



Particle morphology of calcium carbonate precipitated by gas–liquid reaction in a Couette–Taylor reactor

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Abstract

The morphology and size of calcium carbonate particles produced by CO_2 – $\text{Ca}(\text{OH})_2$ reaction precipitation in a Couette–Taylor reactor were investigated experimentally. It was found that the change of particle morphology and size was caused dominantly by the excess species of reactants in the solution. As their measure, the relative enhancement factor Er involving the operation variables was introduced for the first time. The largest mean particle size and the most cube-like particle shape were observed at $Er = 1$, implying the stoichiometric reaction condition. As the Er -value deviates from unity, particle morphology shifted to the spindle-like shape and mean particle size decreased with an increase in excess species concentration in the solution. The effect of excess species on particle size was predicted by the Bliznakov equation based on the monolayer adsorption. The correlation of particle size at various operating conditions represented the experimental data very well. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Calcium carbonate; Couette–Taylor reactor; Gas–liquid reaction precipitation; Particle morphology; Particle size; Relative enhancement factor

1. Introduction

The precipitation of calcium carbonate has attracted much attention because of its numerous applications in various areas of plastics, textiles, rubbers, adhesives, paints and wastewater treatment. In these areas, the morphology and particle size distribution of calcium carbonate play a critical role in determining the product properties (Chakraborty, Agarwal, Bhatia & Bellare, 1994; Tai and Chen, 1998). Because the operating variables such as reactant concentration, mixing, admixture and operating modes, batch or continuous, are interrelated, the mechanism of calcium carbonate precipitation still seems clouded and therefore the present work concentrates on evaluating the effect of excess reactant species in well-known flow of Taylor vortices.

The morphology of a calcium carbonate particle, which is generally classified as rhombic calcite, needle-like aragonite and spherical vaterite, depends on the precipitation condition. Therefore, a considerable

amount of attention and effort has been devoted to elucidate the relationship between the precipitation condition and the particle morphology. It has been observed that calcite, aragonite and vaterite of calcium carbonate particles are formed simultaneously by liquid–liquid reaction precipitation and that each morphological portion depends on the supersaturation and temperature of solution (Wray & Daniels, 1957; Reddy & Nancollas, 1971). The significant change in vaterite crystal shape into calcite in supersaturated solution was reported by Söhnel and Mullin (1982). It is well recognized that vaterite is an unstable precipitate in supersaturated solution. Hostomsky and Jones (1991) reported that the morphology of calcium carbonate could be controlled by the pH of solution in a continuous crystallizer. According to their study, the formation of vaterite in the reaction precipitation of calcium nitrate and sodium carbonate occurs at $\text{pH} \geq 9.5$, but calcite is obtained at $\text{pH} \leq 8.5$. Similarly, the dependency of morphology, nucleation and growth of calcium carbonate particles on the feed concentration and the pH of solution in the reaction precipitation of calcium chloride and sodium carbonate was observed by Tai, Chen and Shih (1993) and Tai and Chen (1995). They attributed the morphological change of

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Nomenclature			
A_n	area of nozzle, m^2	k_L^0	gas-liquid mass transfer coefficient without reaction, m/s
a	gas-liquid interface area per unit reactor volume, m^{-1}	L	reactor length, m
C_A	concentration of CO_2 in solution, mol/m^3	Q_A	volumetric flow rate of CO_2 gas, m^3/s
$C_{A,eq}$	concentration of CO_2 in solution at equilibrium, mol/m^3	Q_B	volumetric flow rate of $Ca(OH)_2$ solution, m^3/s
C_{AG}	concentration of CO_2 in gas phase, mol/m^3	Re	Reynolds number defined as $\omega_i r_i d/v$, dimensionless
C_{Ai}	concentration of CO_2 at gas-liquid interface, mol/m^3	Re_c	critical Reynolds number, dimensionless
C_B	concentration of OH^- in solution, mol/m^3	$\bar{R}$	average absorption rate of CO_2 gas per unit interfacial area, $mol/m^2 s$
C_{B0}	initial concentration of OH^- in solution, mol/m^3	r_A	rate of reaction, $mol/m^3 s$
C_{ex}	concentration of excess species, mol/m^3	r_i	radius of inner cylinder, m
d	gap size between inner and outer cylinder or particle size at a concentration of excess species, m	r_o	radius of outer cylinder, m
d_B	bubble diameter, m	t_G	mean residence time of gas phase in a CSTR, s
d_{eq}	particle size at equilibrium concentration of excess species, m	t_L	mean residence time of liquid phase in a CSTR, s
d_m	mean particle size, m	t_R	actual reaction time, s
d_0	particle size at zero concentration of excess species, m	t_S	mean residence time of solution in Couette-Taylor reactor, s
E	enhancement factor, dimensionless	V_B	bubble volume, m^3
Er	relative enhancement factor, dimensionless	v^*	friction velocity, m/s
f	friction factor, dimensionless	<i>Greek letters</i>	
g	acceleration of gravity, m/s^2	α	empirical constant, dimensionless
K	shape factor defined as ratio of length in major axis to that in minor axis of a particle, dimensionless	ε_G	gas hold-up, dimensionless
K_{ad}	adsorption constant, m^3/mol	ε_L	liquid hold-up, dimensionless
k	rate constant of reaction, $m^3/mol s$	μ	viscosity of solution, $kg/m s$
k_L	actual gas-liquid mass transfer coefficient, m/s	ν	kinematic viscosity of solution, m^2/s
		ρ	density of solution, kg/m^3
		ρ_G	density of CO_2 gas, kg/m^3
		σ	relative supersaturation, dimensionless
		$\tau_{\omega i}$	wall shear stress in Couette-Taylor reactor, Pa
		ω_i	rotating speed of inner cylinder, rad/s

calcium carbonate to the supersaturation level and the pH of solution.

Chakraborty et al. (1994) and Chakraborty and Bhatia (1996) observed polymorphs of calcium carbonate particles produced by aqueous reaction of calcium nitrate and sodium carbonate in a continuous crystallizer. In their studies, polymorphic nuclei of calcite and vaterite were generated simultaneously and unstable vaterite tended to be transformed into stable calcite during the precipitation. Calcite and vaterite had different growth rates and aggregation tendencies influencing on the particle size distribution. These observations were explained in terms of homogeneous and heterogeneous nucleation, which depended on the supersaturation level and ionic ratio of $[Ca^{2+}]/[CO_3^{2-}]$ in solution, and were quantitatively described with the mathematical model. In addition, the extensive study on the effect of operating variables of the reactant concentration, residence time,

specific power input and feed point position on the calcium carbonate precipitation was performed by Franke and Mersmann (1995).

As shown in previous studies that adopted the liquid-liquid reaction systems for calcium carbonate precipitation, it is obvious that the condition of solution is most important in determining the nucleation, growth and morphology of calcium carbonate particles in the precipitation. In these systems, the simultaneous production of a soluble salt as by-product of the reaction, which may significantly influence the precipitation as an admixture in solution, is inevitable. In most studies, however, the influence of by-product on the precipitation process is often not considered. Actually, in the liquid-liquid reaction precipitation of calcium carbonate, it is difficult to judge the influence of by-product on the nucleation, growth and morphology of particles.

CO₂ gas–liquid reaction for calcium carbonate precipitation was examined by Yagi, Iwazawa, Sonobe, Mateubara and Kikita (1984) and Jones, Hostomsky and Li (1992). In their studies, CO₂ gas flowed gently over calcium hydroxide solution agitated in the reactor and was absorbed at a flat gas–liquid interface to react with calcium hydroxide. From their experimental results, a valuable information on the calcium carbonate precipitation could be obtained because the influence of by-product of the reaction on the precipitation was eliminated. Besides, Chen, Tai and Lee (1997) investigated a reaction precipitation of calcium carbonate by feeding CO₂ gas through a gas sparger or a double-tube gas injection nozzle into calcium hydroxide solution in an agitated batch reactor. In their studies, it was observed that particle morphology and growth were closely related to the pH of solution. However, since KOH was used to control the pH in the reactor, it can be hardly said that the effect of admixture on calcium carbonate precipitation is eliminated.

The main purpose of the present study is to investigate the influence of solution conditions, which are determined by the operating variables such as the Ca(OH)₂ feed concentration, CO₂ gas flow rate and wall shear stress in a Couette–Taylor reactor, on the particle morphology and size in the CO₂–Ca(OH)₂ reaction precipitation of calcium carbonate. To create the turbulent Taylor vortex flow the inner cylinder of the Couette–Taylor reactor was rotated. The morphology of calcium carbonate particles is expressed by a shape factor. In addition, the relative enhancement factor, which is composed of the operating variables, is suggested for the first time to classify the morphology and size of particles.

