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Effect of Taylor vortices on calcium carbonate crystallization by gas–liquid reaction

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Abstract

The effects of Taylor vortices on the mean size, size distribution, and morphology of calcium carbonate crystallized by the reaction of gaseous carbon dioxide and aqueous calcium hydroxide were experimentally investigated in a Couette–Taylor reactor. Via the absorption of CO₂ gas into pure water, the mass transfer coefficient of CO₂ at the gas–liquid interface was measured relative to the rotating speed of the inner cylinders in the Couette–Taylor reactor. Polymorphs of rhombohedral-, spindle-, and needle-shaped calcium carbonate crystals were observed with a change in the operating variables, including the reactant concentration and flow rate and the rotating speed of the inner cylinder in the Couette–Taylor reactor. Using a dimensionless parameter consisting of the operating variables, it was demonstrated that the morphological changes in the calcium carbonate crystals in the present reactor could be anticipated from the operating conditions. In the crystallization, the mean crystal size, predominantly controlled by crystal agglomeration, was most influenced by the fluid dynamic conditions related to the rotating speed of the inner cylinder and reactor geometry.

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1. Introduction

Calcium carbonate is one of the most popular crystalline powders applied in various areas of plastics, textiles, rubbers, adhesives, paints, and wastewater treatment. Therefore, many studies have already been performed on the crystallization

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Nomenclature			
a	gas–liquid interface area per unit reactor volume, m^{-1}	Q_G	volumetric flow rate of CO_2 gas, m^3/s
C_A	concentration of CO_2 in solution, mol/m^3	Q_L	volumetric flow rate of $\text{Ca}(\text{OH})_2$ solution, m^3/s
C_{AO}	concentration of CO_2 at entrance to reactor, mol/m^3	Re	Reynolds number defined as $\omega_i r_i d/\nu$, dimensionless
C_A^*	saturation concentration of CO_2 , mol/m^3	r_1	radius of inner cylinder, m
C_{BO}	concentration of $\text{Ca}(\text{OH})_2$ in solution, mol/m^3	r_o	radius of outer cylinder, m
d	gap size between inner and outer cylinder, m	SC	parameter defined as Eq. (5), dimensionless
f	friction factor, dimensionless	T_M	torque at wall of inner cylinder
k_L	actual gas–liquid mass transfer coefficient, m/s	t_S	mean residence time of solution in Couette–Taylor reactor, s
L_C	reactor length, m	u	fluid velocity, m/s
$L_{1,0}$	number-based mean particle size, μm	V_R	reactor volume, m^3
$L_{4,3}$	volume-based mean particle size, μm	x	axial position in reactor, m
$\dot{n}_{G0}$	molar flow rate of CO_2 gas, m^3/s	<i>Greek letters</i>	
P	total power input in reactor, W	ε	energy dissipation, W/kg
		ρ_L	density of suspension, kg/m^3
		τ	mean residence time, s
		τ_ω	shear stress at wall of rotating inner cylinder, Pa

kinetics and processes of calcium carbonate [1–9]. In the reaction crystallization of Kazmlerczak et al. [1], the kinetics of calcium carbonate, including crystal nucleation and growth, were studied using a constant composition method where the activities of ionic species remained constant. Reddy and Nancollas [2] showed that the crystal growth of calcium carbonate is controlled in a second-order supersaturated concentration of the solution, indicating a surface-integration limiting step. Söhnel and Mullin [3] took account of changes in the total external crystal surface area over time to estimate the crystal growth rate. Christoffersen and Christoffersen [4] adopted a spiral growth mechanism for crystal growth in seeded crystallization, while Swinney et al. [5] presented a power law model for the crystal nucleation rate of calcium carbonate.

According to Wray and Daniels [10] and Hostomsky and Jones [11], the crystal morphology of calcium carbonate, including the structural isomers of calcite, aragonite, and vaterite, is determined by the crystallization conditions, such

as the supersaturation, temperature, concentration of the reagents, pH, and residence time in the reactor. Furthermore, the morphological modification of calcium carbonate using an ionic additive during crystallization was suggested by Chakraborty et al. [12] and Tai and Chen [13]. However, predicting the crystal size and morphology of calcium carbonate is still difficult because the crystallization kinetics and processes are intricately linked with the crystallization conditions, including the mixing, reactant concentration, mean residence time, pH of the solution, and reactor configuration, etc.

In particular, when using a gas–liquid reaction system for calcium carbonate crystallization, the interfacial transports between the gas–liquid phases, such as the gas absorption and molecular transfer, create further difficulties in controlling the crystallization when compared with a liquid–liquid reaction system, as adopted in most previous studies. As such, only a limited number of studies investigated calcium carbonate crystallization with a gas–liquid reaction system [14–17].

