

Precipitation of calcium carbonate particles by gas–liquid reaction: Morphology and size distribution of particles in Couette–Taylor and stirred tank reactors

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ABSTRACT

The morphology and size of CaCO_3 precipitated by CO_2 – $\text{Ca}(\text{OH})_2$ reaction in stirred tank and Couette–Taylor reactors were experimentally investigated. The Taylor vortex in CT reactor encouraged more homogeneous mixing conditions, resulting in the production of smaller particles with a uniform shape throughout the reactor. However, in the stirred tank reactor, the local non-homogeneity of the mixing intensity led to the simultaneous production of cube-like and spindle-like particles at a high reactant concentration. The agglomeration of CaCO_3 resulted in a bimodal size distribution. However, the morphology and size of a single particle were predominantly changed by the excess species in the solution. The largest mean size and cube-like particles were observed under stoichiometric reaction conditions. As the excess species concentration increased, the morphology was transformed to a spindle-like shape and the mean size decreased due to selective adsorption of the excess species on the crystal faces.

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1. Introduction

Calcium carbonate is one of the most popular materials for precipitation studies, as it is used in numerous areas, including plastics, textiles, rubbers, adhesives, paints, and wastewater treatment. For industrial applications in the above mentioned fields, the product properties are determined by the morphology and size distribution of the precipitates. Therefore, a considerable amount of attention and effort has been devoted to control these characteristics of calcium carbonate.

The polymorphs and size distribution of calcium carbonate have already been reported to depend on the precipitation conditions, such as the supersaturation, temperature [1,2], solution pH [3,4], ionic ratio of the reactants [5], and polymeric additives [6–8]. Also, an extensive study on the effect of the operating variables, including the reactant concentration, residence time, specific power input and feed point location, on calcium carbonate precipitation was performed [9].

The charged ions in the solution have also been found to change the morphology and size of the particles. Nielsen [10] qualitatively demonstrated the effect of an ionic additive on the

growth and morphology of a particle based on the selective adsorption on the crystal face. Plus, additives such as Mg^{2+} , Ni^{2+} , Co^{2+} and Fe^{3+} were found to favor the formation of aragonite while the formation of calcite was favored in the presence of Mn^{2+} , Ca^{2+} and Pb^{2+} [1,11,12]. Jung et al [13] demonstrated that the monovalent ionic additives of Na^+ , K^+ and NH_4^+ were much effective to the modification of crystal morphology of calcite due to the lattice inclusion. Excess species of reactants in the solution, which may be caused by a deviation from the reaction stoichiometry, can also affect the morphology and size of the particles. However, studies on the effect of excess species are rare, as most experiments are conducted under stoichiometric conditions due to their simplicity.

Besides, most previous studies have adopted liquid–liquid reaction processes, as they are easy to operate and control. However, with this type of system, the simultaneous formation of a by-product from the reaction is inevitable. For example, when using the reaction between calcium chloride and sodium carbonate, sodium chloride is simultaneously produced as a by-product. This by-product salt dissolved in the solution can then influence the precipitation, like an ionic additive, yet this is invariably missed in most studies.

When compared with a liquid–liquid system, a gas liquid reaction system using carbon dioxide and calcium hydroxide is advantageous by eliminating the effect of by-products, plus this

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system is often used in commercial processes. However, studies on the gas–liquid reaction precipitation of calcium carbonate are rare, as the process control is difficult, and the additional variable of the gas–liquid mass transfer makes the theoretical analysis more complex. Juvekar and Sharma were the first to study a calcium carbonate precipitation using gas–liquid reaction [14–18]. However, in these studies, CO₂ gas flowed gently over Ca(OH)₂ solution in an agitated vessel and was absorbed through a flat gas–liquid interface, which has no practical use. Meanwhile, Chen et al [19] introduced CO₂ through a double-tube gas injection nozzle or gas sparger into CaCl₂ solution in an agitated batch reactor, and observed that the morphology was mainly affected by the solution pH and calcium concentration. Also, Tamura and Tsuge [20] induced the calcium carbonate crystallization using gas–liquid reaction in multistage column crystallizer, investigating the operating parameter effects on the particle size distribution. However, they used KOH to control the solution pH.

Accordingly, in the present study, the CO₂–Ca(OH)₂ reaction system without pH control was applied for the calcium carbonate precipitation in the Couette–Taylor (CT) reactor. Here, the characteristics of calcium carbonate precipitation in the CT reactor were investigated with change of the operating conditions, including the aqueous reactant concentration, gas flow rate and agitation rate, and evaluated by comparison with those in a stirred tank. For the variation in the morphology and size distribution, the effects of agglomeration, the presence of excess species in the solution and supersaturation were also considered.

2. Experiments

The CT reactor was composed with two coaxial cylinders, as shown in Fig. 1, where the Taylor vortex flow was induced by the rotation of inner cylinder. The stationary outer cylinder was made of acrylic plastic to ensure visual observation of the Taylor vortices. The rotating inner cylinder was made of stainless steel and polished with an abrasive to prevent any heterogeneous nucleation on the cylinder wall. The ratio of gap between two cylinders to the radius of inner cylinder (d/r_i) was 0.56. In the range of a rotating speed (ω_i) greater than 21 rad/s, a turbulent Taylor vortex flow was exhibited. Meanwhile, the Rushton-type

stirred tank reactor was equipped with six-baffles and made of acrylic resin. The dimensions of both reactors used in the present study are described in Table 1.

To compare the results from both reactors, the operating conditions, including the reactant concentrations, flow rate, and mixing, were first identified. Since a tank reactor of $1 \times 10^{-3} \text{ m}^3$ and a Couette–Taylor reactor of $3 \times 10^{-3} \text{ m}^3$ were employed, the flow rates of the reactants were adjusted and compared in terms of the mean residence times for both phases. For simplicity, the molar gas flow rate ($\dot{n}_{\text{GO}}/V_R$, mol/m³ s) is used in the following discussion, instead of the volumetric gas flow rate (Q_{GO} , m³/s). In addition, the mixing conditions in both the reactors were compared using the power consumption per unit mass of solution (ε) [21,22]. The calculated values of ε at the agitation speed (ω_i and n) in the CT and stirred tank reactors are represented in Table 2.

