Modelling particle growth of calcium carbonate in a pilot-scale pellet fluidized bed reactor

Rui-zhu Hu, Ting-lin Huang, Gang Wen and Shang-ye Yang

ABSTRACT

Pellet fluidized bed reactors have been widely used to soften water. Reports from laboratory-scale research on the particle growth kinetics of calcium carbonate in pellet reactors have been put forward. However, the reports have not been comprehensive as they only consider the influence of supersaturation on the calcium carbonate growth process. The influence of three factors, namely, the superficial velocity (SV), particle size (L₀), and supersaturation (S) on the particle growth rate of calcium carbonate were investigated in a pilot-scale study, and two models of particle growth rate and fixed bed height growth rate were built. The linear particle growth model

\[ G = 3.90 \times 10^{-9} SV^{1.93} L_0^{1.54} S^{1.13} \]

at the bottom of the pellet reactor was built based on a pilot-scale study of particle growth kinetics influenced by SV, L₀, and S. The growth of the fixed bed height is closely related to the particle growth and also influenced by the three factors. The fixed bed growth model

\[ R_h = 5.19 \times 10^{-8} SV^{1.65} L_0^{-0.93} S^{2.58} \]

also incorporates SV, L₀, and S, and provides a method for calculating the fixed bed height. The two models were built based on the pilot-scale experiment and were different from those previously reported. They are applicable as pellet discharge guides and are used in the management of pellet reactors.

Key words | calcium carbonate crystallization, fixed bed height, growth kinetics, linear growth rate, pellet fluidized bed

NOTATION

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>surface area, ( m^2 )</td>
</tr>
<tr>
<td>c</td>
<td>solute concentration, ( mg/L )</td>
</tr>
<tr>
<td>cᵢ</td>
<td>solute concentration in the solution at the crystal–solution interface, ( mg/L )</td>
</tr>
<tr>
<td>c*</td>
<td>equilibrium saturation concentration, ( mg/L )</td>
</tr>
<tr>
<td>[Ca²⁺]</td>
<td>concentration of ( Ca^{2+} ) in water, ( mol/L )</td>
</tr>
<tr>
<td>[CO₃²⁻]</td>
<td>concentration of ( CO₃^{2-} ) in water, ( mol/L )</td>
</tr>
<tr>
<td>( d_p )</td>
<td>average diameter of the particles, ( mm )</td>
</tr>
<tr>
<td>( d_{pi} )</td>
<td>the average diameter of particles trapped in the ( i ) sieve net layer, ( mm )</td>
</tr>
<tr>
<td>( G_u )</td>
<td>mass growth rate, ( kg/s )</td>
</tr>
<tr>
<td>( G )</td>
<td>linear particle growth rate, ( m/s )</td>
</tr>
<tr>
<td>( k_d )</td>
<td>mass transfer coefficient, ( m/s )</td>
</tr>
<tr>
<td>( k_r )</td>
<td>surface reaction coefficient, ( m/s )</td>
</tr>
<tr>
<td>( K_g )</td>
<td>coefficient of linear growth rate</td>
</tr>
<tr>
<td>( K_{sp} )</td>
<td>solubility product of calcium carbonate</td>
</tr>
<tr>
<td>( L )</td>
<td>particle size, ( mm )</td>
</tr>
<tr>
<td>( L_0 )</td>
<td>pellet size of seed, ( mm )</td>
</tr>
<tr>
<td>( m )</td>
<td>the mass of solid deposited, ( kg )</td>
</tr>
<tr>
<td>( R_b )</td>
<td>fixed bed height growth rate, ( cm/d )</td>
</tr>
<tr>
<td>( S )</td>
<td>supersaturation, ( kg solute/kg water )</td>
</tr>
<tr>
<td>( SV )</td>
<td>superficial velocity, ( m/h )</td>
</tr>
<tr>
<td>( t )</td>
<td>time, ( h )</td>
</tr>
<tr>
<td>( x_i )</td>
<td>the mass fraction of particles trapped in the ( i ) sieve net layer, ( % )</td>
</tr>
</tbody>
</table>

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doi: 10.2166/ws.2016.158
INTRODUCTION

Crystallization in a pellet fluidized bed reactor is used as a water and wastewater treatment method. Pellet reactors have been developed for water softening (Graveland et al. 1983; Veen & Graveland 1988), phosphate removal (Battistoni et al. 2003), and fluoride removal (Aldaco et al. 2007a, 2007b) from drinking water and for heavy metal recovery from wastewater (Lee et al. 2004). Pellet reactors have been used to soften water since the 1980s (Chen et al. 2000). Compared to traditional methods of water softening, pellet reactors do not produce waste; on the contrary, they produce recyclable raw materials that are used in industries and agricultural processes (Schetters et al. 2015).