However, a gas (CO_2)–liquid ($\text{Ca}(\text{OH})_2$) reaction system is advantageous in crystallization studies, as the influence of ionic by-products on the crystallization, which are inevitable in a liquid–liquid reaction system, can be eliminated, as demonstrated by Jung et al. [18].

The fluid dynamic conditions are an important factor determining the crystal size and morphology in crystallization. Due to the macro- and micro-fluid motion involved in the crystallization processes, the crystal size distribution changes significantly with the reactor configuration and geometry as well as the mixing intensity in the reactor [19]. While the residence time distribution in the reactor is influenced by the macro-fluid motion, the reaction and crystal growth are predominantly controlled by the micro-fluid motion. In a gas–liquid reaction system, the interfacial transport between gas–liquid phases is dependent on the fluid dynamic conditions. In addition, fluid dynamic motion causes the simultaneous occurrence of crystal collision leading to crystal aggregation and fluid shear resulting in the breakage of aggregated crystals.

In contrast to previous studies utilizing batch and stirred tank reactors, the present study employed a Couette–Taylor reactor to investigate the influence of fluid dynamic conditions on gas–liquid reaction crystallization. As shown in Fig. 1, the radial fluid motion is induced by rotation of the inner cylinder, while the outer cylinder remains stationary. When the rotating speed of the inner cylinder exceeds a certain critical value, the radial

fluid motion creates periodic macroscopic flow patterns, called Taylor vortices. The geometry of the Couette–Taylor reactor is represented by the aspect ratio, d/r_i , where d denotes the annular gap width between the inner and outer cylinder and r_i is the radius of the inner cylinder. Taylor vortices exhibit a unique mixing behavior of excellent radial mixing combined with minimal longitudinal mixing [20]. Accordingly, in the current study, the reactor geometry, reactant concentration, rotating speed of the inner cylinder, and reactant flow rate were all varied and a dimensionless parameter consisting of such operating variables introduced to predict modifications in the crystal morphology resulting from the crystallization.

2. Experimental procedure

The calcium carbonate crystallization in the Couette–Taylor reactor was driven by a reaction with a gaseous CO_2 (higher than 99.99% purity) and aqueous $\text{Ca}(\text{OH})_2$ (ACS Grade, Shinyo Co., Japan) solution. The stationary outer cylinder of the Couette–Taylor reactor was made of acrylic resin to allow visual observation of the Taylor vortices. The inner cylinder was made of stainless steel and rotated with a variable-speed DC motor (NSH-55, Bodine, USA). Two kinds of reactor geometry with gap sizes of $d/r_i = 0.25$ and 0.56 , respectively, were used for the crystallization. A detailed description of the Couette–Taylor reactors used in the current study is given in Table 1.

As shown in Fig. 2, the reactor was placed horizontally to eliminate any hydrostatic pressure effect, and eight sample ports were installed on the outer cylinder to take the sample suspension along the axial direction of the reactor. To minimize the effect of the heterogeneous surface on the crystallization, the reactor wall and inner cylinder were carefully rinsed with distilled water after washing with dilute acetyl acid. The CO_2 gas and $\text{Ca}(\text{OH})_2$ aqueous solution was continuously fed into the Couette–Taylor reactor while monitoring the rate. To eliminate any fluctuation in the flow rate, a damper was installed in the gaseous feed line and the head tank used to feed the aqueous solution. Since the solubility of CO_2 gas in an aqueous

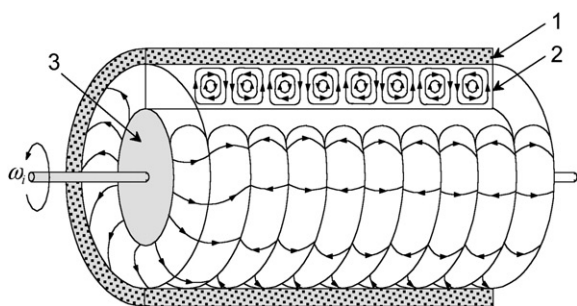


Fig. 1. Conceptual diagram of Taylor vortices in Couette–Taylor reactor (1, stationary outer cylinder; 2, Taylor vortices; and 3, rotating inner cylinder).

solution depends on the temperature, the feed solution was carefully controlled at 20°C.