The calcium carbonate precipitation in both reactors was driven by the reaction between gaseous carbon dioxide (more than 99.9% purity) and aqueous calcium hydroxide. The aqueous reactant solution was prepared by dissolving calcium hydroxide (ACS Grade, Shinyo Co., Japan) in distilled water and its concentration was measured using a conductivity meter (Cole-Parmer, model 1481-60). As shown in Fig. 1, reactants were continuously fed into the reactor and the flow rates were monitored. To eliminate fluctuations in the flow rates, a damper was used for the gaseous feed stream and a by-pass valve installed in the aqueous feed line. The molar flow rates of CO₂ gas were changed from 0.0062 to 0.149 mol/m³ s, while those of the aqueous reactant were fixed to have the same mean residence time of 600 s in both reactors. The variations of the operating variables in the present study are summarized in Table 3.

Samples of the product suspension were taken at a steady state after 10 times mean residence time. The steady state was

Table 1
Dimensions of tank and Couette–Taylor reactors used for experiment.

Couette–Taylor reactor	
Radius of inner cylinder, r_i	0.032 m
Radius of outer cylinder, r_o	0.050 m
Gap size, d	0.018 m
Length of reactor, L_C	0.70 m
Volume of reactor, V_R	$3.0 \times 10^{-3} \text{ m}^3$
Tank reactor	
Diameter of impeller, D_i	0.036 m
Height of impeller, H_i	0.036 m
Width of impeller blade, W_i	0.007 m
Length of impeller blade, L_i	0.009 m
Width of baffle, B	0.009 m
Diameter of reactor, D_R	0.108 m
Height of reactor, H_R	0.108 m
Volume of reactor, V_R	$1.0 \times 10^{-3} \text{ m}^3$

Table 2
Calculated values of power input per unit mass of solution (ε) at each angular velocity of inner cylinder (ω_i) in Couette–Taylor reactor and corresponding agitation speed of impeller (n) in the tank reactor.

Couette–Taylor reactor		ε (W/kg)	Tank reactor	
ω_i			n	
(rpm)	(rad/s)		(rev/s)	(rpm)
250	26.2	0.055	5.25	320
400	41.9	0.18	7.72	460
600	62.8	0.48	10.8	650
800	83.8	0.97	13.7	820
1000	105	1.69	16.4	990

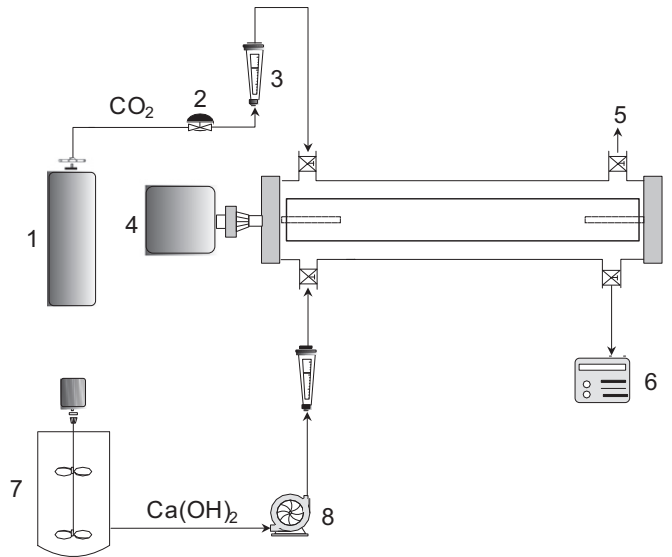


Fig. 1. Schematic of experimental apparatus with Couette–Taylor reactor (1. gas tank; 2. gas valve; 3. flow meter; 4. motor; 5. sample port; 6. pH-meter; 7. solution storage tank; 8. metering pump).

Table 3
Variation of operating variables in present experiments.

Operating variables	Couette-Taylor reactor	Tank reactor
OH [−] ion concentration, C_{B0} (mol/m ³)	5, 16, 24, 32, 40, 48, 64, 100	5, 12, 24, 36, 48
CO ₂ gas flow rate, $Q_{CO} \times 10^7$ (m ³ /s)	4.17, 6.67, 8.33, 11.7, 15.0	2.78, 8.33, 16.7, 25.0, 33.3
$\dot{n}_{CO}/V_R \times 10^2$ (mol/m ³ s)	0.62, 0.99, 1.24, 1.74, 2.23	1.24, 3.72, 7.44, 11.2, 14.9
Agitation rate, n or ω_i (rpm)	250, 400, 600, 800, 1000	320, 460, 650, 820, 990
Ca(OH) ₂ solution flow rate, $Q_L \times 10^7$ (m ³ /s)	5.0	1.67
Mean residence time, τ (s)	600	600

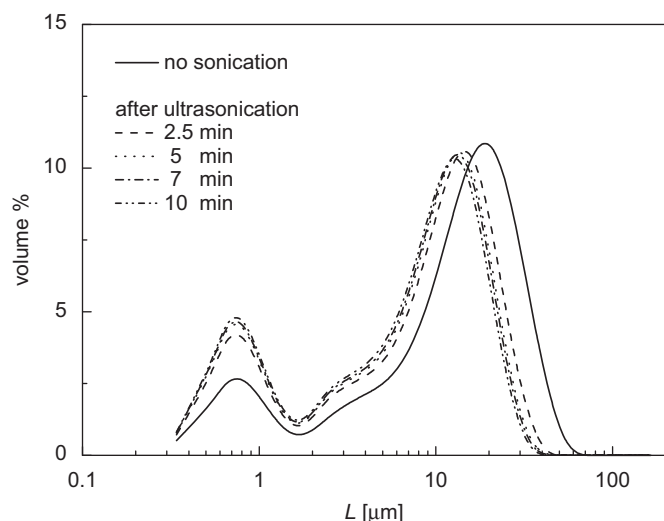


Fig. 2. Effect of ultrasonication on particle size distribution measured by PSA (tank reactor, $C_{B0}=48$ mol/m³, $\dot{n}_{CO}/V_R=0.0124$ mol/m³ s, $n=650$ rpm).

continuously checked based on the solution pH using an ion-meter (Orion, EA 940). After each sampling, the suspension was quickly diluted by adding about five times the sample volume of distilled water.

The morphology and size distribution of the sampled products were analyzed using a scanning electron microscope (SEM; JSM-820, Jeol, Japan) and particle size analyzer (PSA; Malvern, Mastersizer/E, UK) respectively. The bimodal size distribution of the agglomerated precipitates was observed using the PSA instrument with a light scattering method, as shown in Fig. 2. As ultrasonication prior to the measurements produced slightly smaller particles, indicating aggregation over time. The effect of aggregation was excluded by applying ultrasonication until the mean particle size became invariant. For the measurement of individual particle size of the precipitates, each sample was completely dried and several SEM micrographs taken. About 200 justifiable particles were then read directly from the images. Since both the morphology and the size of the calcium carbonate varied simultaneously with the operating conditions, the characteristic length for a quantitative representation of the particle size was defined here as the diameter of a sphere, the volume of which was equivalent to that of the actual particle [21].