2. Theoretical backgrounds

The overall process of the precipitation of calcium carbonate is well known as



According to Juvekar and Sharma (1973), this reaction consists of four elementary steps and the rate-controlling step is the following elementary reaction between CO₂ and OH[−]:



In Eq. (2) the forward reaction is second order and the reverse reaction is first order. Then, the net rate of reaction at non-equilibrium is given (Danckwerts, 1970) as

$$r_A = kC_B(C_A - C_{A,\text{eq}}), \quad (3)$$

where C_A and $C_{A,\text{eq}}$ denote the CO₂ concentrations in solution at non-equilibrium and equilibrium, respectively, and C_B the concentration of OH[−] in solution. The rate constant k at 20°C is 12.4 m³/mol s (Astarita, 1967).

In the present system, since the absorbed CO₂ reacts with OH[−] instantaneously to produce CaCO₃, $C_{A,\text{eq}}$ can be expected to be nearly zero; that is, the reaction seems to be irreversible. Therefore, the rate of reaction is expressed as the simple second-order reaction of CO₂ and OH[−].

The flow in a Couette–Taylor reactor is characterized by the existence of toroidal vortex cells spaced periodically along the cylindrical axis. At a given operating condition, this vortex regime appears when the rotating speed of the inner cylinder is larger than the critical value. Each flow element consists of counter-rotating vortices and an axial length of each cell is approximately equal to the annular gap width. Therefore, a Couette–Taylor reactor can be simplified as continuous-stirred tank reactors (CSTRs) connected in series (Campero & Vigil, 1997; Lee, M.O. Kim, W.S. Kim & Choi, 1998b). It is assumed that all these tank reactors have the same size individually and the mean residence time of each reactor is the same. When CSTRs in series are run at steady state and operated so as to be completely mixed, mass balance equations for CO₂ based on the gas phase and liquid phase and for OH[−] in the j th reactor can be expressed (Amundson & Luss, 1992) as

$$\varepsilon_G \frac{C_{AG,j-1} - C_{AG,j}}{t_G} = k_L a (C_{Ai} - C_{A,j}), \quad (4)$$

$$\varepsilon_L \frac{C_{A,j-1} - C_{A,j}}{t_L} + k_L a (C_{Ai} - C_{A,j}) = \varepsilon_L r_{A,j}, \quad (5)$$

$$\varepsilon_L \frac{C_{B,j-1} - C_{B,j}}{t_L} = \varepsilon_L r_{A,j}, \quad (6)$$

where ε_G , ε_L , t_G , and t_L are the gas hold-up, the liquid hold-up, the mean residence time in the gas phase, and that in the liquid phase, respectively. C_{AG} denotes the concentration of CO₂ in the gas phase, C_{Ai} that at the gas–liquid interface, k_L the gas–liquid mass transfer coefficient and a the interfacial area per unit reactor volume.

When the absorbed gas reacts with a reactant dissolved in an aqueous solution, the absorption of gas can be facilitated by the chemical reaction in solution. It is often convenient to present the effect of a chemical reaction on the gas absorption in terms of the enhancement factor E . E is defined as the ratio of the rate of gas absorption into a reacting liquid to that without chemical reaction. The enhancement factor can be expressed as

$$E = \frac{\bar{R}a}{k_L^0 a (C_{Ai} - C_A)}, \quad (7)$$

where $\bar{R}$ is the average rate of absorption of CO₂ gas per unit interfacial area and k_L^0 the mean mass transfer coefficient when no reaction occurs.

In the present system the reaction is so fast that all CO₂ absorbed is consumed within the thin liquid film near the gas–liquid interface. Therefore, there is little

amount of CO_2 in the bulk of liquid and C_A terms in (4) and (5) are negligible. The concentration of CO_2 at the interface uniformly remains C_{Ai} and then the reaction becomes first order in C_B . If CSTRs in series are operated at the same temperature, the reaction rate constants of each tank reactor are the same. Therefore, the effluent concentration of OH^- in the j th reactor is reduced from Eq. (6) by

$$C_{B,j} = \frac{C_{B0}}{(1 + t_L k C_{Ai})^j}, \quad (8)$$

where C_{B0} is the initial concentration of OH^- in solution. If all CO_2 bubbles are dissolved and reacted completely until the n th reactor, substituting Eq. (8) into Eq. (3) and applying the above assumptions produce the following equation from Eq. (5):

$$\bar{R}a = \varepsilon_L \sum_{j=1}^n r_{A,j} = \varepsilon_L k C_{Ai} C_{B0} \sum_{j=1}^n \frac{1}{(1 + t_L k C_{Ai})^j}. \quad (9)$$

This means that the rate of absorption of CO_2 is equal to the rate of reaction of CO_2 . Substituting the above equation into Eq. (7) leads to

$$E = \frac{\varepsilon_L k C_{B0}}{k_L^0 a} \sum_{j=1}^n \frac{1}{(1 + t_L k C_{Ai})^j}. \quad (10)$$

It is generally known that the mass transfer coefficient increases with the rotating speed of the inner cylinder in the Couette–Taylor reactor. The mass transfer coefficient k_L^0 is given by the equation of Metzner and Friend (1958), which can be simplified in good approximation to

$$k_L^0 = \alpha v^* = \alpha \sqrt{\tau_{oi}/\rho}, \quad (11)$$

where α is the dimensionless empirical constant, v^* the friction velocity, and ρ the density of solution. The shear stress at the wall of the rotating inner cylinder (τ_{oi}) is defined by

$$\tau_{oi} = \frac{f \rho r_i^2 \omega_i^2}{2}, \quad (12)$$

where r_i and ω_i are the radius and the rotating speed of the inner cylinder, respectively. The friction factor f is given as a function of d/r_i and the Reynolds number Re , which was experimentally suggested by Atsumi et al. (1988):

$$f = 0.80 \left(\frac{d}{r_i} \right)^{0.35} Re^{-0.53} \quad \text{for } Re \geq Re_c \quad (13)$$

where $Re = \omega_i r_i d / \nu$. Here, d is the gap size between the inner and outer cylinder, and ν the kinematic viscosity of solution. The critical Reynolds number Re_c , at which Taylor vortices begin to appear, is given by

$$Re_c = 41.2 \left(\frac{d}{r_i} \right)^{-0.5} + 27.2 \left(\frac{d}{r_i} \right)^{0.5} + 2.8 \left(\frac{d}{r_i} \right)^{1.5}. \quad (14)$$

Table 1

Calculation of Reynolds number Re , friction factor f and wall shear stress τ_{oi} with rotating speed of inner cylinder ω_i for $d/r_i = 0.57$ with $r_i = 3.1$ cm

ω_i		$Re \times 10^4$	$f \times 10^3$	τ_{wi}
(rev/min)	(rad/s)			[Pa]
250	26.2	1.50	3.95	1.39
400	41.9	2.40	3.43	3.08
600	62.8	3.60	3.04	6.14
800	83.8	4.81	2.78	9.99
1000	104.7	6.01	2.60	14.6

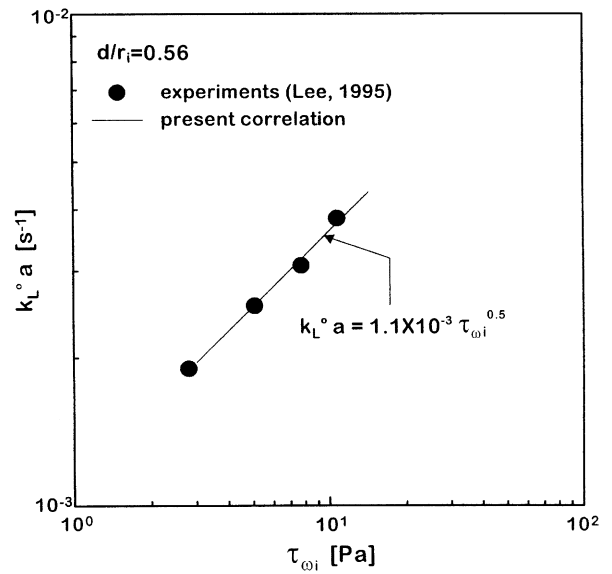


Fig. 1. Relation of mass transfer coefficient $k_L^0 a$ with wall shear stress τ_{oi} in present experiments of pure CO_2 absorption into water by Lee (1995).

In the range of the present experiments, where $d/r_i = 0.57$ and $Re_c = 76.6$, the calculated Re , f and τ_{oi} are listed in Table 1, as a function of the rotating speed of the inner cylinder.

In the present three-phase system it is difficult to determine k_L^0 and a separately by measurements of absorption because, in a system containing bubbles, the interfacial area is not known. Thus, the quantity measurable directly by absorption experiments under the fixed volumetric flow rate of solution (Q_B) and that of CO_2 gas (Q_A) is $k_L^0 a$. The experimental values of averaged $k_L^0 a$ obtained by Lee (1995) are shown in Fig. 1. In his experiments CO_2 gas was dissolved partially into water in the Couette–Taylor reactor. The CO_2 -absorption data for $d/r_i = 0.56$ without reaction were well correlated by

$$k_L^0 a = 1.1 \times 10^{-3} \tau_{oi}^{0.5}. \quad (15)$$

Therefore, it seems evident that the mass transfer coefficient k_L^0 is enhanced by the wall shear stress with the power of 0.5, as shown in Eq. (11).