The particles must be maintained at an optimum size range. The crystallization rate decreases if the particles grow too big, and consequently, the water quality of the outlet is degraded resulting in an increase in water treatment costs. Particle discharge times increase and seed consumption increases if the discharged particles are smaller in size; correspondingly, the water treatment cost also increases (Schagen et al. 2008). Therefore, mastering the kinetics in pellet reactors and monitoring the state of particles in them would not only improve outlet water quality but also reduce water treatment costs. The ratio of calcium carbonate to pellets discharged in a reactor is about 98% (Chen et al. 2000); the study of particle growth kinetics is linked to the study of calcium carbonate growth kinetics. Many scholars have studied calcium carbonate growth kinetics in different systems. Tai et al. (1999, 2006) and Tai & Hsu (2001) studied the growth kinetics of calcite crystals in a batch fluidized bed using a pH-stat apparatus and obtained the growth rate expression of calcite crystals based on the two-step growth model by exploring the influence factors of superficial velocity, supersaturation, particle size of the seed, ionic strength, and pH. However, the values of mass transfer coefficient $K_d$ and surface reaction coefficient $K_r$ needed to be determined experimentally using a laboratory-scale fluidized bed (Tai et al. 1999; Tai & Hsu 2001; Tai et al. 2006). Zhu et al. (2015) studied crystal growth kinetics in a multistage mixed suspension mixed product removal crystallizer in a highly alkaline, supersaturated system and proposed a growth kinetic correlation between growth rate and supersaturation, where only the influence of supersaturation on the calcium carbonate growth process (Zhu et al. 2015) was considered. Razmi et al. (2014) studied the calcium carbonate growth kinetics in a cooling crystallizer unit; they also considered only the influence of supersaturation on the calcium carbonate growth process (Razmi et al. 2014). Schagen et al. (2008) did not study the crystallization process, but they simulated the change process of particle size and bed height using a nonlinear control method. This calculation process was complicated and incapable of predicting particle growth processes in practical engineering (Schagen et al. 2008; Van Schagen et al. 2008).

In summary, past research on particle growth kinetics possessed two problems, as follows. (1) The research content was incomprehensive. The crystal growth process is influenced by factors such as $S$, $L_0$, and $S$ (Bravi & Mazzarotta 1998; Aldaco et al. 2007a, 2007b; Jiang et al. 2014); however, the research only considered the influence of supersaturation on the calcium carbonate growth process. (2) The models were built under laboratory-scale conditions and the model parameters were determined by a relatively stable fluidized bed, which is difficult to measure in practical engineering. The particle growth rate models lacked guidance value because of the above-mentioned problems and needed to be rebuilt on a pilot scale.

Expanded bed height is an important design index in pellet reactor design (Veen & Graveland 1988). It is influenced by fixed bed height and particle size. Traditional calculation methods of fixed bed height require porosity and pre- and post-expansion particle size values, which are difficult to measure in practical engineering (Rietveld 2003), or require reactor models that simulate and calculate change process of bed height to be built (Schagen et al. 2008). The traditional method is complicated and has universal applicability. Practically, fixed bed height growth is attributed to particle size growth and is also influenced by $S$, $L_0$, and $S$; it can be predicted by building a fixed bed height growth rate model using the three factors.

In this study, we explore the influence of $S$, $L_0$ and $S$ on the particle growth of calcium carbonate in a pilot-scale experiment. We also build a particle growth rate model and a fixed bed height growth rate model using the three factors, which provides an easy and universally relevant particle size and fixed bed height calculation method. The two models are useful in practical engineering, where they are used to guide particle discharge and design and operate pellet reactors.
THEORETICAL BACKGROUNDS

Two-step growth model

The two-step growth model is a common mechanism used to explain the calcium carbonate crystallization process (Tai 1999; Aldaco et al. 2007a, 2007b; Jiang et al. 2014). The model divides the calcium carbonate crystallization process into a diffusion process and a first-order surface reaction. The former considers that the mass transport of solute molecules occurs by diffusion and convection from the bulk of the fluid phase to the solid surface (Aldaco et al. 2007a, 2007b). The latter considers that the solute molecules begin to grow on the surface of the seed and arrange themselves to form a regular crystal lattice structure. The two processes are illustrated in Figure 1.