3. Results and discussion

In the case of reaction precipitation, the reactant concentration, flow rate and agitation rate were all important variables to control the product properties. For example, the nucleation and growth processes varied with the reactant concentration and flow rate. In addition, the mixing of the solution significantly affected the reaction as well as the mass transfer processes. Therefore, the

present gas–liquid reaction precipitation of calcium carbonate investigated the effects of concentration of the aqueous solution (C_{B0}), molar gas flow rate ($\dot{n}_{CO}/V_R$) and power consumption (ε) on the morphology and size of the particles.

In the present gas–liquid reaction system, the pH value of the solution would provide valuable information on the reaction stoichiometry. The isoelectric point (IEP) of calcite was known to be pH 8.2 [23]. Therefore, at pH higher than 8.2, an oversupply of Ca(OH)₂ and excess of Ca²⁺ ions would be expected in the solution, whereas an excess of CO₂ would be anticipated at pH lower than 8.2.

The variation of the solution pH in the tank reactor is illustrated in Fig. 3. Here, θ (t/τ) represented dimensionless reaction time and the mean residence time of the solution (τ) was fixed at 10 min. As shown in Fig. 3(a), the solution pH became constant at higher values with an increase in C_{B0} and the reaction seemed to approach a steady state after 4–5 T. When dissolving whole CO₂ gas into the solution at the given gas flow rate, the C_{B0} value for the stoichiometric reaction was estimated to be 5 mol/m³. However, in an actual stirred tank, the stoichiometric value of C_{B0} was lower due to the slow and partial dissolution of CO₂ gas. Thus, within the range of C_{B0} given in Fig. 3(a), excess Ca²⁺ ions in the solution were expected from pH values higher than 8.2. Fig. 3(b) showed that the solution pH decreased with an increase in $\dot{n}_{CO}/V_R$ and the stoichiometric reaction occurred near $\dot{n}_{CO}/V_R=0.112$ mol/m³ s, when the pH $\approx$ 8.2. It was also found that an increase in the agitation rate enhanced the absorption rate of CO₂, resulting in a reduction of the solution pH, as shown in Fig. 3(c).

A similar dependency of the solution pH on the operating variables was observed in the CT reactor. In addition, variation of the solution pH with the axial length of the steady CT reactor was also observed. A typical example is shown in Fig. 4, where x denoted the dimensionless axial position in the reactor. The solution pH decreased with an increase in $\dot{n}_{CO}/V_R$. A significant decrease in the pH value during the early period of the reaction indicated a very fast chemical reaction.

3.1. Comparison of mixing conditions in stirred tank and Couette-Taylor reactors

As shown in Fig. 5, the morphology of calcium carbonate varied according to C_{B0} . In both reactors, rhombic (cube-like) calcite was produced at a low C_{B0} , where a nearly stoichiometric reaction occurred. However, the morphology became spindle-like with an increase in the C_{B0} , i.e. as the concentration of excess Ca²⁺ ion increased. A more detailed analysis of the morphological variation would be discussed later. X-ray diffraction confirmed that the above morphologies were all calcite, which is consistent with the previous experimental study by Tai and Chen [24].

The difference in the mixing conditions between the stirred tank and CT reactors was more evident at a high C_{B0} (48 mol/m³), in which case all the precipitates in the CT reactor were spindle-like, whereas rhombic and spindle-like particles were simultaneously produced in the tank reactor. Therefore,