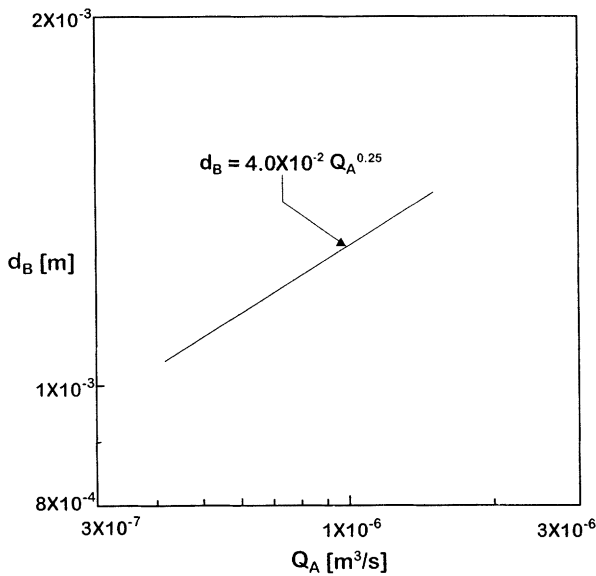


Fig. 2. Prediction of bubble diameter d_B with CO_2 gas flow rate Q_A by using Eq. (16).

Assuming an approximately spherical bubble of diameter d_B , the gas–liquid interfacial area per unit reactor volume is simply given by

$$a = 6 \frac{\varepsilon_G}{d_B} \quad (16)$$

The bubble size is characterized by the bubble flow pattern. In the present system, in which the gas velocity is large, the momentum flux from the nozzle is somewhat significant. The bubble volume V_B ($= 4d_B^3/3$) is obtained from the force balances (Wallis, 1969):

$$(36\pi)^{1/3} = \frac{2g(\rho - \rho_G)}{5\mu Q_A} V_B^{4/3} + \frac{Q_A \rho_G}{A_n \mu} V_B^{1/3}, \quad (17)$$

where g is the acceleration due to gravity, ρ_G the density of CO_2 gas, μ the viscosity of solution, Q_A the volumetric flow rate of CO_2 gas and A_n the area of the nozzle. From the calculation of V_B according to the above equation, it should be noted that the bubble size d_B increases with Q_A approximately by the power of 0.25, as shown in Fig. 2, in the range of the present experiments.

In addition, $\varepsilon_L/\varepsilon_G \cong Q_B/Q_A$ is a good approximation under the assumption of $t_G \cong t_L$ in Eqs. (4)–(6). If the reaction is finished at the similar position in the Couette–Taylor reactor, n in Eq. (10) can be assumed to be a constant in the present system. Substituting the above relationships of $d_B \propto Q_A^{0.25}$, $k_L^0 \propto \tau_{oi}^{0.5}$ and $\varepsilon_L/\varepsilon_G \cong Q_B/Q_A$ into Eq. (10), the enhancement factor is reduced by

$$E \propto \frac{Q_B}{Q_A^{0.75}} \frac{C_{B0}}{\tau_{oi}^{0.5}} \quad (18)$$

Since the reaction leading to precipitation is controlled by the absorption of CO_2 gas, the enhancement factor plays an important role as a significant operating parameter in the precipitation processes. The above enhancement factor also consists of the operating variables which can be easily measured and calculated. In this work the following relative enhancement factor Er is introduced by normalizing the above enhancement factor:

$$Er = \frac{Q_B C_{B0} / Q_A^{0.75} \tau_{oi}^{0.5}}{(Q_B C_{B0} / Q_A^{0.75} \tau_{oi}^{0.5})_{C_{ex}=0}} \quad (19)$$

The condition of $C_{ex} = 0$ means that no excess species exists. At this stoichiometric reaction the maximum particle size of CaCO_3 appears, that will be seen later.

The charged ions such as admixtures, impurities and excess ions have frequently been believed to modify the morphology and size of particles. Nielsen (1964) observed the morphological change of particles by the charged ion in solution. Nancollas and Purdie (1957) and Howard and Nancollas (1957) showed the reduction of the particle growth in non-stoichiometric reaction precipitation of BaSO_4 and Ag_2CrO_4 , respectively, and attributed these experimental phenomena to the blockage of growth site (kinks) by the excess species adsorbed on the particle surface. The similar effect of ionic additives on the particle growth in ADP and KCl precipitation was also reported by Davey and Mullin (1974) and König, Emons and Nyvlt (1987). The excess ion in solution seems to be adsorbed on preferred faces of a CaCO_3 particle due to the interaction between particle faces and charged ions. Then, the adsorbed ion will inhibit the face growth of a particle and bring modification of particle morphology. Also, since the adsorption of excess ion on the particle surface is proportional to the excess species concentration in solution, it can be expected that particle morphology changes and particle size is reduced until the equilibrium of the adsorption is reached. Then, particle morphology and size become insensitive to the excess species concentration.

To predict the effect of excess species on the particle growth the following model equation, which was suggested originally by Bliznakov under the assumption of the monolayer adsorption of excess species on the particle surface (Punin & Franke, 1998), is employed:

$$\frac{d - d_0}{d_{eq} - d_0} = \frac{K_{ad} C_{ex}}{1 + K_{ad} C_{ex}}, \quad (20)$$

where d denotes the particle size at an excess species concentration C_{ex} in solution and K_{ad} the adsorption constant. d_0 and d_{eq} are the particle sizes at zero and equilibrium concentration of excess species, respectively. d_0 is expected to be the maximum value of particle size. In Eq. (20) the term on the right-hand side means the coverage of the growth site on the particle surface by excess species.

Since calcium carbonate reaction is very fast, the excess species concentration C_{ex} in the Couette–Taylor reactor is estimated from Eqs. (3), (5), (9) and (11) by

$$C_{\text{ex}} = \frac{C_{B0}}{2} - \frac{1}{\varepsilon_L} C_{Ai} k_L a t_R, \quad (21)$$

where t_R is the actual reaction time. According to simplification of CSTRs in series, t_R represents nt_L . The initial Ca^{2+} -ion concentration corresponds to $C_{B0}/2$ (see Eq. (1)) and $C_{Ai} k_L a$ indicates the rate of dissolution of CO_2 into solution with $C_A \cong 0$. $k_L a$ indicates the actual mass transfer coefficient with chemical reaction. In the case of no reaction, it is represented as $k_L^0 a$ ($< k_L a$) and t_R will be equivalent to the mean residence time of solution (t_S) in the present Couette–Taylor reactor. Then, $C_{Ai} k_L a t_R$ means the average amount of CO_2 consumed by the reaction per unit reactor volume with $t_G = t_L$ (see Eq. (4)) during t_R .

3. Experiments

In the present experiments the CaCO_3 reaction precipitation was driven with gaseous carbon dioxide (more than 99.9% of purity) and aqueous calcium hydroxide (ACS grade). The aqueous solution of calcium hydroxide was prepared with distilled water. The concentration of calcium hydroxide feed solution was measured with a conductivity meter (Cole-Parmer, model 1481-60), and C_{B0} was varied from 5 to 100 mol/m³, as summarized in Table 2. To remove solid impurities in solution it was filtered with the microbag filter prior to storage in the feed tank.

As shown in Fig. 3(a), CO_2 gas and Ca(OH)_2 solution were fed into the Couette–Taylor reactor and the flow rates were monitored by rotameters. To eliminate fluctuations in flow rates a damper was used for the gaseous feed and a by-pass valve was installed in the aqueous feed line. The flow rate of the gaseous feed was changed from 4.17×10^{-7} to 1.50×10^{-6} m³/s while that of the aqueous feed was fixed. Since the solubility of CO_2 in aqueous solution is sensitive to temperature, the temperatures of both gaseous and aqueous feed were carefully controlled at 20°C.