To quantitatively evaluate the fluid dynamic conditions in the Couette–Taylor reactor, the energy dissipation (ε) caused by the fluid motion was used, defined as the power input (P) per unit mass of suspension in the reactor. The power input to the Couette–Taylor reactor was defined as the product of the torque and angular velocity of the rotating inner cylinder [20],

$$P = \omega_i T_M, \quad (1)$$

where ω_i is the angular velocity of the rotating inner cylinder and T_M is the torque defined as $2\pi L_C r_i^2 \tau_\omega$ at the wall of the inner cylinder. From the relationship between the shear stress at the wall

of the rotating inner cylinder (τ_ω) and the friction factor (f) [18], the energy dissipation in the Couette–Taylor reactor was derived as

$$\varepsilon = \pi L_C r_i^4 \omega_i^3 f / V_R, \quad (2)$$

where L_C is the reactor length and r_i is the radius of the inner cylinder. Here, ε is related to P as $\varepsilon = P/(\rho_L V_R)$, where ρ_L is the density of the suspension and V_R is the volume of the reactor.

To compare the crystallization conditions between in the two reactor geometries, the flow rates of the aqueous reactant solution (Q_L) were

Table 1
Physical dimensions of Couette–Taylor reactors

Reactor geometry	$d/r_i = 0.25$	$d/r_i = 0.56$
Radius of inner cylinder, r_i	4.0 cm	3.2 cm
Radius of outer cylinder, r_o	5.0 cm	5.0 cm
Annular gap width, d	1 cm	1.8 cm
Reactor length, L_C	70 cm	70 cm
Reactor volume, V_R	2.41	31

Table 2
Experimental conditions in Couette–Taylor reactors

Operating variables	$d/r_i = 0.25$	$d/r_i = 0.56$
CO ₂ gas molar flow rate, $\dot{n}_{G0}/V_R$ (mol/m ³ -s)	0.00775	0.00775, 0.0124, 0.01736
Aqueous Ca(OH) ₂ concentration, C_{B0} (mol/m ³)	16	8, 16
Aqueous solution flow rate, Q_L (ml/min)	240	300, 600
Mean residence time, τ (min)	10	5, 10
Rotating speed of inner cylinder, ω_i (rpm)	400, 700, 900, 1100	400, 600, 800, 1000

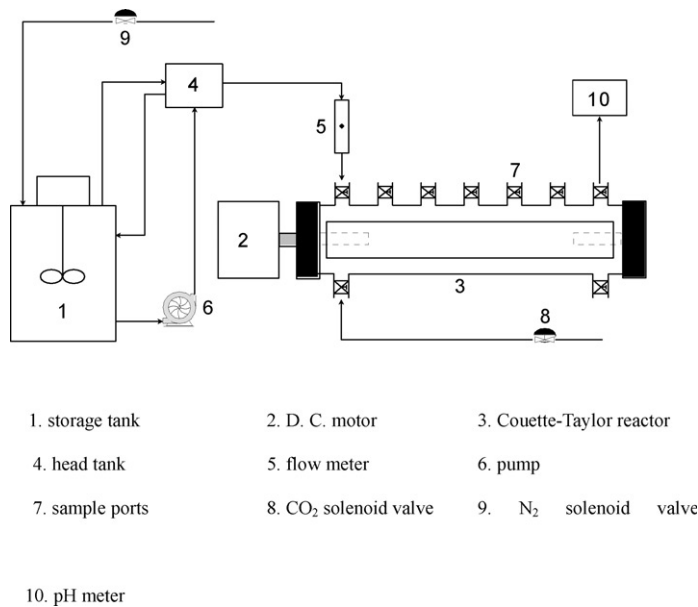


Fig. 2. Schematic diagram of experimental system with Couette–Taylor reactor.

Table 3

Calculation of Reynolds number Re , friction factor f , wall shear stress τ_w and energy dissipation ε at various rotating speeds of inner cylinder in Couette–Taylor reactors

Reactor type	rpm (rev/min)	ω_i (rad/s)	$Re \times 10^{-3}$	$f \times 10^3$	τ_w (Pa)	ε (W/kg)
$d/r_i = 0.56$	400	41.9	24.0	3.11	2.80	0.18
	600	62.8	36.0	2.51	5.07	0.48
	800	83.8	48.1	2.15	7.73	0.97
	1000	104.7	60.1	1.91	10.7	1.69
$d/r_i = 0.25$	400	41.9	16.78	2.839	4.0	0.49
	700	73.3	29.32	2.112	9.08	1.95
	900	94.2	37.68	1.849	13.13	3.63
	1100	115.1	46.04	1.663	17.63	5.95

adjusted with the same mean residence time (τ) in both reactors, the molar flow rate of CO_2 gas per unit reactor volume ($\dot{n}_{\text{G0}}/V_{\text{R}}$) and concentration of aqueous calcium hydroxide (C_{B0}) were changed from 0.00775 to 0.01736 mol/m³-s and from 8 to 16 mol/m³, respectively, to modify the stoichiometric ratio for the chemical reaction, and the rotating speed of the inner cylinder (ω_i) was varied from 400 to 1100 rpm. The variation ranges for the operating variables in the experiments are summarized in Table 2. The estimated ε values relative to ω_i for both reactors are summarized in Table 3 along with the calculated values of f and τ_w for the Couette–Taylor reactor.