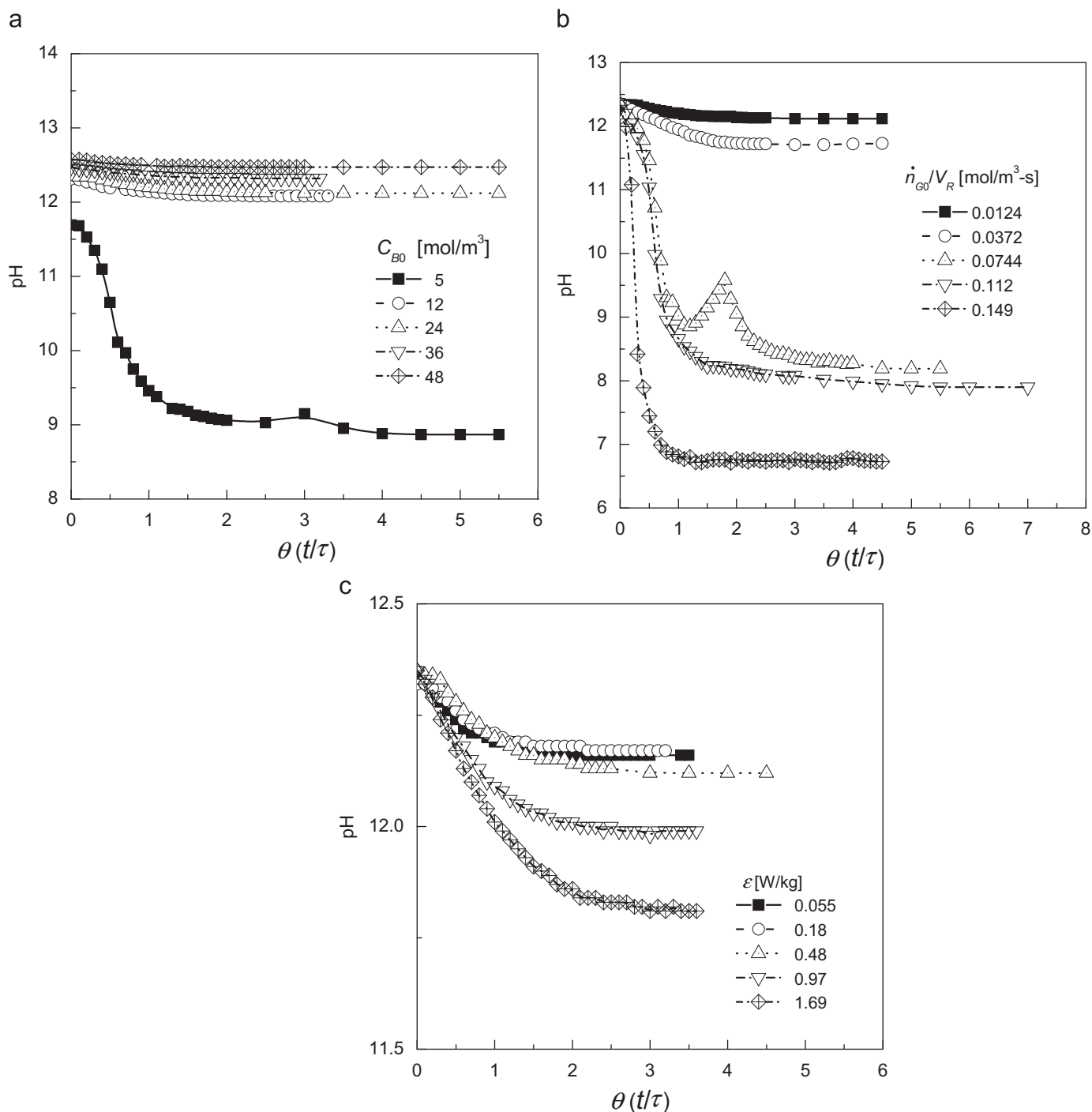


Fig. 3. pH profiles with reaction time in tank reactor (a) at various C_{B0} ($\dot{n}_{G0}/V_R = 0.0124$ mol/m³ s, $\varepsilon = 0.48$ W/kg), (b) at various $\dot{n}_{G0}/V_R$ ($C_{B0} = 24$ mol/m³, $\varepsilon = 0.48$ W/kg), and (c) at various ε ($C_{B0} = 24$ mol/m³, $\dot{n}_{G0}/V_R = 0.0124$ mol/m³ s).

these results indicated that a local fluctuation of mixing intensity occurred in the stirred tank reactor [25]. In contrast, the CT reactor encouraged more homogeneous mixing through the rotation of the inner cylinder, thereby producing particles with a uniform shape throughout the reactor.

A comparison of the size distributions from both reactors is represented in Fig. 6. Both distributions measured by light scattering method were almost similar as bimodal one, although the particles produced in the CT reactor showed slightly narrower distribution. The bimodal distribution of the crystals size was due to the agglomeration of individual particles [26–28], being described in the following section in detail. In light scattering

and SEM image reading analyses, it was also found that the particles produced in the CT reactor had smaller mean size than those produced in the stirred tank reactor under the same conditions. It was due to the fact that the Taylor vortex providing more uniform mixing in the CT reactor was more effective to enhance the nucleation and produce smaller particles than the turbulent motion in the stirred tank reactor [9].

3.2. Effect on agglomeration

In the present study, the mean size and size distribution of the calcium carbonate precipitates were first measured using a light

scattering instrument (PSA). Under the given conditions in both reactors at a steady state, the mean particle size was found to vary with the operating variables, as shown in Fig. 7, where $\bar{L}_{4,3}$ denotes the volume-based mean size. The mean sizes in Fig. 7 ranged from 5–15 μm . However, in the SEM images in Fig. 5, most individual particles were 0.1–1 μm in size and never exceeded

2 μm . Therefore, this overestimated mean size from the light scattering method was seemingly due to particle agglomeration.

Agglomerates were found in the SEM images in Fig. 5 and the occurrence of agglomeration was also supported by the size distributions in Fig. 6. The calcium carbonate exhibited a bimodal size distribution, where the first peak was located at 0.3–2 μm and the second at about 10 μm . As mentioned earlier, the aggregates were re-dispersed using ultrasonication which was applied until the mean size became invariant. However,

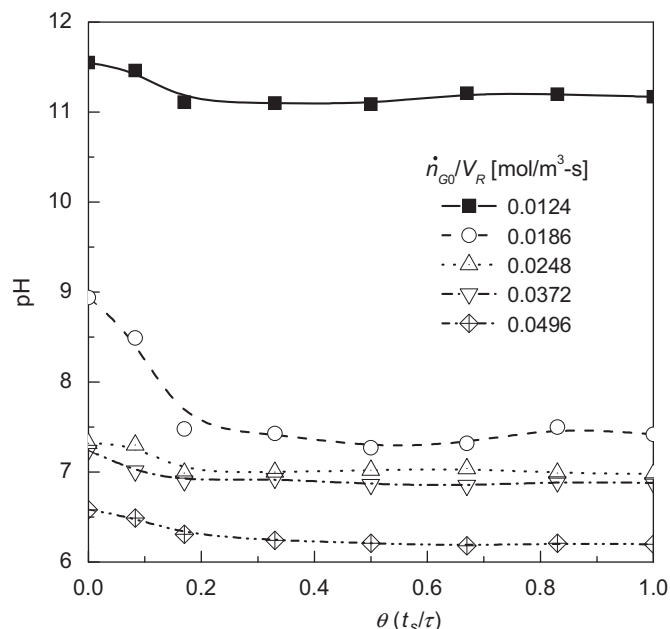


Fig. 4. pH profiles along with reactor length at various $\dot{n}_{\text{CO}}/V_R$ in steady Couette-Taylor reactor ($C_{\text{B}0}=10 \text{ mol/m}^3$, $\varepsilon=0.48 \text{ W/kg}$).

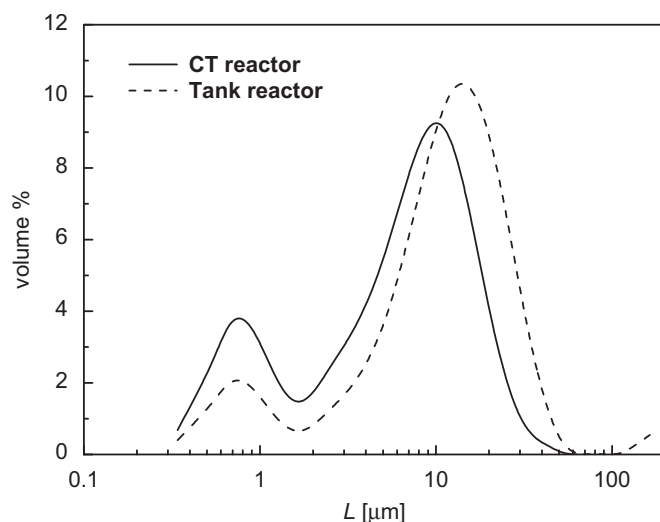


Fig. 6. Comparison of size distributions of calcium carbonate produced in Couette-Taylor and tank reactors ($C_{\text{B}0}=24 \text{ mol/m}^3$, $\dot{n}_{\text{CO}}/V_R=0.0124 \text{ mol/m}^3 \text{ s}$ and $\varepsilon=0.48 \text{ W/kg}$).