Table 2
Variation of operating variables

OH^- concentration, C_{B0}	5, 16, 24, 32, 40, 48, 64, 100 mol/m ³
CO_2 gas flow rate, $Q_A \times 10^7$	4.17, 6.67, 8.33, 11.7, 15.0 m ³ /s
Rotating speed of inner cylinder, ω_i	26.2, 41.9, 62.8, 83.8, 104.7 rad/s
Ca(OH)_2 solution flow rate, $Q_B \times 10^6$	5.0 m ³ /s
Mean residence time, t_S	600 s

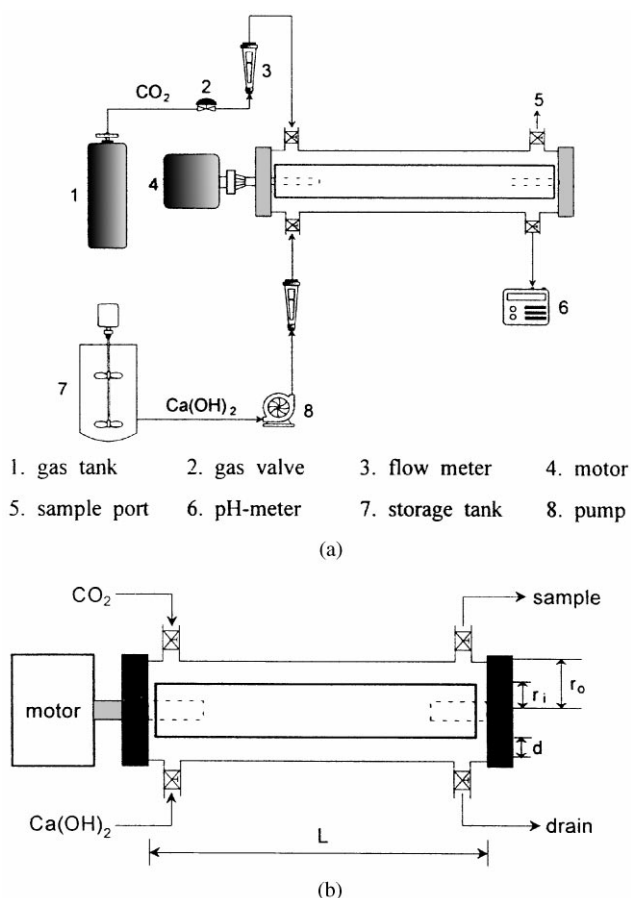
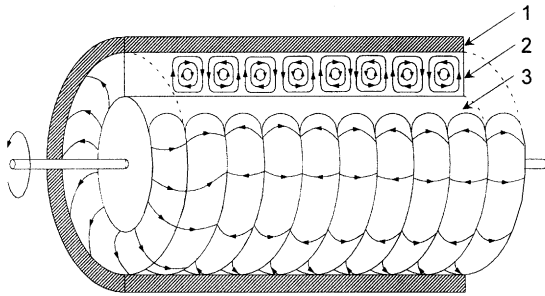


Fig. 3. Schematic diagram of experimental system for calcium carbonate reaction precipitation.

The Couette–Taylor reactor was composed of two coaxial cylinders, as shown Fig. 3(b). Its d/r_i -value was 0.56, which is consistent with that of correlation (15). The outer cylinder at rest was made of lucid acrylic plastic. The rotating inner cylinder was made of stainless steel and was polished with abrasive to prevent heterogeneous nucleation on the cylinder wall. The dimensions of the Couette–Taylor reactor are described in Table 3. In the range of the rotating speed greater than $\omega_i = 21$ rad/s a homogeneous suspension of particles and dispersion of gas in the reactor were achieved and turbulent Taylor vortex flow was exhibited, as shown in Fig. 4. After conducting an experiment, the reactor was washed with 10% HCl solution to get rid of calcium carbonate sticking on the reactor wall and then rinsed with distilled water. Samples of product suspension were taken at the end position of the reactor after waiting for 10 times the mean residence time to achieve the steady state. The steady state was continuously checked with a pH-meter (Orion, EA 940) at the end position of the reactor. At each sampling, the suspension was quickly diluted to quench the precipitation processes of nucleation and growth. Since these processes are dominantly determined

Table 3
Dimensions of present Couette–Taylor reactor

Radius of inner cylinder, r_i	3.1×10^{-2} m
Radius of outer cylinder, r_o	5.0×10^{-2} m
Gap size, d	1.9×10^{-2} m
Reactor length, L	7.0×10^{-1} m



- 1 : stationary outer cylinder
2 : Taylor vortices
3 : rotating inner cylinder

Fig. 4. Conceptual diagram of Taylor vortices in Couette–Taylor reactor.

by the concentration of calcium carbonate, i.e. supersaturation, the sample was diluted to decrease the supersaturation by adding about five times the sample volume. The relative supersaturation σ was calculated from the equation suggested by Nielsen and Toft (1984). Concentration of ionic species were computed from the experimental pH-value, total calcium concentration and total carbonate concentration by successive approximation, using the mass action equations, mass balance equations and the modified Debye–Hückel equation for the calculation of activity coefficients (Tai et al., 1993). The experimental pH-values ranged in 7–11. For simplicity the σ -value was calculated with pH = 8. Assuming that all of CO_2 feed was dissolved into the solution, the σ -value in the present experiments ranged in 3.0–8.6. Its maximum value was 17.4, based on the solubility of $\text{Ca}(\text{OH})_2$ in water (25 mol/m^3) and that of CO_2 (33.5 mol/m^3).

The particle size distribution was analyzed by two methods: light scattering method (Malvern, Masterizer/E) and micrographs reading using a scanning electron microscope (Jeol, JSM-820). The former method resulted in bimodality as is shown in Fig. 5. Ultrasonication produced smaller particles but their resulting size distributions were almost the same at $t_s = 25, 50, 150$ and 300 s. The residence time t_s represents each sample port located along the reactor length. It seems that the actual reaction time $t_R < 25$ s, which is consistent with Eq. (21). The sample before ultrasonication produced much larger

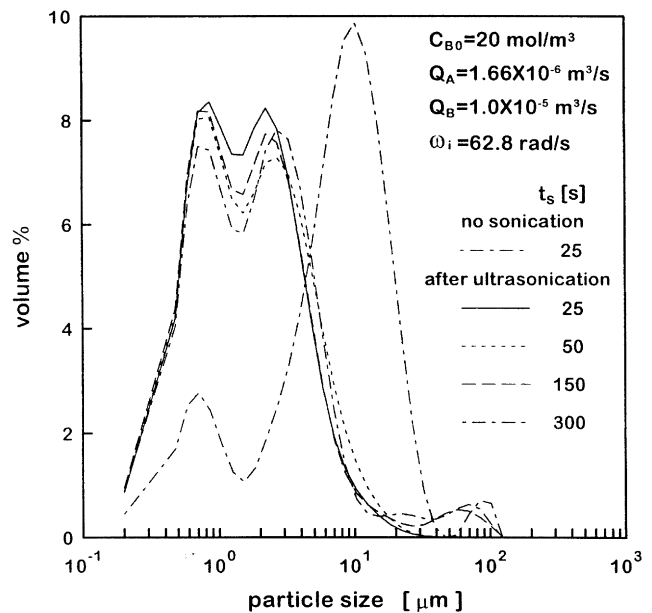


Fig. 5. Variation of particle size distributions along reactor length.

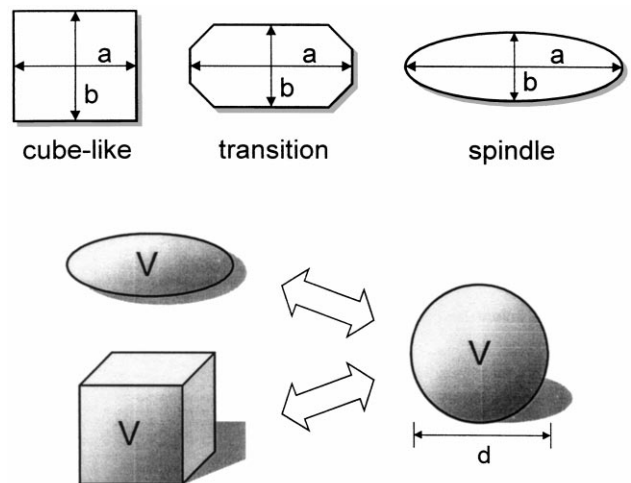


Fig. 6. Determination of shape factor K ($= a/b$) and particle size d for various shapes of particles.

particles due to aggregation with time. Therefore, the latter method using the microscope was used in analyzing the present experimental data under the operating conditions in Table 2. Each sample was completely dried and micrographs were taken. Then, about 200 particles justifiable as the whole were read directly from the micrographs taken. Their particle size distribution also showed the bimodal pattern but its mean particle size was much lower than that obtained from the former method.

Since morphology and size of calcium carbonate particles simultaneously varied with the operating conditions, a shape factor and a characteristic length for quantitative description of particle morphology and size, respectively, were introduced, as shown in Fig. 6. The

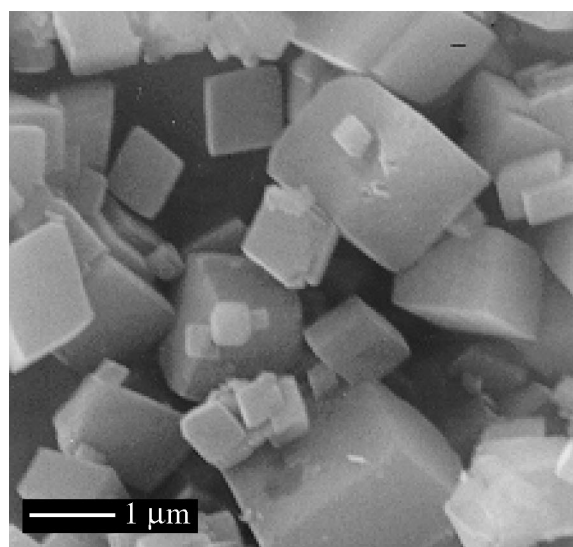
shape factor K was defined as the ratio of particle size in a major axis a to one in a minor axis b , as illustrated Fig. 6(a). Thus, the K -value would approach unity if the morphology of a particle is close to the cube-like shape and become a higher value as particle morphology is shifted to the spindle-like shape. The characteristic length d for particle size was defined here as a diameter of the sphere of which the volume V was equivalent to that of an actual particle, as shown in Fig. 6(b).