Samples of the product suspension were taken at the ports after waiting for longer than 10 times the mean residence time to achieve a steady state. The steady state was checked with a pH meter (Model 940, Orion, USA) at the end position of the reactor. The crystal size distribution in the suspension was analyzed using a particle size analyzer (Model 3300, Malvern, UK) and the morphology examined using a scanning electron microscopy (JSM-820, JEOL, Japan).

Prior to the crystallization study, the gas–liquid mass transfer was evaluated via a measurement of CO_2 absorption into pure water in the same Couette–Taylor reactors. Therefore, when the current experiment was in a steady state, the aqueous CO_2 concentration profile was measured along the axial direction of the reactor using a CO_2 selective electrode (Model 9502BN, Orion, USA).

3. Results and discussion

3.1. Gas–liquid mass transfer

In a gas–liquid reaction system, the overall mass transfer coefficient, $k_L a$, which is the product of the interfacial mass transfer coefficient (k_L) and the area (a), can be directly measured via the CO_2 absorption, as suggested by Jhaveri and Sharma [21]. When CO_2 gas is absorbed into pure water in a Couette–Taylor reactor, the description of the aqueous CO_2 concentration in a steady state Couette–Taylor reaction can be simplified as a plug flow reactor model,

$$\frac{dC_A}{d(x/u)} = k_L a (C_A^* - C_A), \quad (3)$$

where x is the axial position in the reactor, u the mean fluid velocity, and C_A^* the saturation concentration of CO_2 in pure water (34 mol/m³ at 20°C). Integrating the above equation leads to

$$\ln \left(1 - \frac{C_A}{C_A^*} \right) = -k_L a \left(\frac{x}{u} \right) + \ln \left(1 - \frac{C_{A0}}{C_A^*} \right), \quad (4)$$

where C_{A0} denotes the concentration of CO_2 at the entrance to the reactor. Therefore, when comparing the CO_2 concentration profile with Eq. (4), $k_L a$ can be extracted from the slope of a semi-log plot of $\ln(1 - C_A/C_A^*)$ vs. x/u , as shown in Fig. 3. The CO_2 concentration profiles in the reactor varied with the rotating speed of the inner cylinder. When the energy dissipation increased, the CO_2 concentration along the axial direction was significantly

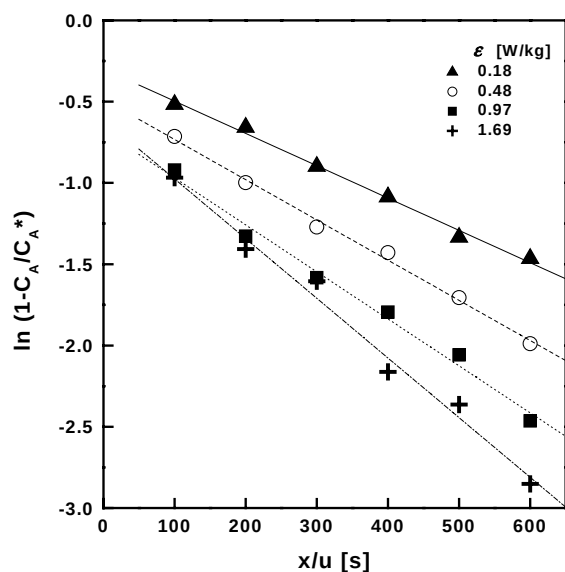


Fig. 3. Semi-logarithmic plots of $\ln(1 - C_A/C_A^*)$ vs. x/u at various energy dissipation of inner cylinder in Couette–Taylor reactor ($d/r_i = 0.56$, $\dot{n}_{G0}/V_R = 0.00775 \text{ mol/m}^3\text{-s}$ and $\tau = 10 \text{ min}$).

reduced, indicating an enhanced mass transfer rate at the gas–liquid interface. The overall mass transfer coefficients for the whole range of rotating speeds for the inner cylinder with the two reactor geometries are displayed in Fig. 4. The overall mass transfer coefficient was found to be more sensitive to the energy dissipation with the reactor geometry of $d/r_i = 0.56$ than with $d/r_i = 0.25$, because the higher shear stress (τ_ω) caused by the larger gap size of the reactor resulted in a larger interfacial area. It was interesting that the simple plug flow model could be used to estimate the gas–liquid mass transfer in the turbulent vortex regime of a Couette–Taylor reactor.