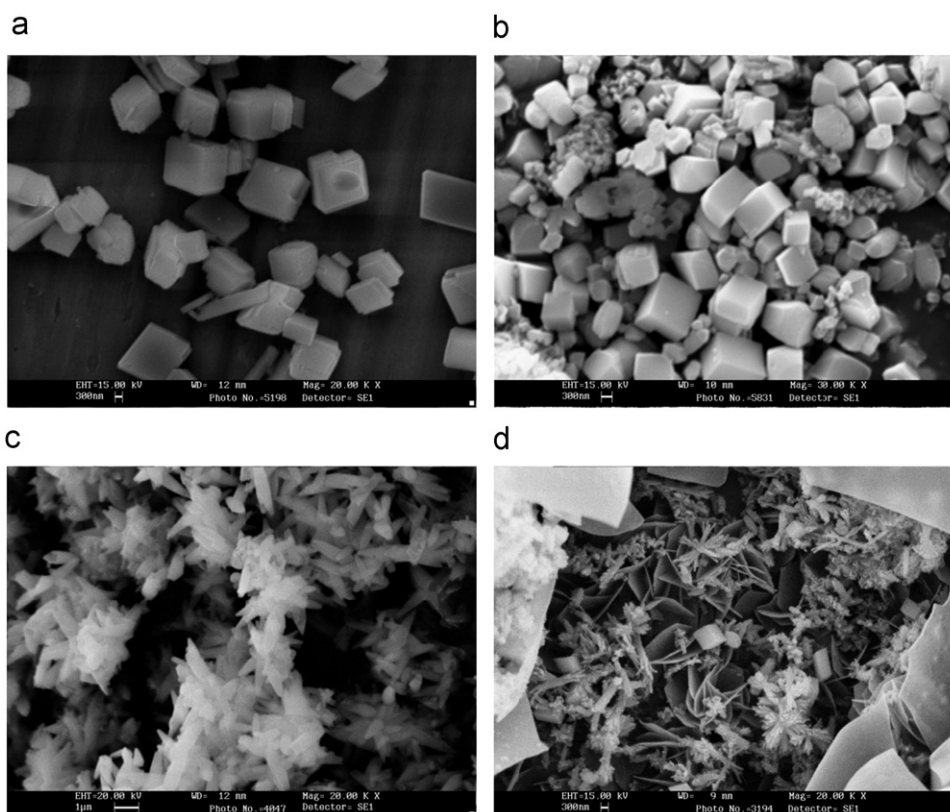


Fig. 5. Comparison of morphologies of calcium carbonate produced in Couette-Taylor and tank reactors ($\dot{n}_{\text{CO}}/V_R=0.0124 \text{ mol/m}^3 \text{ s}$ and $\varepsilon=0.48 \text{ W/kg}$). (a) $C_{\text{B}0}=5 \text{ mol/m}^3$ in Couette-Taylor reactor, (b) $C_{\text{B}0}=5 \text{ mol/m}^3$ in tank reactor, (c) $C_{\text{B}0}=48 \text{ mol/m}^3$ in Couette-Taylor reactor, (d) $C_{\text{B}0}=48 \text{ mol/m}^3$ in tank reactor.