4. Results and discussion

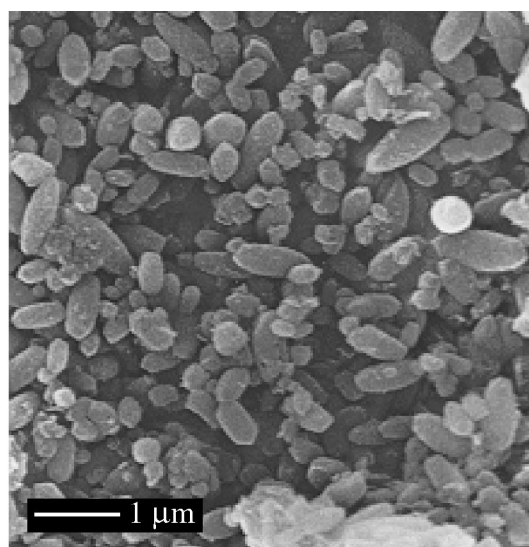
In reaction precipitation, the feed concentration, feed flow rate and mixing of solution are the important oper-

ating variables to control product properties. The particle formation and growth processes in the precipitation, which depend directly on the supersaturation of solution, vary with the feed concentration and flow rate. The reaction rate as well as the mass transfer rate in the particle growth is critically determined by the mixing of solution. In addition, a modification of particle morphology and variation of particle size can occur from an excess species in solution, which is caused by a non-stoichiometric reaction condition.

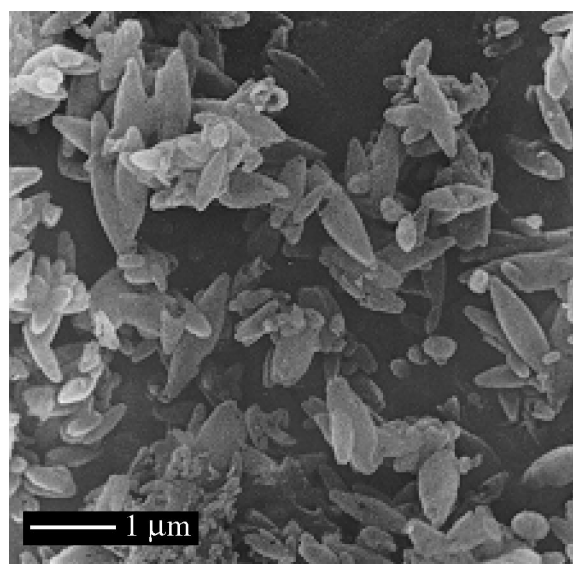
In the present CO_2 - $\text{Ca}(\text{OH})_2$ reaction precipitation of calcium carbonate in the Couette-Taylor reactor the effects of the concentration of feed solution (C_{B0}) and the CO_2 flow rate (Q_A) on particle morphology and size were investigated. When Q_A and Q_B were fixed as



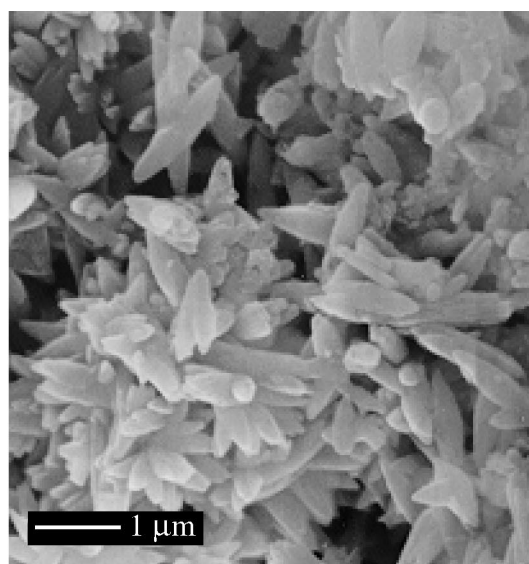
(a) 5 mol/m³



(b) 24 mol/m³



(c) 40 mol/m³



(d) 100 mol/m³

Fig. 7. Variation of calcium carbonate particle morphology with OH^- concentration C_{B0} at $Q_A = 8.33 \times 10^{-7} \text{ m}^3/\text{s}$ and $\omega_i = 62.8 \text{ rad/s}$.

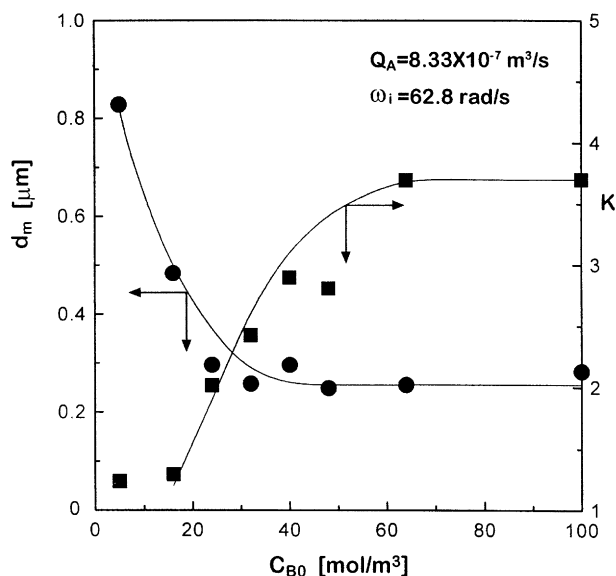


Fig. 8. Variation of mean particle size d_m and shape factor K with OH^- concentration C_{B0} at $Q_A = 8.33 \times 10^{-7} \text{ m}^3/\text{s}$ and $\omega_i = 62.8 \text{ rad/s}$.

8.33×10^{-7} and $5.0 \times 10^{-6} \text{ m}^3/\text{s}$, respectively, variations of particle morphology and size with C_{B0} were observed, as shown in Figs. 7 and 8. Fig. 7 shows that at low C_{B0} calcium carbonate particles are shaped like cubes and with increasing C_{B0} the morphology of particles changes to the spindle-like shape. Aggregates are seen but their presence during precipitation processes in the present reactor is not clear because the micrographs and Fig. 5 are not on-line real-time results. It is stressed that the present study focuses on the individual particle. Fig. 8 shows that mean particle size d_m decreases with increasing C_{B0} . It should be noted that even though particle morphology changed markedly with C_{B0} , the crystal system of all particles was confirmed as rhombic calcite by the XRD analysis (Lee, Jung, Kim & Choi, 1998a). This is supported by experimental observations of Tai and Chen (1998).

The variation of particle morphology and size with C_{B0} can be explained in terms of excess Ca^{2+} -ions in the solution. With dissolution of whole CO_2 gas into the solution, it is estimated that at the flow rates given above, the C_{B0} -value for the stoichiometric reaction of calcium carbonate is 14.8 mol/m^3 . In the actual precipitation system, however, the stoichiometric value of C_{B0} will be lower than the above value because of slow dissolution of CO_2 gas. Thus, within the range of C_{B0} given in Fig. 8, the excess of $\text{Ca}(\text{OH})_2$ in the reaction is expected to result in the excess Ca^{2+} -ions in solution. The excess Ca^{2+} -ion seems to be adsorbed on the preferred faces of the cube-like calcium carbonate particle. Then the adsorbed ion inhibits the face growth of a particle and brings modification of particle morphology into the spindle-like shape. Therefore, the shape factor K increases, as shown in Fig.

8, and mean particle size decreases until the equilibrium of the adsorption, which is expected to reach around $C_{B0} = 50 \text{ mol/m}^3$. Then, particle morphology and size become insensitive to C_{B0} . This scenario based on the present experimental results is consistent with the studies of Söhnel and Mullin (1982) and Nielsen and Toft (1984) that calcite precipitation is surface controlled.

In Figs. 9 and 10, the influence of the CO_2 gas flow rate Q_A on the morphology and size of calcium carbonate particles is exhibited. Under the assumption of dissolution of whole CO_2 gas into solution, the theoretical Q_A -value for the stoichiometric reaction with $C_{B0} = 24 \text{ mol/m}^3$ is about $13.3 \times 10^{-7} \text{ m}^3/\text{s}$. Due to limitation of CO_2 gas dissolution in the actual situation the higher Q_A -value than its theoretical one is definitely required. Therefore it can be considered that within the range of Q_A in Fig. 10, Ca^{2+} -ion is also an excess species and its concentration is reduced with increase in Q_A . Thus, with increasing Q_A the particle morphology changes from the spindle-like shape to the cube-like shape (Fig. 9) and the mean particle size increases (Fig. 10) because of concentration reduction of the excess ion and its adsorption on the particle surface. This variation of particle morphology and mean size with Q_A is coincident with that with C_{B0} .

