess species on the crystal size, a Bliznakov and Kirkova equation based on a Langmuir isotherm¹⁴ was applied as

$$\frac{d_{ad} - d_p}{d_{eq} - d_p} = \frac{K_{ad}C_{ex}}{1 + K_{ad}C_{ex}} \quad (1)$$

where d_p , d_{ad} , and d_{eq} are the mean diameters of the crystals obtained under stoichiometric reactant conditions (no excess species), nonstoichiometric reactant conditions, and with an equilibrium concentration of excess species, respectively.³ C_{ex} is the concentration of the excess species in the solution, defined as $|C_{A0} - C_{B0}|/2$ for a L–L reaction, and K_{ad} is the affinity constant. From the present experimental results, d_p was $0.978 \mu\text{m}$ for the mean crystal size obtained under stoichiometric conditions, while d_{eq} was $0.417 \mu\text{m}$ for the mean crystal size obtained under extreme excess conditions of $\text{Ca}(\text{OH})_2$. From these data, K_{ad} as the affinity constant in the Langmuir isotherm was estimated as $0.3 \text{ m}^3/\text{mol}$ (Figure 6), which was consistent with the values previously reported by Jung et al.³ and Huang et al.¹⁵

In the present study, the morphological change was apparently brought about by the selective adsorption of the excess Ca^{2+} species on the crystal surfaces, stemming from the atomic array of the crystal structure.^{16–18} However, with excess CO_3^{2-} , there was only a little selective adsorption on the crystal faces, resulting in only a slight morphological change, yet a significant reduction in the crystal size. In contrast to the morphology, the crystal structure was not affected by any excess species, as shown from the XRD patterns in Figure 7. All of the crystals obtained via the $\text{Ca}(\text{OH})_2$ – H_2CO_3 reaction system were calcite in the concentration range of 0.007 – 0.125 M $\text{Ca}(\text{OH})_2$ at 10 min (residence time).

Previous studies also found that crystal morphology and size were significantly influenced by the excess condition of reactants. For example, vaterite was predominantly crystallized under Ca^{2+} excess conditions, while calcite was favorably formed under CO_3^{2-} excess conditions.^{1,9} Plus, the crystal size of BaSO_4 was sensitively reduced when increasing the ionic concentration

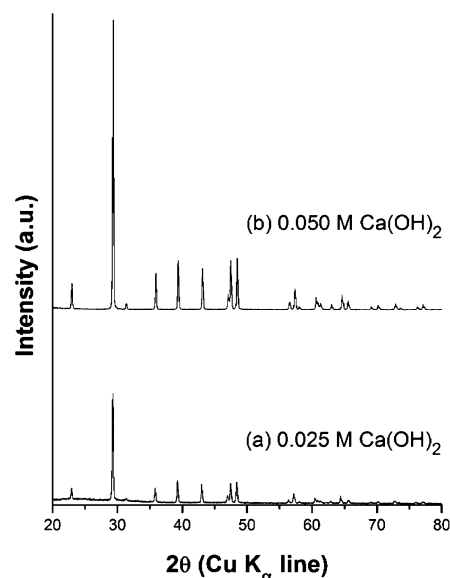


Figure 7. XRD pattern of CaCO_3 produced by the crystallization at various stoichiometric conditions for reaction.

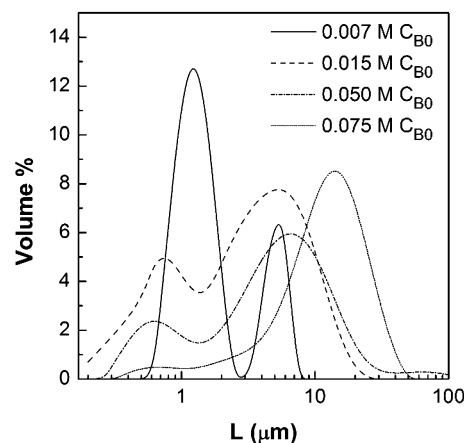


Figure 8. Agglomerate size distributions of CaCO_3 produced by crystallization at various stoichiometric conditions for reaction.

of the excess species during crystallization.¹⁹ However, all of these studies used an L–L reaction system for the crystallization and the contribution of the ionic byproduct was not carefully considered.