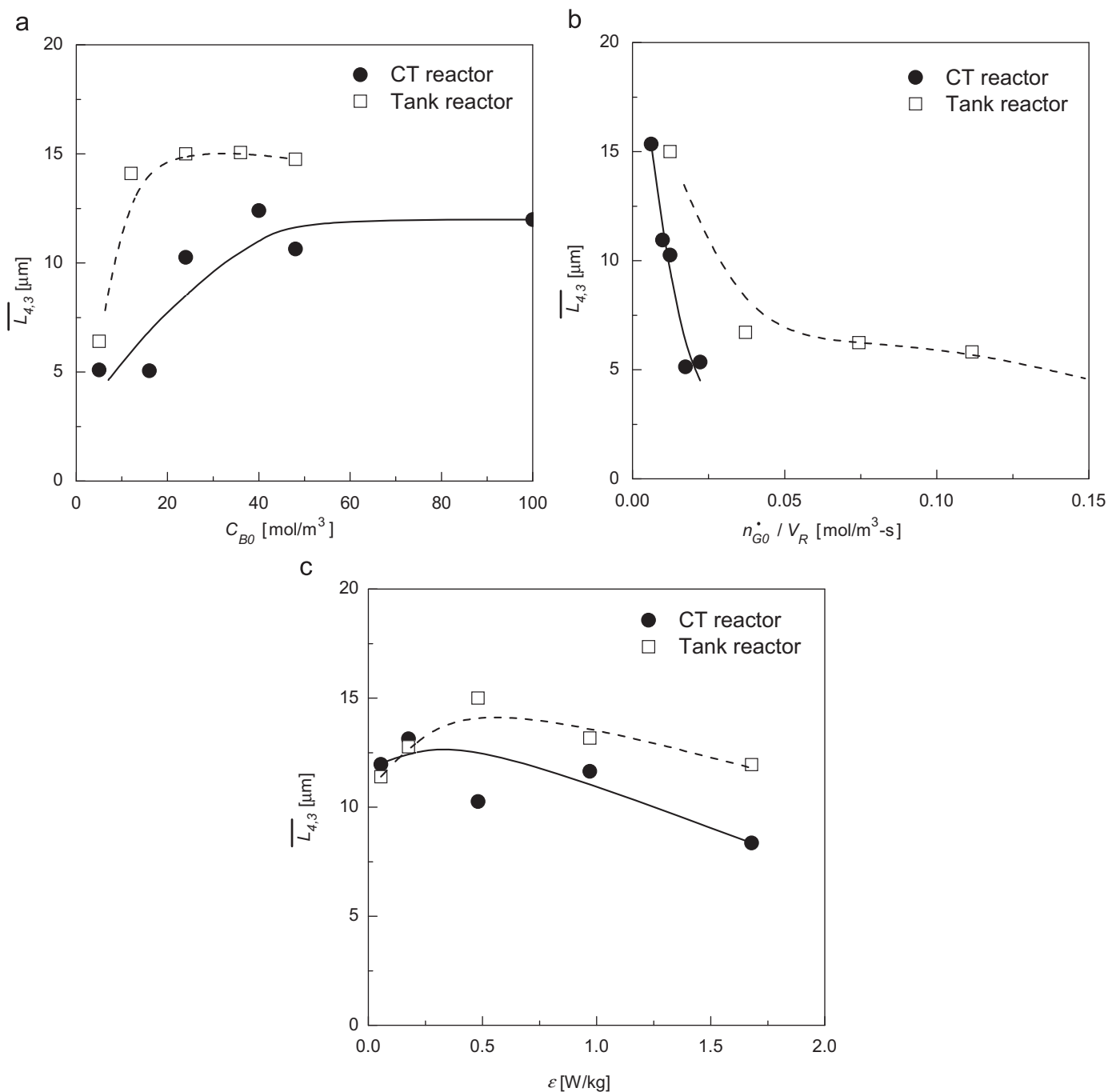


Fig. 7. Mean sizes of agglomerated particles, measured by light scattering method (PSA), produced in steady Couette-Taylor and tank reactors (a) at various C_{B0} ($\dot{n}_{G0}/V_R=0.0124$ mol/m³ s, $\varepsilon=0.48$ W/kg), (b) at various $\dot{n}_{G0}/V_R$ ($C_{B0}=24$ mol/m³, $\varepsilon=0.48$ W/kg), and (c) at various ε ($C_{B0}=24$ mol/m³, $\dot{n}_{G0}/V_R=0.0124$ mol/m³ s).

agglomerates flocked by chemical forces could not be re-dispersed by ultrasonication and the size distributions after ultrasonication also showed a bimodality (Fig. 2). Thus, it seemed that the light scattering instrument recognized agglomerates as particles, thereby overestimating the mean size. From the bimodal distribution, it was also inferred that the first peak at 1 μm mainly represented individual particles formed by nucleation and growth, as shown in the SEM images, whereas the second peak at 10 μm represented agglomerates. The agglomeration of calcium carbonate has already been reported in other studies [3,17,21,24,25]. Thus, agglomeration, rather than particle growth, clearly had an overriding effect when determining the mean size using a light scattering method.

Fig. 7(a) showed that increase in C_{B0} enhanced the agglomeration, which was also confirmed by the SEM images in Fig. 5, yet the agglomeration decreased with an increase in $\dot{n}_{G0}/V_R$, as shown in Fig. 7(b). It was already well known that a high supersaturation produced a high suspension density and enhanced the frequency of particle collision, resulting in agglomeration [29,30]. Therefore, the effect on agglomeration when varying the supersaturation with the C_{B0} and $\dot{n}_{G0}/V_R$ should also be considered. The relative supersaturation (σ) was calculated from the equation suggested by Nielsen and Toft [31]. The ionic species concentrations were computed from the experimental pH value, total calcium and carbonate concentrations by successive approximation using mass action equations mass balance equations and the modified

Debye–Hückel equation in order to calculate the activity coefficients [4]. Under the assumption of the complete absorption of carbon dioxide gas into the solution, the estimated σ -values for each set of experimental conditions are listed in Table 4. Since the σ -value increased with C_{B0} , the results in Fig. 7(a) supported the above viewpoint. Yet, when there is an increase in $\dot{n}_{CO}/V_R$, the estimated σ -value in Table 4 exhibited a maximum, while the agglomeration was reduced, as shown in Fig. 7(b), thereby deviating from the above viewpoint. Thus, the supersaturation seemed to play an important role in the particle agglomeration according to the $\dot{n}_{CO}/V_R$ value.

In addition, agglomeration depends on the surface charge of the particles. All the results in Fig. 7(a) and (b) showed that the agglomeration increased with an increase in the pH value, i.e. an excess Ca^{2+} ion concentration. As such, it could be deduced that the excess Ca^{2+} ions were adsorbed on the negatively charged surface of the particles, thereby reducing the repulsion force sufficiently for the particles to agglomerate.

Finally, agglomeration was also affected by the mixing resulting from the agitation. Thus, the effect of the agitation rate in both reactors, represented by the power consumption, on the mean size measured by the light scattering method is illustrated in Fig. 7(c). An increase in ε was expected to enhance the agglomeration, due to the increased frequency of particle collision. However, the mean size exhibited a maximum at a certain ε value in both reactors, indicating that attrition or breakage, as well as agglomeration, became important at a high agitation rate.

3.3. Effect of excess species in solution

To investigate the effect of excess species on the size of individual particles, the size of individual particles was analyzed by direct reading from the SEM images. It should be noted that this method focuses on a single individual particle. The resulting size distribution also showed a bimodal pattern, yet the mean size was much lower than that obtained using the former method.

The variations of the volume-based mean size, when measured by SEM image reading, with the operating variables in both reactors at a steady state are presented in Fig. 8. When $\dot{n}_{CO}/V_R$ and ε were fixed at 0.0124 mol/m³ s and 0.48 W/kg, respectively, the

mean size decreased with an increase in C_{B0} , as shown in Fig. 8(a). This tendency was opposite to the result in Fig. 7(a) when using the light scattering method. Also, the mean size of individual particles was smaller than 2 μ m, in contrast to agglomerates of 5–15 μ m in Fig. 7(a). For the morphology, cube-like rhombic calcium carbonate was produced with a low C_{B0} , while spindle-like particles were favored with a high C_{B0} (Fig. 5).

The variation in the morphology and size with C_{B0} could be explained in terms of selective adsorption of the excess Ca^{2+} ions on the crystal face, as demonstrated in an earlier study by the present authors [21]. At a pH value higher than 8.2, as shown in Fig. 3(a), excess Ca^{2+} ions was expected in the solution within the range of C_{B0} given in Fig. 8(a). Thus, at a low C_{B0} (5 mol/m³), nearly stoichiometric reaction conditions, cube-like rhombic calcite with well-formed faces was favored. However, as C_{B0} increased, the excess Ca^{2+} ions were adsorbed on the preferred faces of the calcium carbonate, thereby inhibiting the face growth of a particle and modifying the morphology. Consequently, the mean size in Fig. 8(a) decreased until the adsorption reached an equilibrium around C_{B0} =50 mol/m³. As a result of this selective adsorption, inclined faces were observed as the transition shape of the particles produced in the Couette–Taylor reactor. Then, with a high C_{B0} , these inclined faces became dominant and the morphology became spindle-like in shape. After the adsorption reached equilibrium, the morphology and size became almost independent of C_{B0} . This explanation based on the present experimental results was also consistent with previous reports [11,31].