Since the nucleation and growth process directly depend on the supersaturation in solution, the effect of variations of the supersaturation with C_{B0} and Q_A on the precipitation may be considered. According to the kinetic studies of calcium carbonate precipitation (Garside & Shah, 1980; Swinney, Stevens & Peters, 1982; Tai et al., 1993), a higher supersaturation produces smaller particles because the nucleation process is more sensitive to the supersaturation than the growth process. Since the estimated relative supersaturation σ is (a) 3.0, (b) 6.4, (c) 8.0 and (d) 8.4 in Fig. 7, the data in Fig. 8 support this viewpoint. But the estimated σ -value is (a) 4.3, (b) 5.7, (c) 7.6 and (d) 8.6 in Fig. 9, and under the conditions shown in Fig. 10, d_m increases with an increase in σ . This is contradictory to the above viewpoint. Therefore, the supersaturation seems to play the important role in nucleation or growth of particles, depending on the Q_A -value.

In the Couette–Taylor reactor, the hydrodynamic conditions depend on the rotating speed of the inner cylinder. Within the present experimental range of the rotating speed, the flow regime in the Couette–Taylor reactor belongs to turbulent Taylor vortex flow. The dissolution rate of CO_2 gas into solution will be enhanced by increasing the rotating speed using Eq. (18). Thus when the feed conditions were fixed as $Q_A = 8.33 \times 10^{-7} \text{ m}^3/\text{s}$, $Q_B = 5 \times 10^{-6} \text{ m}^3/\text{s}$ and $C_{B0} = 24 \text{ mol/m}^3$, the particle morphology and mean particle size varied with the wall shear stress $\tau_{\omega i}$, as shown in Figs. 11 and 12. Since the excess Ca^{2+} -ion concentration is expected to decrease with an increase in $\tau_{\omega i}$, the

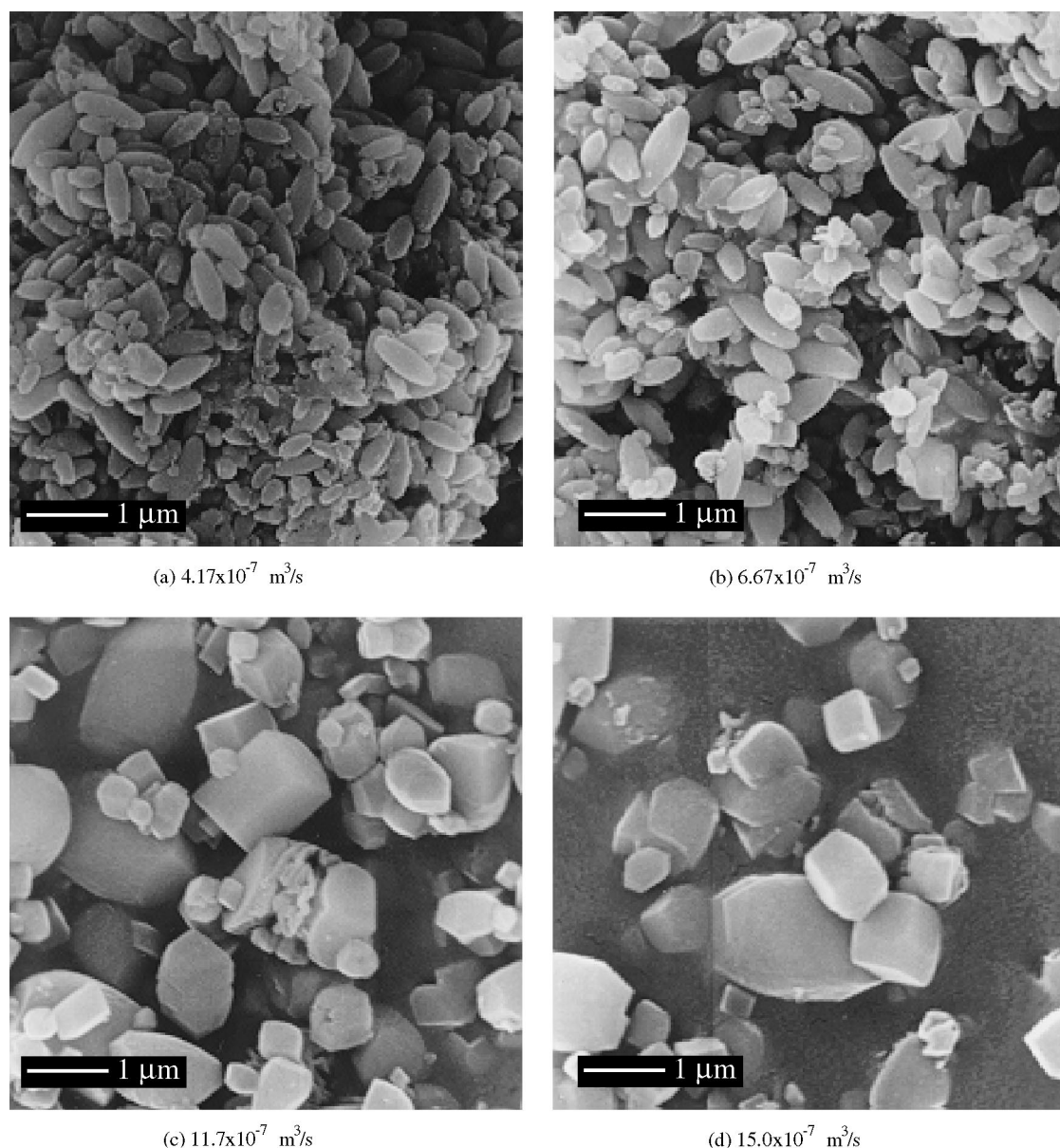


Fig. 9. Variation of calcium carbonate particle morphology with CO_2 gas flow rate Q_A at $C_{B0} = 24 \text{ mol/m}^3$ and $\omega_i = 62.8 \text{ rad/s}$.

particle morphology seems to approach the cube-like shape of $K = 1$, and therefore, mean particle size becomes larger.

When C_{B0} was lowered as 5 mol/m^3 , as shown in Fig. 13, mean particle size showed the maximum with the minimum K -value around $\tau_{oi} = 4 \text{ Pa}$. These experimental results imply that the dissolution of CO_2 gas into solution is enhanced with an increase in τ_{oi} and the stoichiometric reaction condition is almost achieved by producing the most cube-like shape around $\tau_{oi} = 4 \text{ Pa}$. For $\tau_{oi} > 4 \text{ Pa}$, CO_2 becomes oversupplied into the local solution at the early stage of reaction and remains as an excess species. Then similar to the influence of excess Ca^{2+} -ion on the precipitation (Figs. 8 and 10), excess

CO_2 results in modification of particle morphology and reduction of the particle size. The excess CO_2 dissolved can simply be expected from the fact that with dissolution of whole CO_2 gas a theoretical Q_A -value for the stoichiometric reaction with $C_{B0} = 5 \text{ mol/m}^3$ is estimated as $2.67 \times 10^{-7} \text{ m}^3/\text{s}$. In the present system, Q_A of $8.33 \times 10^{-7} \text{ m}^3/\text{s}$ may be enough to satisfy the stoichiometric reaction with the given C_{B0} at $\tau_{oi} = 4 \text{ Pa}$. The corresponding maximum size $d_{\max}$ of $0.87 \mu\text{m}$ at $\tau_{oi} = 4 \text{ Pa}$ is the largest mean particle size in the entire range of the present experiments.

The hydrodynamic conditions affect the particle growth. According to Kim and Tarbell (1996), the micromixing is important in determining the nucleation in

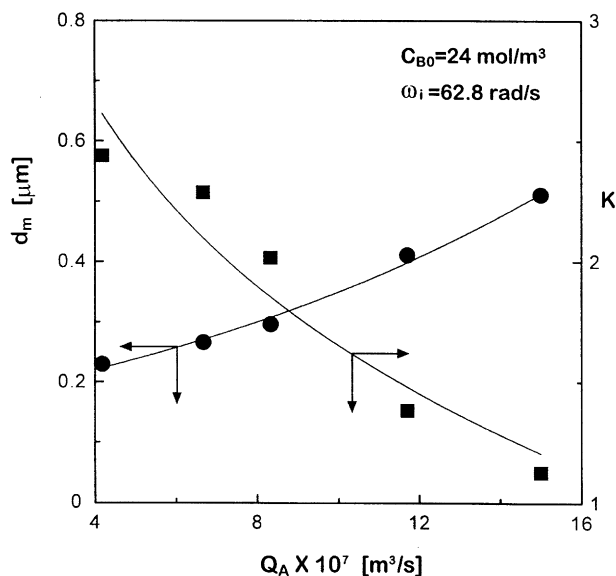


Fig. 10. Variation of mean particle size d_m and shape factor K with CO_2 gas flow rate Q_A at $C_{B0} = 24 \text{ mol/m}^3$ and $\omega_i = 62.8 \text{ rad/s}$.

the premixing region while in the homogeneous mixing region the precipitation is dominantly controlled by the mass transfer process around the particles. Then with increasing the intensity of turbulent flow the convective mass transfer resistance around particles is reduced and the particle growth is promoted. From the variation of mean particle size with τ_{oi} at $C_{B0} = 24 \text{ mol/m}^3$ (Fig. 12), the increase of mean particle size with τ_{oi} results from the enhanced mass transfer rate in particle growth process as well as from reduction of the excess Ca^{2+} -ion concentration. At $C_{B0} = 5 \text{ mol/m}^3$ (Fig. 13), however, mean particle size is reduced with increasing τ_{oi} beyond 4 Pa, even though the mass transfer around a particle is expected to be facilitated by turbulent vortices. These experimental results in addition to those in Figs. 8 and 10 indicate that the particle growth is inhibited by the effect of the excess species rather than the mass transport affected by the hydrodynamic conditions.