3.2. Crystal morphology

Morphology is one of the most important factors determining the characteristics of crystals. The crystal morphology of the calcium carbonate produced in the Couette–Taylor reactor clearly changed when adjusting the crystallization operating conditions, such as the rotating speed of the inner cylinder, reactant concentration, and flow rate, etc., as observed in Fig. 5. With a Ca(OH)_2

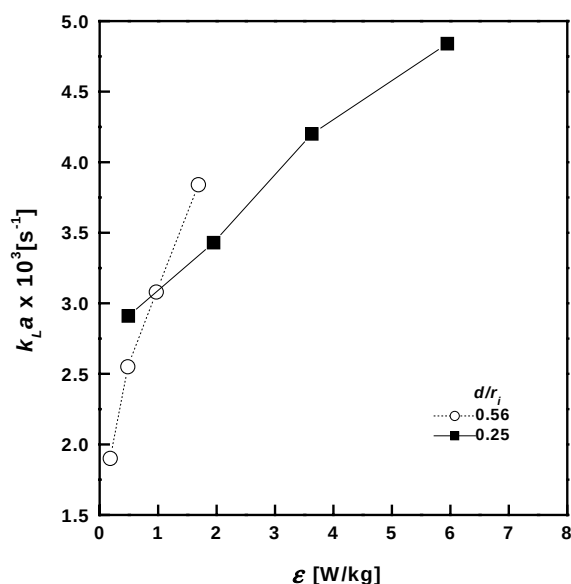


Fig. 4. Effect of energy dissipation of inner cylinder on gas–liquid mass transfer of CO_2 in Couette–Taylor reactors ($\dot{n}_{G0}/V_R = 0.00775 \text{ mol/m}^3\text{-s}$ and $\tau = 10 \text{ min}$).

feed concentration and flow rate of 8 mol/m^3 and $5 \times 10^{-6} \text{ m}^3/\text{s}$, respectively, and CO_2 flow rate of $11.0 \times 10^{-7} \text{ m}^3/\text{s}$, the calcium carbonate crystals were favorably shaped like a rhombohedron (Fig. 5(a)), however, their shape gradually changed to one of a spindle (Fig. 5(b)) as the Ca(OH)_2 molar feeding rate increased and CO_2 flow rate decreased. A similar change in shape of calcium carbonate crystals was reported by Jung et al. [18] and attributed to the effect of excess ions on the calcium carbonate growth. That is, the excess calcium ions resulting from increasing the Ca(OH)_2 molar feeding rate and decreasing the CO_2 flow rate caused a change in the crystal morphology from a rhombohedron to a spindle shape.

When decreasing the energy dissipation, the interfacial transport of CO_2 was significantly diminished, leading to in a high excess of ions in the solution and the production of needle-like crystals of calcium carbonate (Fig. 5(c)). The creation of needle-like aragonite in crystallization has been previously reported to depend on the temperature, supersaturation, and pH of the solution [8]. For example [8], a high pH in the