These two stages can be described by the equations:

\[ G_w = \frac{dm}{dt} = k_d A (c - c_i) \] (mass transport) (1)

\[ = k_r A (c - c^*)^{\gamma} \] (surface reaction) (2)

The growth rate of the crystal can be expressed as a linear growth rate, as described by the equations:

\[ G = \frac{dL}{dt} \] (3)

As shown in Equations (1)–(3), particle growth process is influenced by supersaturation, superficial velocity, and particle size of the seed. Previous studies (Bravi & Mazzarotta 1998) have put forward an empirical model, which takes into account the three factors as shown in Equation (4). Previous studies (Aldaco et al. 2007a, 2007b; Jiang et al. 2014) created a calcium fluoride growth linear model using Equation (4). Therefore, calcium carbonate particle growth kinetics and fixed bed height growth rate can both be expressed as the equation below.

\[ G = K_g \cdot L^{m_v} \cdot SV^n \cdot S^j \] (4)

Description of the process of crystallization of calcium carbonate

Crystallization and precipitation occur when a solution gets supersaturated, and the solute precipitates in solid form from the solution. Crystallization first needs nucleation that divides the products into homogeneous nucleation and heterogeneous nucleation (Tai et al. 2009; Hanhoun et al. 2013). The former are the reaction products of nucleation in the homogeneous phase, while the latter are the reaction products of nucleation on the surface of particle impurities or solids in the solution. The solution prioritizes heterogeneous nucleation at low supersaturation levels (Garea et al. 2009). Conversely, homogeneous nucleation is predominant when the homogeneous nucleation rate increases. The pellet reactor prioritizes heterogeneous nucleation (Neira-Carrillo et al. 2012).

Figure 2 shows the process of heterogeneous nucleation where the superficial velocity is 70 m/h, supersaturation is 125.5, and the particle sizes of the seeds are 0.1 mm–0.25 mm. Garnets of variable sizes and uneven surfaces, are put into the pellet reactor to act as nucleation sites for crystal growth. Calcium carbonate molecules adhere to the garnet’s surface by diffusion, then expand and aggregate (Figure 2(c)). The adsorption and aggregation between seeds and fine crystals are the main mechanisms of calcium carbonate growth. In the early crystallization stages, the surface of the pellet is rougher, but becomes dense and smooth after constant adsorption and aggregation. The shape of the pellets approaches a sphere as it matures, and the crystallization rate decreases. The mature pellets are discharged from the bottom of the pellet reactor. New seeds are added to the reactor and the process is repeated.
The mass formation of fine crystals is unavoidable at high supersaturations due to discrete precipitation and homogeneous nucleation. The shapes of fine crystals are hexahedral and their quantities increase as supersaturation levels increase. At low supersaturation, pellet reactors prioritize heterogeneous nucleation; the crystals here are small and most of them attach to the particle’s surface (Hanhoun et al. 2015).

MATERIALS AND METHODS

Pilot-scale system

The pellet reactor (shown in Figure 3) used in the pilot-scale experiment was 4.0 metres high with an effective reaction height of 3.7 metres, an inner diameter of 90 cm, and was filled with garnets. Hard water was pumped up into the pellet reactor from the water storage tank. Valves and a flow meter that were used to adjust the superficial velocity were installed in the water inlet. A softening agent was added to the reactor and mixed with inlet water through a dosing pump installed at the bottom of the reactor. The garnets were added to the pellet reactor by a seed dosing pipe and the mature particles were discharged through a particle discharge pipe.
Materials

The hard water used in the pilot-scale experiment was groundwater from Guodu County, Xi’an City, Shaanxi Province, China. The total hardness ranged between 260 and 465 mg/L, the concentration of Ca$^{2+}$ and carbonate alkalinity range were about 75–150 mg/L and 280 mg/L, respectively. Garnets were used as seeds in the pellet reactor, and their sizes ranged from 0.1 mm to 0.4 mm and they had densities of 3.93 g/cm$^3$. Sodium hydroxide (NaOH) of mass concentration 30% was adopted as a softening agent.

Pilot-scale experiment process description

In the pilot-scale experiment, variable control methods were used to study the effect of $SV$, $L_0$, and $S$ on linear particle growth rate. Superficial velocity was controlled at 50 m/h–70 m/h. The particle sizes of the seeds were controlled at 0.1 mm–0.4 mm and the supersaturation levels were controlled at 84–125 at 14–15°C. Table 1 shows the pilot-scale experimental conditions.