Fig. 14 shows the distribution of mean particle size normalized by $d_{\max} = 0.87 \mu\text{m}$ with the relative enhancement factor Er defined by Eq. (18). In the present experiments the maximum of mean particle size appears around $Er = 1$ at which the stoichiometric reaction condition might be accomplished. Therefore, for $Er < 1$ the excess dissolution of CO_2 gas into the solution is expected while $Er > 1$ the excess Ca^{2+} -ion exists possibly. As Er is far from unity, which means the increase of excess species concentration, mean particle size seems to be reduced.

The relationship of the shape factor K with the operating variables of the Couette–Taylor reactor is also described by Er , as displayed in Fig. 15. The shape factor K indicates that particle morphology is the cube-like

shape (see Fig. 6) for $Er < 4$ and then it seems to be shifted to the transient shape until the Er -value reaches 8. For $Er > 8$, particle morphology belongs to the spindle-like shape. In the distribution of the shape factor K , it is supposed that its minimum value occurs around $Er = 1$ due to the stoichiometric reaction. This is consistent with the dependency of mean particle size d_m on Er . It is interesting that in the region of cube-like shape, even though the shape factor is almost independent of Er (Fig. 15), mean particle size varies sensitively with Er (Fig. 14). However, in the range of transient and spindle-like shape, these trends of the shape factor and mean particle size with Er are reverse. These experimental results imply the complicated influence of the excess species on particle morphology and growth.

In general, when the growth rate of each particle face is differently influenced by ionic admixture due to its selective adsorption, particle morphology is dominantly determined by faces having low growth rates (Nielsen, 1964; Sarig, 1994). For the present experimental results, thus, the selective adsorption of excess species on calcium carbonate particle faces may be considered as a plausible reason. At a low excess species concentration, each face of a particle is little different in the adsorption selectivity of excess species and undergoes a similar magnitude of growth inhibition by the adsorbed excess species. Then, particles show well-formed cube-like shape even though mean particle size is significantly reduced. As the excess species concentration in solution increases, an inclined face appears in the transient particle shape due to the selectivity in adsorption. At a high excess species concentration, the inclined faces become dominant and particle morphology is modified to spindle-like shape. As the adsorption of excess species is close to equilibrium, the particle morphology and size become insensitive to excess species concentration.

The excess species concentration C_{ex} in solution at various operating conditions can be estimated from Eq. (21). If $C_{\text{ex}} > 0$, C_{ex} indicates the excess Ca^{2+} -ion concentration in the solution. Otherwise, C_{ex} implies the excess CO_2 concentration. In this calculation, however, k_{La} and t_R are unknown variables and can be replaced by known k_{La}^0 and t_S , respectively. From the premise that the stoichiometric reaction, i.e., $C_{\text{ex}} = 0$ would be expected at the condition where $d_{\max}$ appears, $k_{La}t_R$ at $C_{\text{ex}} = 0$ can be estimated from Eq. (21). In the present experiments it is found that $k_{La}t_R \cong 0.056k_{La}^0t_S$, which was used in Eq. (21). This relation looks reasonable since $k_{La} \geq k_{La}^0$ and $t_R = O(10 \text{ s}) \leq t_S = (600 \text{ s})$ due to the fast reaction, and it seems that most of nucleation occurs in the front region of the reactor and the remaining region contributes mainly to the growth of particles. If this relation is used in calculating the relative supersaturation σ , its value ranges in 14–37. With this relation the estimated σ -value is (a) 2.9, (b) 3.7, (c) 4.7 and (d) 5.3 in Fig. 9. It is mentioned that its exact value is not easily obtained but almost the same

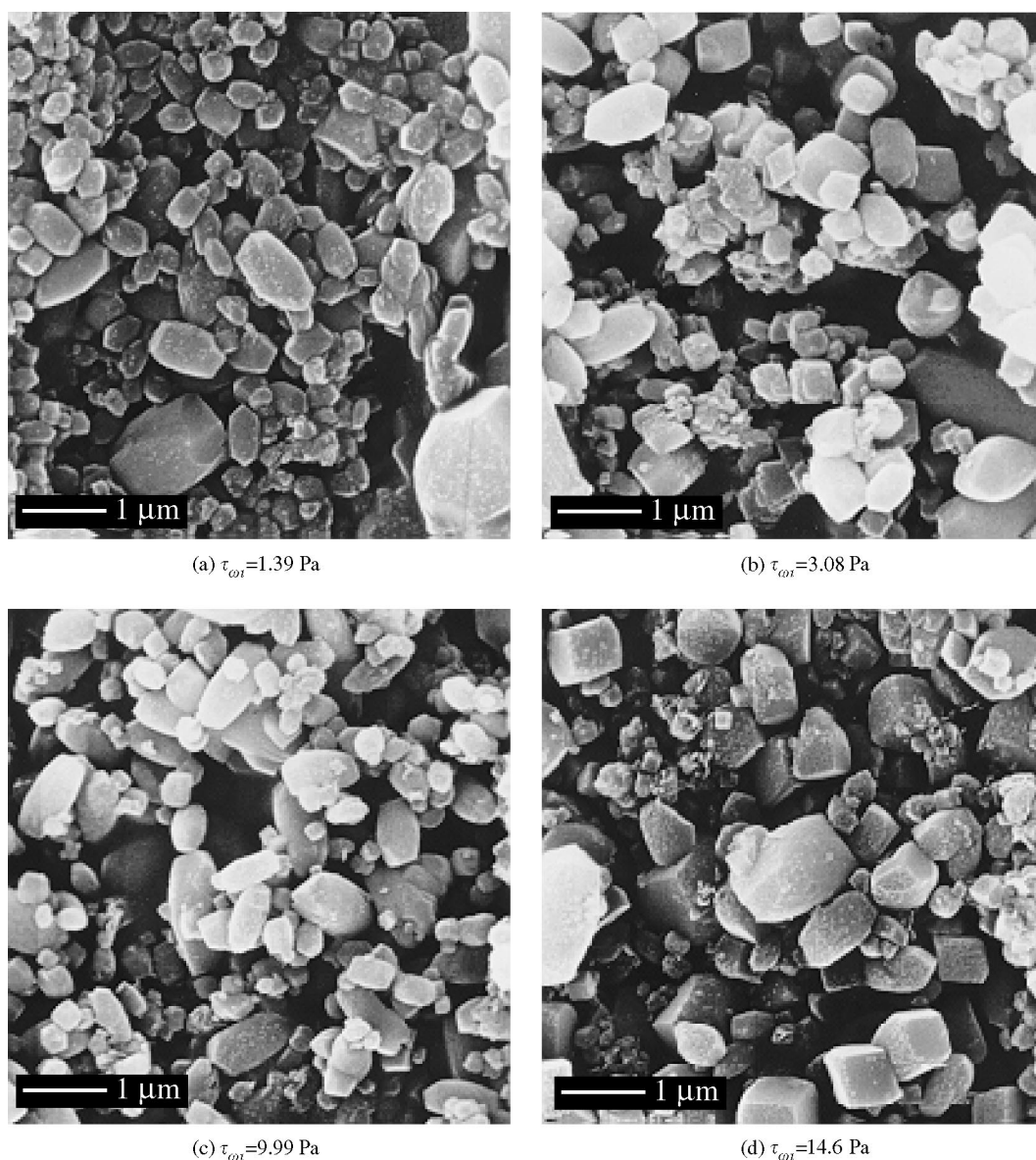


Fig. 11. Variation of calcium carbonate particle morphology with wall shear stress τ_{oi} at $C_{B0} = 24 \text{ mol/m}^3$ and $Q_A = 8.33 \times 10^{-7} \text{ m}^3/\text{s}$.

trend of supersaturation is seen from the present two assumptions: dissolution of whole CO_2 gas into the solution during t_s and its partial dissolution during t_R . By assuming $d_0 = 0.87 \mu\text{m}$ and $d_{eq} = 0.22 \mu\text{m}$ (see Fig. 14) the estimated C_{ex} profile is plotted as the solid line in Fig. 16. This represents that at a low C_{ex} the particle size is very sensitive to the adsorption of excess species. As the adsorption approaches the equilibrium with an increase of C_{ex} , the particle size becomes independent of C_{ex} . Comparison of the model prediction with the experimental data showed good agreement within 12.8% in relative errors.