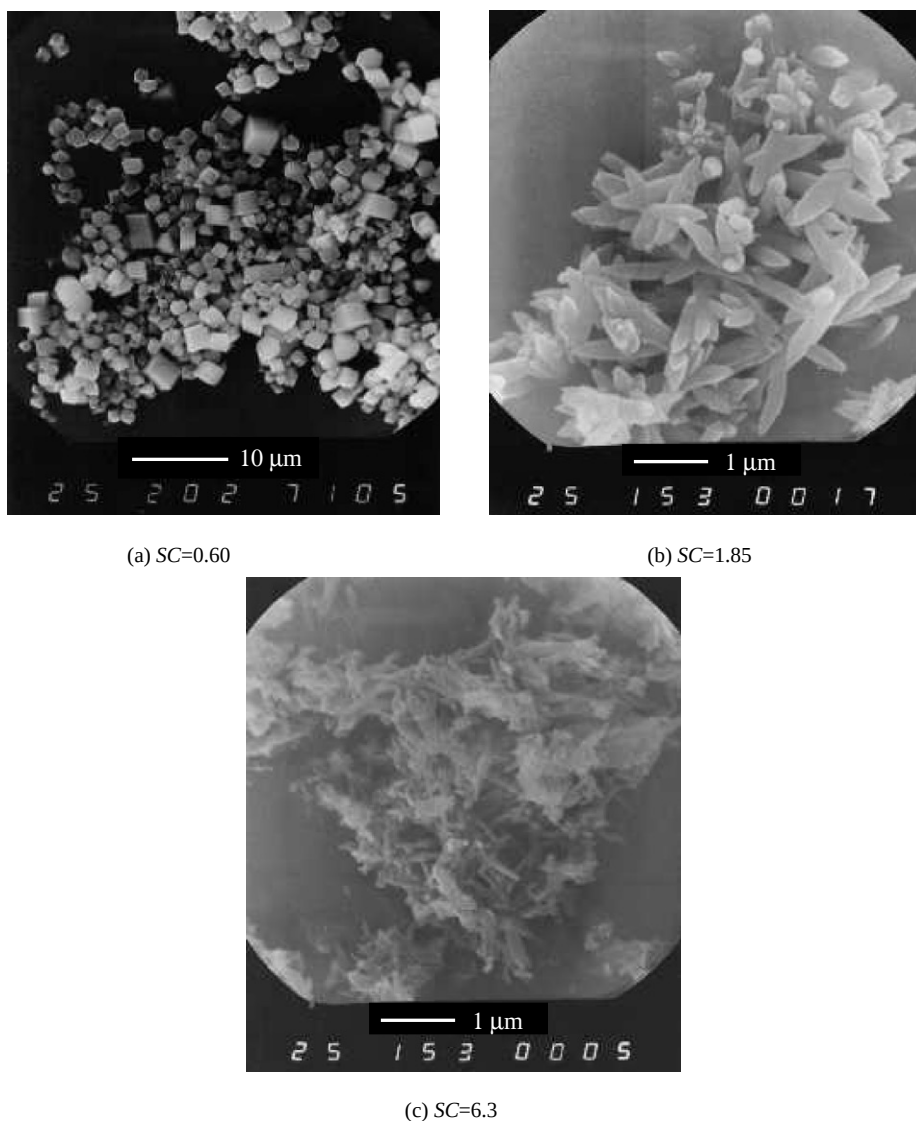


Fig. 5. Scanning electron micrographs of calcium carbonate: (a) $d/r_i = 0.56$, $\dot{n}_{G0}/V_R = 0.01736 \text{ mol/m}^3\text{-s}$, $\tau = 10 \text{ min}$ and $C_{B0} = 8 \text{ mol/m}^3$, (b) $d/r_i = 0.25$, $\dot{n}_{G0}/V_R = 0.00775 \text{ mol/m}^3\text{-s}$, $\tau = 10 \text{ min}$ and $C_{B0} = 16 \text{ mol/m}^3$, and (c) $d/r_i = 0.56$, $\dot{n}_{G0}/V_R = 0.0124 \text{ mol/m}^3\text{-s}$, $\tau = 5 \text{ min}$ and $C_{B0} = 16 \text{ mol/m}^3$.

crystallization solution ($8.75 < \text{pH} < 10.0$) favors the generation of needle-like aragonite. As such, in the current study, it would appear that the overdosage of Ca(OH)_2 to CO_2 during crystallization created an excess of Ca^{2+} , thereby increasing the pH and producing a significant change in the crystal morphology from a rhombohedron to needle shape.

To predict the crystal morphology produced in a Couette–Taylor reactor with variations in the operating conditions, a dimensionless group (tentatively called a ‘shape criterion’) was suggested as

$$\text{SC} = \frac{C_{B0} Q_L / \tau}{C_A^* Q_G k_L a} \quad (5)$$

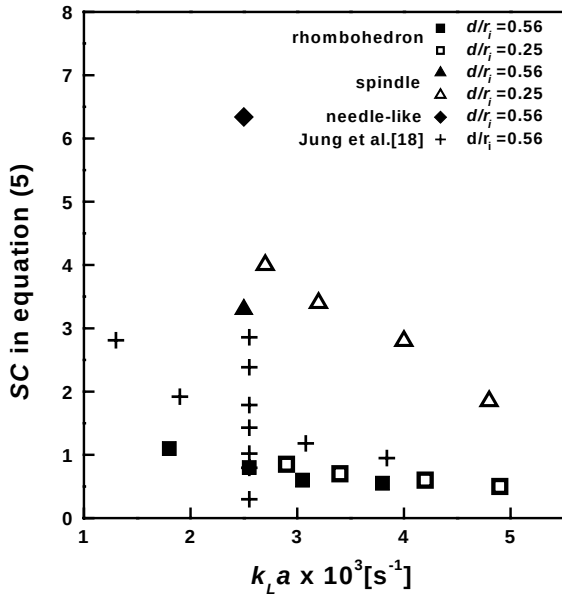


Fig. 6. Morphology of calcium carbonate related to Eq. (5) in present crystallization system.