In Fig. 8(b), the effect of the gas flow rate on the mean size of individual particles was exhibited under the same conditions in Fig. 7(b). The mean size in Fig. 8(b), measured from image reading, exhibited a maximum with an increase in $\dot{n}_{CO}/V_R$, deviating from the results in Fig. 7(b). As mentioned in Fig. 3(b), the pH value decreased with an increase in $\dot{n}_{CO}/V_R$ and a nearly stoichiometric reaction occurred at $\dot{n}_{CO}/V_R$ =0.112 mol/m³ s when the pH $\approx$ 8.2. Therefore, within the range of $\dot{n}_{CO}/V_R$ < 0.112 mol/m³ s, there was also an excess of Ca^{2+} ions. Thus, the mean size increased with an increase in $\dot{n}_{CO}/V_R$ due to a reduction in the excess Ca^{2+} ion concentration. It was also found from the SEM images that the calcium carbonate morphology was transformed from being spindle-like to cube-like with an increase in $\dot{n}_{CO}/V_R$. This variation in the morphology and mean size with $\dot{n}_{CO}/V_R$ was also coincident with that with C_{B0} . In contrast, within the range of $\dot{n}_{CO}/V_R$ > 0.112 mol/m³ s, there was an oversupply of CO_2 into the local solution. Thus, the excess of CO_3^{2-} ion resulted in the mean size reduction, yet no significant change was observed in the particle morphology.

The nucleation and growth process directly depended on the supersaturation which varied with C_{B0} and $\dot{n}_{CO}/V_R$. According to kinetic studies of calcium carbonate crystallization [32,33], a higher level of supersaturation produced smaller particles, as the nucleation was more sensitive than the particle growth. From the estimated σ -values in Table 4, Fig. 7(a) supported this viewpoint, whereas the tendency in Fig. 7(b) did not. Therefore, it would be inferred that the excess species present in the solution were more dominant than the supersaturation in determining the mean size.

It was already well known that increase in the agitation rate enhanced the absorption rate of CO_2 , which was experimentally confirmed by a decrease in the pH value with increment of ε . Also under the same conditions as in Fig. 7(c), the mean size of individual particles varied with ε , as shown in Fig. 8(c), where excess of Ca^{2+} ions also existed. Since the excess ion concentration decreased with an increase in ε , the mean particle size became larger, although only slightly, and the morphology approached a rhombic shape. As shown in an earlier study using a CT reactor [18], the mean size showed a maximum and mainly

Table 4
Estimated values of relative supersaturation (σ) under assumption of dissolution of whole CO_2 gas into solution.

Operating conditions		σ	
C_{B0} (mol/m ³)	$\dot{n}_{CO}/V_R$ (mol/m ³ s)	Couette–Taylor	Tank
5	0.0124	8.3	8.4
12			25.1
16		27.6	
24		30.1	30.2
32		31.1	
36			31.4
40		31.6	
48		31.8	31.8
64		31.9	
24	0.0062	21.7	
		0.0099	
		27.3	
		0.0124	30.2
		0.0174	
		34.7	
		0.0223	
		37.7	
		0.0372	41.4
	0.0744		15.9
	0.112		11.6
	0.149		2.4

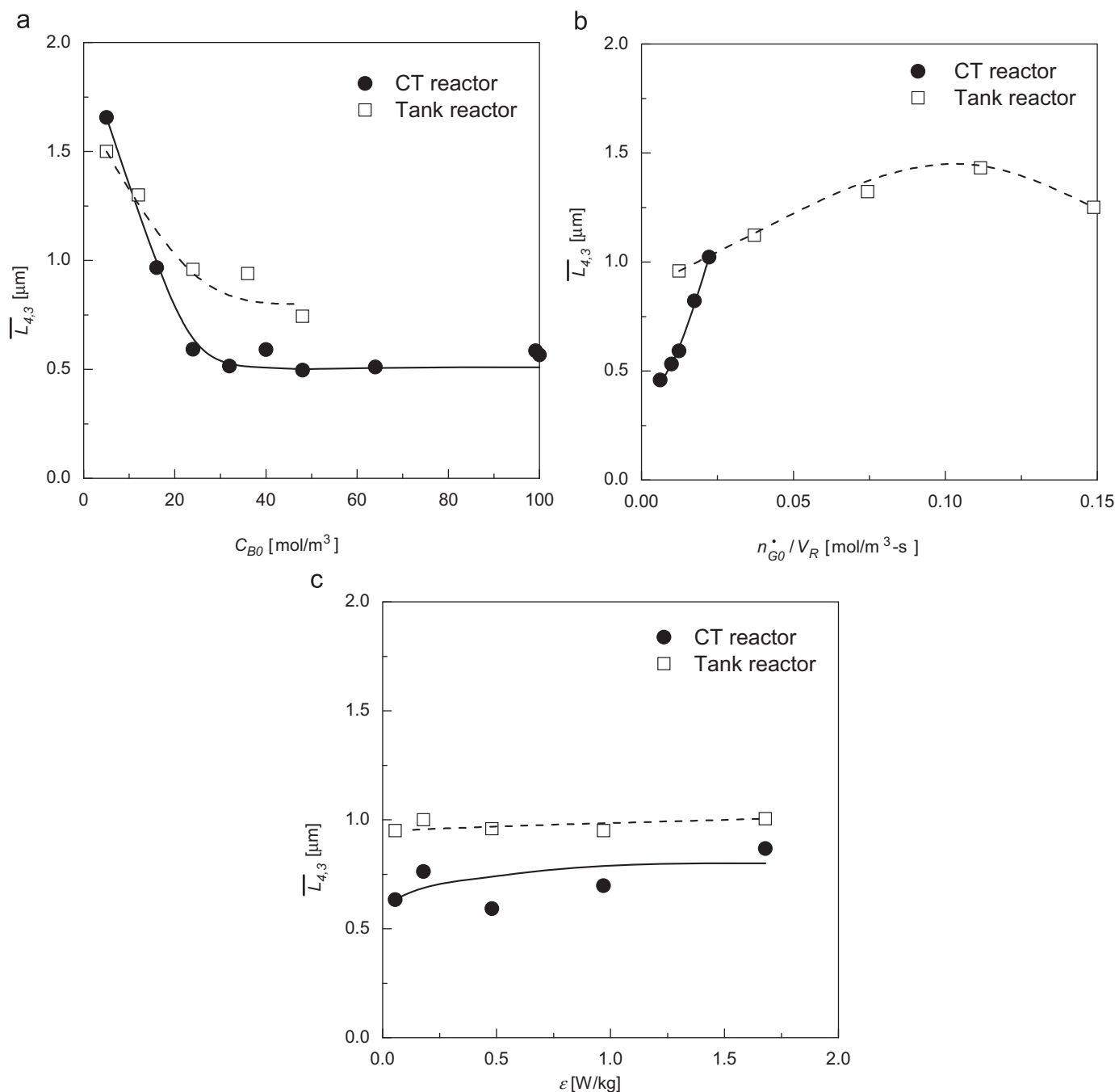


Fig. 8. Mean sizes of individual particles, measured from SEM images, produced in steady Couette-Taylor and tank reactors (a) at various C_{B0} ($\dot{n}_{G0}/V_R = 0.0124$ mol/m³ s, $\varepsilon = 0.48$ W/kg), (b) at various $\dot{n}_{G0}/V_R$ ($C_{B0} = 24$ mol/m³, $\varepsilon = 0.48$ W/kg), and (c) at various ε ($C_{B0} = 24$ mol/m³, $\dot{n}_{G0}/V_R = 0.0124$ mol/m³ s).

cube-like shape around $\varepsilon = 0.3$ W/kg with a low C_{B0} of 5 mol/m³, when the stoichiometric reaction conditions were satisfied.