In the present experiments the effect of operating conditions on CaCO_3 precipitation was explained to a certain degree in terms of the selective adsorption of excess

species. This was possible that in the Couette–Taylor reactor the product nucleation and its subsequent particle growth occur along the reactor length under the fixed wall shear stress, similar to the well-known CSTRs. This reactor excludes the effect of the impeller in a usual reactor and the wall shear stress is easily controllable. Therefore, it will be very useful in investigating the mechanism of processes involving slow reaction and aggregation.

5. Conclusions

The morphology and size of calcium carbonate particles produced by CO_2 – $\text{Ca}(\text{OH})_2$ reaction precipitation

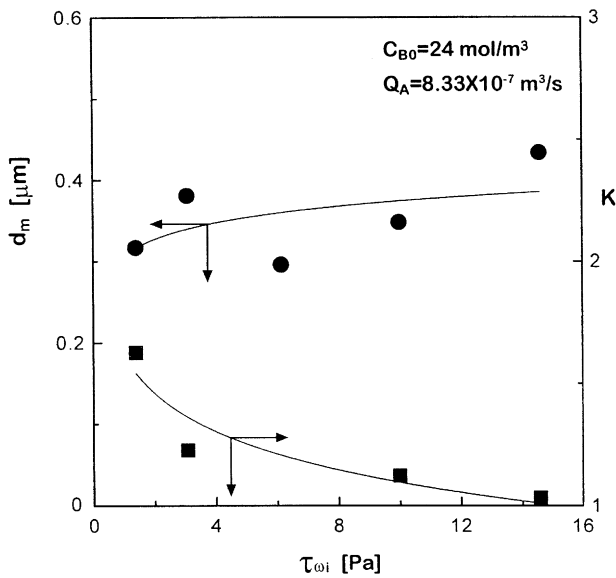


Fig. 12. Variation of mean particle size d_m and shape factor K with wall shear stress τ_{wi} at $C_{B0} = 24 \text{ mol/m}^3$ and $Q_A = 8.33 \times 10^{-7} \text{ m}^3/\text{s}$.

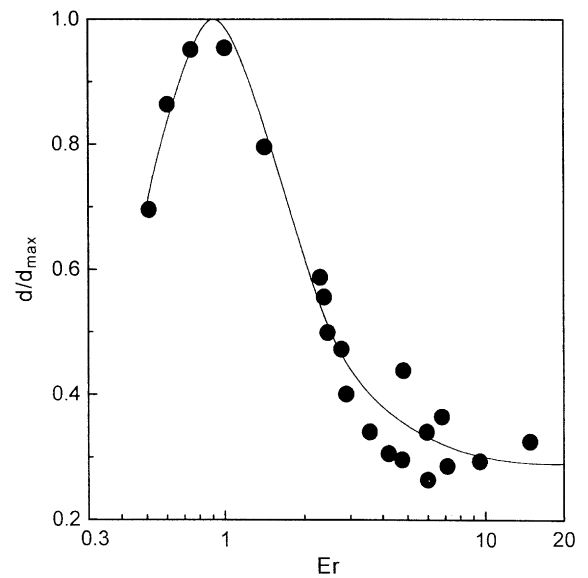


Fig. 14. Distribution of normalized mean particle size $d/d_{\max}$ by $d_{\max} = 0.87 \mu\text{m}$ with relative enhancement factor Er .

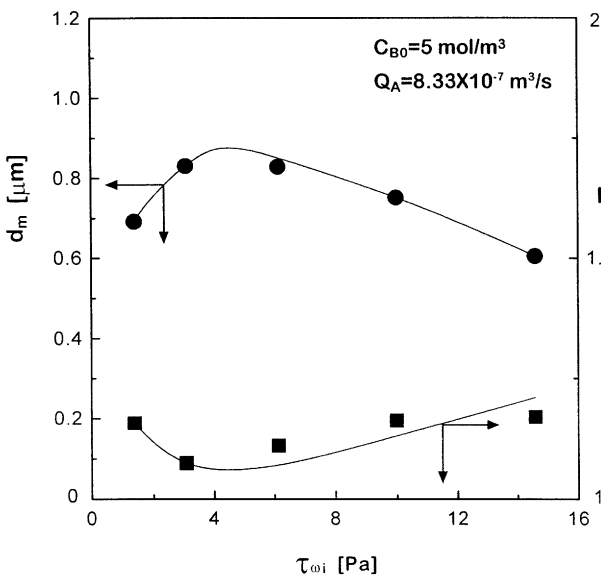


Fig. 13. Variation of mean particle size d_m and shape factor K with wall shear stress τ_{wi} at $C_{B0} = 5 \text{ mol/m}^3$ and $Q_A = 8.33 \times 10^{-7} \text{ m}^3/\text{s}$.

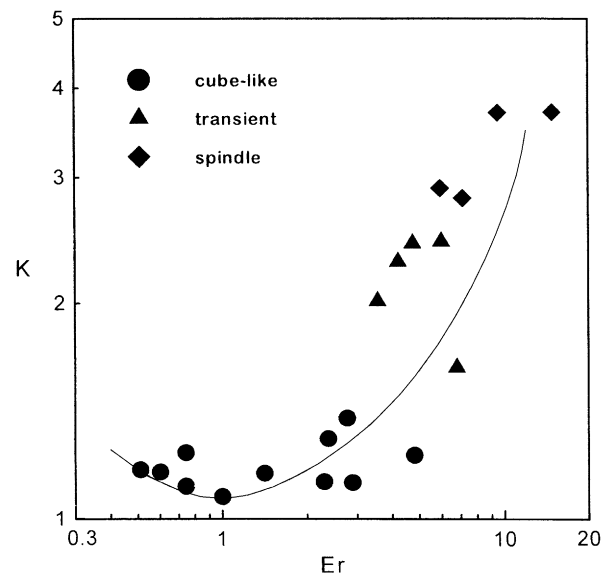


Fig. 15. Distribution of shape factor K with relative enhancement factor Er .

in the Couette–Taylor reactor varied significantly with operating variables of the $\text{Ca}(\text{OH})_2$ feed concentration, CO_2 gas flow rate and wall shear stress. It was found that particle morphology and size are influenced mainly by excess species. It seems that the modification of particle morphology is induced by the different growth rates of particle faces due to the different adsorption of excess species and the particle growth rate was retarded by excess species. The probable explanation is that the growth site is blocked and the surface integration step is mainly inhibited by the adsorbed excess species. It is

interesting that, as the excess species concentration increases, particle morphology is modified from the cube-like to the spindle-like shape and mean particle size decreases. As the adsorption approaches the equilibrium, particle morphology and mean size become almost independent of the excess species concentration.

The influence of operating variables on particle morphology (shape factor) and mean particle size was described by the relative enhancement factor rather than supersaturation. Mean particle size seems to be maximum by showing the most cube-like shape at the relative

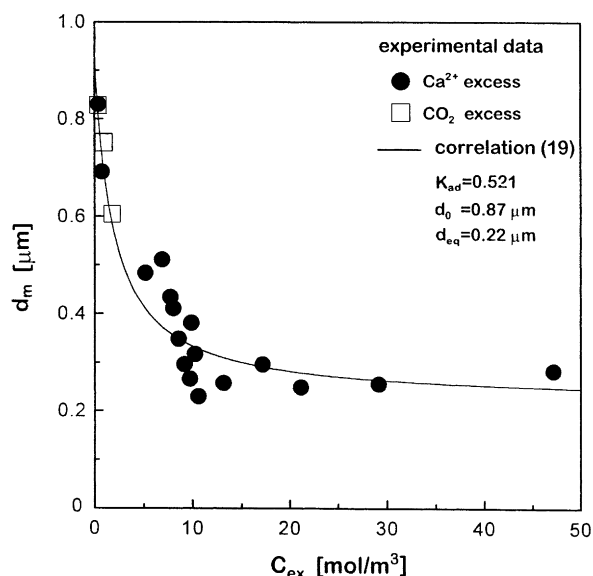


Fig. 16. Comparison of mean particle size d_m with concentration of excess species C_{ex} estimated from Eq. (20).

enhancement factor $Er = 1$, where the stoichiometric reaction condition was expected to be achieved. As the Er -value was far away from unity, the shape factor K increased and mean particle size decreased due to the excess species. Changes of the shape factor and mean size of particles with the operating variables were well illustrated by Er .

The influence of excess species on particle size was predicted by the model equation based on the monolayer adsorption. The excess species concentration was calculated from the operating variables. According to the prediction of size of particles grown in the excess species solution, it was suggested that the adsorption of excess species on the particle surface obeys the Blaznakov isotherm and the decrease of particle size is due to the coverage of growth sites by the adsorbed excess species. The resulting correlation of particle size represented the experimental data well. It was also shown that the basic concept for the model equation was consistent with the present hypothesis to explain the CaCO_3 precipitation.

Acknowledgements

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