In the present study, the shape criterion ranged from 0.4 to 7 when varying the operating conditions. Based on this criterion, the morphology of calcium carbonate was classified as shown in Fig. 6. Accordingly, a rhombohedral crystal was favored when $SC < 1$, while a spindle-like crystal was predominantly produced when $1 < SC < 5$. Then, a needle-like crystal appeared when $SC > 6$. Due to the limitations of the current experimental system, such as the solubility of $\text{Ca}(\text{OH})_2$, the minimum rotating speed of the turbulent vortex, feed flow, etc., a $SC > 7$ was hard to achieve in order to confirm any further morphological modification. It should be noted that the above morphological classification of calcium carbonate based on a shape criterion was in good agreement with previous results achieved with a gas–liquid reaction [18,22].

3.3. Crystal size

The crystallization of calcium carbonate along the axial direction of the Couette–Taylor reactor was measured, as displayed in Fig. 7. The profiles of the mean crystal size based on the crystal

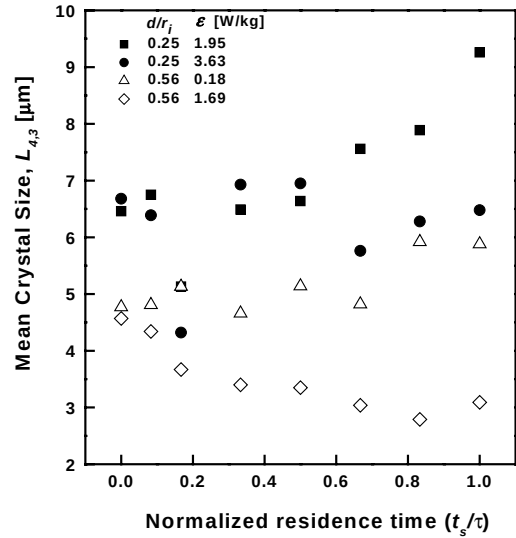


Fig. 7. Variation of mean size with axial position at various reactor geometry and energy dissipation of inner cylinder ($\dot{n}_{\text{G0}}/V_{\text{R}} = 0.00775 \text{ mol/m}^3\text{-s}$, $\tau = 10 \text{ min}$ and $C_{\text{B0}} = 16 \text{ mol/m}^3$).

volume ($L_{4,3}$) at the axial positions of the reactor varied with the energy dissipation and reactor geometry. For the reactor with a smaller gap size ($d/r_i = 0.25$), the mean crystal size increased along the reactor with a low energy dissipation ($\varepsilon = 1.95$), yet slightly decreased with a high energy dissipation ($\varepsilon = 3.63$). Similar profile trends relative to the energy dissipation were also observed for the reactor with a larger gap size ($d/r_i = 0.56$).

As shown in the microscopic images in Fig. 5, the resulting crystals were found to be seriously agglomerated. The crystal agglomeration was also confirmed by the bimodal distribution of the crystal sizes, obtained using a crystal size analyzer based on exploiting the light scattering, as shown in Fig. 8. According to Hostomsky and Jones [11], the bimodality of the crystal size distribution originates from the agglomeration of individual crystals, thereby increasing the large-size crystal population and reducing the small-size crystal population. Meanwhile, crystal agglomeration is also influenced by the fluid dynamic conditions of the suspension, as it results from the collision and breakage of crystals due to turbulent force [23,24].

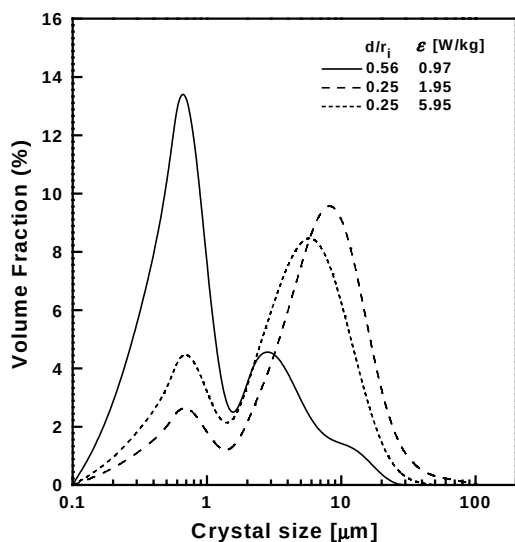


Fig. 8. Effect of reactor geometry on crystal size distribution ($\dot{n}_{G0}/V_R = 0.00775 \text{ mol/m}^3\text{-s}$, $\tau = 10 \text{ min}$ and $C_{B0} = 16 \text{ mol/m}^3$).