The supersaturation was calculated using Equation (5) (Tai et al. 1999; Aldaco et al. 2007a, 2007b; Jiang et al. 2014):

$$S = \left( \frac{[Ca^{2+}] [CO_3^{2-}]}{K_{sp}} \right)^{1/2} - 1$$

In every pilot-scale experiment, the particles were taken out from the bottom of the pellet reactor at a certain time in the experiment. The diameters of the particles at different times were calculated using the following equation Equation (6), which was then fitted to get the linear particle growth rate $G$ under every experimental condition. Finally, all the linear particle growth rates $G$ were fitted to Equation (4).

$$d_p = \frac{1}{\sum (x_i/d_{pi})}$$\

Analytical methods

The calcium concentration of inlet water and outlet water was determined by EDTA titration (Jiang et al. 2019). After drying, the particles were observed under a microscope (Nikon 50i). The diameters of the particles were determined by the ASTM sieving method (Tai et al. 1999). The fixed bed height after expansion was measured using a metre ruler.

RESULTS AND DISCUSSION

Figures (4)–(6) show the particle size at the bottom of the pellet reactor and fixed bed height as a function of time when $SV$, $L_0$, and $S$ change according to Table 1.

Influence of supersaturation

Figure 4 shows the influence of supersaturation on the linear particle growth rate (Figure 4(a)) of calcium carbonate and a fixed bed height growth rate (Figure 4(b)) in the pellet reactor. It can be seen from the figure that $G$ and $R_b$ increase from $1.96 \times 10^{-10}$ m/s to $3.66 \times 10^{-9}$ m/s and 20.74 cm/d to 52.58 cm/d, respectively. The supersaturation levels increase from 84.4 to 125.5. As seen in Figure 4, the particle sizes of the seeds and fixed bed height both increase linearly as supersaturation increases. Moreover, the growth rate of calcium carbonate follows first-order kinetics regarding the supersaturation, as supersaturation is a driving force for calcium carbonate crystallization. From the two-step growth model of crystallization, we observe that increasing supersaturation leads to the increase of mass transfer (Equation (1)) and surface reaction (Equation (2)), therefore, the linear growth rate and fixed bed height growth rate increase. The influence of supersaturation on the linear growth rate is in agreement with that proposed by several studies on other
crystallization processes, including a previous study on calcium phosphate crystallization (Neira-Carrillo et al. 2012) and a few others on calcium fluoride crystallization (Aldaco et al. 2007a, 2007b; Jiang et al. 2014).

Influence of superficial velocity

For a given particle size of a seed and supersaturation level, the linear growth rate (Figure 5(a)) and fixed bed height (Figure 5(b)) increase with the superficial velocity. It can be seen from the figure that $G$ and $R_h$ vary from about $8.58 \times 10^{-10}$ m/s to $2.14 \times 10^{-9}$ m/s and 12.46 cm/d to 26.11 cm/d, respectively, as the superficial velocity increases from 50 m/h to 70 m/h. The following aspects are probable reasons why $G$ is proportional to superficial velocity. (1) The increase of superficial velocity increases the diffusion ability of calcium carbonate. Molecular strength increases and mass transfer rates accelerate resulting in the enhancement of the rate of adsorption and aggregation between calcium carbonate crystals and seeds. (2) As the superficial velocity increases, the expansion ratio and porosity of the expanded bed increase, and the corresponding number of seeds available per reactor volume decreases. Under this condition, a single seed can provide surface area for more calcium carbonate molecules, thereby increasing the growth rate. A previous study (Aldaco et al. 2007a, 2007b) on calcium fluoride crystallization confirms this theory.

Influence of particle size of the seeds

Figure 6 depicts the effects of the particle size of the seeds on linear particle growth rates (Figure 6(a)) and fixed bed
growth rate (Figure 6(b)) at a superficial velocity of 60 m/h and a supersaturation of 84.4. It can be seen from the figure that $G$ and $R_h$ rise from $1.08 \times 10^{-10}$ m/s to $1.96 \times 10^{-9}$ m/s and 14.81 cm/d to 20.74 cm/d, respectively, when the particle size of the seed increases from 0.1 mm to 0.4 mm. From the figures, $G$ and $R_h$ have a higher growth rate at a smaller particle size of seeds. It is apparent that smaller particle sizes have bigger specific surface areas that result in the increase in the growth rate of the particles.