4. Conclusion

The operating variables affecting the morphology and size of the calcium carbonate produced by a CO₂–Ca(OH)₂ reaction in stirred tank and CT reactors were identified as the aqueous reactant concentration, gas flow rate and power consumption (agitation rate).

In the stirred tank reactor, the coexistence of cube-like and spindle-like particles with a high concentration of excess Ca²⁺ ions indicated that the mixing driven by the impeller agitation

resulted in local differences in the mixing intensity. In contrast, in the CT reactor, the unique mixing behavior of the Taylor vortices effectively encouraged homogeneous mixing conditions, resulting in smaller particles with a uniform shape throughout the reactor.

The bimodal distribution of the particles size measured using a conventional light scattering method was due to the agglomeration of individual particles that were measured in the range of 0.1–1 μm from SEM image reading. Also, the agglomeration was affected by the supersaturation and surface charge depending on the operating variables of reactant concentration, stoichiometric condition, agitation, etc.

However, the SEM images revealed that the morphology and size of individual particles were mainly influenced by the excess species of reactants in the solution. As such, modification of the

particle morphology was seemingly caused by different growth rates of the crystal faces due to selective adsorption of the excess species, where the growth site was blocked and the surface integration step inhibited by the adsorbed excess species. Therefore, stoichiometric conditions produced the most cube-like particles with the largest mean size. As in the excess Ca^{2+} ion concentration increased, the morphology transformed to a spindle-like shape and the mean size decreased.

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References

- [1] J.L. Wray, F. Daniels, *J. Am. Chem. Soc.* 79 (1957) 2031.
- [2] M.M. Reddy, G.H. Nancollas, *J. Colloid Interface Sci.* 36 (1971) 166.
- [3] J. Hostomsky, A.G. Jones, *J. Phys. D: Appl. Phys.* 24 (1991) 165.
- [4] C.Y. Tai, P.C. Chen, S.M. Shih, *AIChE J.* 39 (1993) 1472.
- [5] D. Chakraborty, V.K. Agarwal, S.K. Bhatia, *J. Bellare, Ind. Eng. Chem. Res.* 33 (1994) 2187.
- [6] I.W. Kim, R.E. Robertson, R. Zand, *Cryst. Growth Des.* 5 (2005) 513.
- [7] G. Falini, S. Manara, S. Fermani, N. Roveri, M. Goisis, G. Manganelli, L. Cassar, *Cryst. Eng. Commun.* 9 (2007) 1162.
- [8] H. Matahwa, V. Ramiah, R.D. Sanderson, *J. Cryst. Growth* 310 (2008) 4561.
- [9] J. Franke, A. Mersmann, *Chem. Eng. Sci.* 50 (1995) 1737.
- [10] A.E. Nielsen, *Kinetics of Precipitation*, Pergamon Press, Oxford, 1964.
- [11] O. Söhnel, J.W. Mullin, *J. Cryst. Growth* 60 (1982) 239.
- [12] H. Roques, A. Girou, *Water Res.* 8 (1974) 907.
- [13] T. Jung, W.-S. Kim, C.K. Choi, *Cryst. Res. Technol.* 40 (2005) 586.
- [14] V.A. Juvekar, M.M. Sharma, *Chem. Eng. Sci.* 28 (1973) 825.
- [15] H. Yagi, A. Iwazawa, R. Sonobe, T. Mateubara, H. Kikita, *Ind. Eng. Chem. Fundam.* 23 (1984) 153.
- [16] S. Wachi, A.G. Jones, *Chem. Eng. Sci.* 46 (1991) 1027.
- [17] S. Wachi, A.G. Jones, *Chem. Eng. Sci.* 46 (1991) 3289.
- [18] A.G. Jones, J. Hostomsky, Z. Li, *Chem. Eng. Sci.* 47 (1992) 3817.
- [19] P.C. Chen, C.Y. Tai, K.C. Lee, *Chem. Eng. Sci.* 52 (1997) 4171.
- [20] K. Tamura, H. Tsuge, *Chem. Eng. Sci.* 61 (2006) 5818.
- [21] W.M. Jung, S.H. Kang, W.-S. Kim, C.K. Choi, *Chem. Eng. Sci.* 55 (2000) 733.
- [22] W.L. McCabe, J.C. Smith, P. Harriott, in: *Unit Operations of Chemical Engineering*, 4th ed., McGraw-Hill, New York, 1985.
- [23] P. Somasundaran, G.E. Agar, *J. Colloid Interface Sci.* 24 (1967) 433.
- [24] C.Y. Tai, P.C. Chen, *AIChE J.* 41 (1995) 68.
- [25] J. Villiermaux, R. David, *Chem. Eng. Commun.* 21 (1983) 105.
- [26] W.-S. Kim, W.S. Kim, K.-S. Kim, J.-S. Kim, M.D. Ward, *Mater. Res. Bull.* 39 (2004) 283.
- [27] M.H. Sung, I.S. Choi, J.S. Kim, W.-S. Kim, *Chem. Eng. Sci.* 55 (2000) 2173.
- [28] T. Serra, X. Casamitjana, *AIChE J.* 44 (1998) 1724.
- [29] J.A. Wójcik, A.G. Jones, *Trans. Inst. Chem. Eng.* 75 (1997) 113.
- [30] M.J. Hounslow, R.L. Ryall, V.R. Marshall, *AIChE J.* 34 (1988) 1821.
- [31] A.E. Nielsen, J.M. Toft, *J. Cryst. Growth* 67 (1984) 278.
- [32] A. Packter, *J. Chem. Soc. (A): Inorg. Phys. Theory.* (1968) 859.
- [33] L.D. Swinney, J.D. Stevens, R.W. Peters, *Ind. Eng. Chem. Fundam.* 21 (1982) 31.