3.2. Agglomeration. The crystal agglomeration was measured using PSA based on the principle of dynamic light scattering. Bimodality in size distribution is always observed in all concentrations of reactants, as shown in Figure 8. In the bimodal distribution patterns, the small size peak (first peak) was about 0.5 – $1.0 \mu\text{m}$, corresponding closely to the individual crystal size (Figure 3), whereas the large peak (second peak) ranged from 4 to $20.0 \mu\text{m}$, depending on the $\text{Ca}(\text{OH})_2$ concentration, and was related to the agglomeration of the individual crystals. As such, it appeared that the crystal agglomeration brought about the bimodality in the size distribution,^{20,21} which was also visually confirmed by SEM images of the present results.

When increasing the $\text{Ca}(\text{OH})_2$ concentration, the fraction of the first peak in the distribution was reduced, while the fraction of the second peak was increased. Essentially, the mean size of the agglomerates (d_{agg})

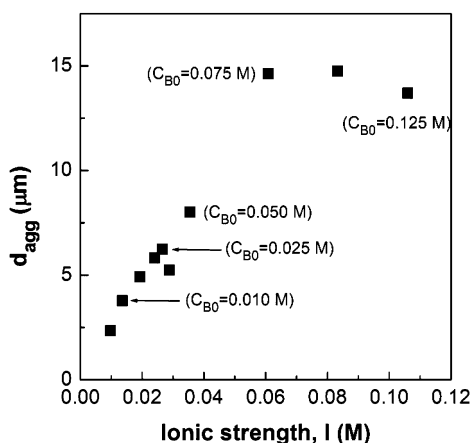


Figure 9. Mean size of aggregates (d_{agg}) relative to ionic strength.

increased when increasing the Ca(OH)_2 concentration, as shown in Figure 9, although the mean size of the individual crystals decreased (Figure 3), which indicates that the Ca^{2+} species had a different influence on crystal agglomeration than on the molecular growth of the crystals. According to Collier et al.,²² the collision efficiency for crystal adhesion depends on the electric double layer thickness controlled by the ionic strength of the solution. Therefore, the ionic strength (I) of the solution is an important factor in determining the crystal agglomeration in CaCO_3 crystallization. For example, when the ionic strength is low, contact with other crystals for adhesion is difficult and it takes time for the adhered crystals to agglomerate because of the thick electrical double layer on the crystals. However, with a high ionic strength, the electrostatic repulsion force between the crystals is reduced and the van der Waals attraction is enhanced due to a thin double layer. Accordingly, an increase in the ionic strength encourages the agglomeration of individual crystals. In the present study, an increase in the Ca(OH)_2 concentration caused an increase in the ionic strength of the solution, thereby resulting in the efficient agglomeration of individual crystals, as demonstrated in Figure 9, where the mean agglomerate size was approximately proportional to the ionic strength, which is consistent with the measurements of Collier et al.²² It should also be mentioned that the agglomerate size and distribution in the Couette–Taylor reactor were much smaller and narrower than those in an MSMPR reactor due to more uniform residence time distribution.²³

4. Conclusion

When using an L–L [Ca(OH)_2 – H_2CO_3] reaction system for the crystallization of CaCO_3 in a Couette–Taylor reactor, it was found that the morphology and mean size of individual crystals significantly varied with the reactant conditions. As a result of the high radial mixing effect of the Taylor vortex, homogeneous crystallization conditions could be achieved in the reactor. The largest rhombohedral crystals were obtained under stoichiometric reaction conditions. When the Ca^{2+} species was in excess, the individual crystal size rapidly

reduced and the morphology gradually shifted from a rhombohedral shape to a spindle and eventually to a needle shape. An excess of the CO_3^{2-} species also reduced the individual crystal size, yet did not significantly modify the crystal morphology. This was ascribed to the influence of the excess reactants on the molecular growth of the crystals via preferential adsorption on the crystal faces, especially in the case of an excess of the Ca^{2+} species. The experimental results of the crystal size reduction were quantitatively described by a Langmuir isotherm, allowing the affinity constant to be estimated as $0.3 \text{ m}^3/\text{mol}$, which is consistent with other reported values. In addition, the agglomeration of individual crystals was promoted when increasing the excess species concentration, as the surface charge of the crystals was reduced relative to the ionic concentration of the excess species. Consequently, the mean agglomerate size was approximately proportional to the ionic strength of the solution.

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