As such, crystal breakage is linearly proportional to the energy dissipation of the turbulence, whereas crystal collisions increase relative to the square root of the energy dissipation [23]. This implies that at a low energy dissipation, crystal collision for crystal agglomeration is promoted rather than the breakage of the crystal agglomerates, while at a high energy dissipation, the breakage of agglomerates exceeds crystal agglomeration. Consequently, this dependency of crystal agglomeration on the fluid dynamic conditions resulted in the two distinct profiles for the mean crystal size along the reactor at the two different energy dissipations (Fig. 7).

It should also be mentioned that the mean size based on the crystal numbers ($L_{1,0}$) remained constant at $0.5\text{--}0.7 \mu\text{m}$ regardless of the operating conditions, reactor geometry, and position in the reactor, although the mean size based on the crystal volume ($L_{4,3}$) clearly varied. This number-based mean size was coincident with the size of the first peak (peak of small crystals) in the bimodal size distribution of crystals (Fig. 8) and also the size of the individual crystals estimated from the microscopic images. These results imply that the crystallization kinetics of crystal nucleation and

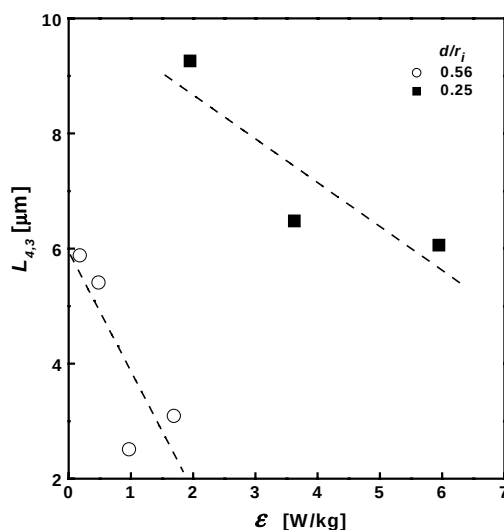


Fig. 9. Effect of energy dissipation of inner cylinder on mean size in steady Couette–Taylor reactors ($\dot{n}_{G0}/V_R = 0.00775 \text{ mol/m}^3\text{-s}$, $\tau = 10 \text{ min}$ and $C_{B0} = 16 \text{ mol/m}^3$).

growth were almost completed in the entry region of the reactor due to the Taylor vortices providing maximum mixing in the radial direction and minimum mixing in the axial direction. In addition, crystal agglomeration was found to be involved in the calcium carbonate crystallization in the Couette–Taylor reactor as the major process determining the mean crystal size.

Fig. 9 shows the mean crystal size in the product suspension relative to the energy dissipation. When the energy dissipation increased, the mean crystal size was reduced due to the promotion of agglomerate breakage by the turbulent fluid force. The crystal agglomeration was more effectively inhibited in the reactor with the larger gap (d/r_i), thereby leading to a smaller mean crystal size than in the reactor with the smaller gap geometry. This result was most likely due to the shear stress of the Taylor vortices relative to the reactor geometry.

4. Conclusion

The current study investigated the changes in crystal morphology and size when varying the operating conditions of gas (CO_2)–liquid

(Ca(OH)₂) reaction crystallization in a Couette–Taylor reactor. The morphological changes in the calcium carbonate in the present crystallization were due to the influence of excess Ca²⁺ ions on the crystal growth. The condition of excess Ca²⁺ was predominantly controlled by the interfacial transport of CO₂ and stoichiometric feeding balance. Therefore, when increasing the Ca(OH)₂ concentration and decreasing the interfacial transport rate, the crystal morphology of the calcium carbonate shifted from a rhombohedron to a needle shape. Of course, the interfacial transport of CO₂ was clearly promoted by the rotating speed of the inner cylinder in the Couette–Taylor reactor. The predicted morphological changes according to the operating conditions, attempted based on a dimensionless parameter (SC), matched fairly well with the experimental results.

Due to the unique behavior of Taylor vortices, it was apparent that the kinetics of crystallization, such as crystal nucleation and growth, were almost completed at the entry region of the reactor, followed by crystal agglomeration. Therefore, the profile of the mean crystal size along the axial direction of the reactor depended on the turbulent energy dissipated due to the rotation of the inner cylinder. When the energy dissipation was increased, the mean crystal size tended to decrease along the reactor, because crystal agglomeration was inhibited by the turbulence force.

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