**Model establishment**

**Linear particle growth rate model at the bottom of a reactor**

According to the empirical model adopted by previous studies (Bravi & Mazzarotta 1998; Aldaco et al. 2007a, 2007b; Jiang et al. 2014) (Equation (4)), the growth rate data given in Table 2 had been fitted to Equation (4) to calculate the coefficient of linear growth rate $K_g$ using Matlab software R2013b; the growth rate orders $m$, $n$, and $j$ referred to the particle size, the superficial velocity, and supersaturation, respectively. The linear particle growth rate model at the bottom of a pellet reactor can be expressed as the following equation.

$$G = 3.90 \times 10^{-9} SV^{1.93} L_0^{1.56} S^{2.13} \quad (7)$$

As Equation (7) shows, the index of supersaturation in the linear particle growth model is about 2, which is in agreement with previous studies (Tai 1999; Tai et al. 1999). The correlation between the experiment and the predicted values of $G$ are shown in Figure 7. The correlation

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**Table 2 | Results of the linear particle growth rate ($G$) and fixed bed height growth rate ($R_h$) experiments**

<table>
<thead>
<tr>
<th>Run no</th>
<th>Superficial velocity $SV$ (m/h)</th>
<th>Particle size $L_0$ (mm)</th>
<th>Supersaturation ($S$)</th>
<th>Linear growth rate $G$ (m/s)</th>
<th>$R^2$</th>
<th>$R_h$ (cm/d)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>50</td>
<td>0.1–0.25</td>
<td>84.4</td>
<td>$8.58 \times 10^{-10}$</td>
<td>0.99</td>
<td>12.46</td>
<td>0.98</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>0.1–0.25</td>
<td>84.4</td>
<td>$1.96 \times 10^{-9}$</td>
<td>0.99</td>
<td>20.74</td>
<td>0.99</td>
</tr>
<tr>
<td></td>
<td>70</td>
<td>0.1–0.25</td>
<td>84.4</td>
<td>$2.14 \times 10^{-9}$</td>
<td>0.99</td>
<td>26.11</td>
<td>0.99</td>
</tr>
<tr>
<td>2</td>
<td>60</td>
<td>0.1–0.25</td>
<td>84.4</td>
<td>$1.96 \times 10^{-9}$</td>
<td>0.99</td>
<td>20.74</td>
<td>0.99</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>0.15–0.4</td>
<td>84.4</td>
<td>$1.48 \times 10^{-9}$</td>
<td>0.98</td>
<td>14.83</td>
<td>0.99</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>0.2–0.4</td>
<td>84.4</td>
<td>$1.08 \times 10^{-9}$</td>
<td>0.97</td>
<td>14.81</td>
<td>0.99</td>
</tr>
<tr>
<td>3</td>
<td>60</td>
<td>0.1–0.25</td>
<td>84.4</td>
<td>$1.96 \times 10^{-9}$</td>
<td>0.99</td>
<td>20.74</td>
<td>0.99</td>
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<tr>
<td></td>
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<td>0.1–0.25</td>
<td>107.77</td>
<td>$2.86 \times 10^{-9}$</td>
<td>0.98</td>
<td>43.22</td>
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<td></td>
<td>60</td>
<td>0.1–0.25</td>
<td>125.50</td>
<td>$3.66 \times 10^{-9}$</td>
<td>0.94</td>
<td>52.58</td>
<td>0.98</td>
</tr>
</tbody>
</table>
The correlation between the experiment results and the predicted values of $R_h$ are shown in Figure 8. The correlation coefficient of the fitting is 0.953, which indicates well-correlated data. From the empirical model of fixed bed growth in a pellet reactor, it is possible to explain the influence of the selected variables.

The model provides a simple calculation method. The fixed bed height growth rate can be calculated if the conditions of superficial velocity, supersaturation, and particle size of the seeds are known. The fixed bed height after a certain point of time in the operation can be predicated using the initial fixed bed height and the fixed bed height growth rate. The calculation method is simple and suitable for fixed bed height prediction in practical engineering.

**CONCLUSIONS**

The following conclusions were drawn based on this study:

1. The linear particle growth rate is proportional to the superficial velocity and supersaturation, but inversely proportional to the particle size of the seeds in the pellet reactor. The particle growth prioritizes heterogeneous nucleation in the pellet reactors.

2. When the superficial velocity is 50–70 m/h, the supersaturation range is 84.4–125.5, the particle size of the seeds is 0.1–0.4 mm, and the linear particle growth rate model at the bottom of the pellet reactor is $G = 3.90 \times 10^{-9}SV^{1.95}L_0^{-1.56}S^{2.13}$.

3. When the superficial velocity range is 50–70 m/h, the supersaturation range is 84.4–125.5, the particle size of the seeds is 0.1–0.4 mm, and the fixed bed growth rate model is $R_h = 5.19 \times 10^{-8}SV^{1.65}L_0^{-0.93}S^{2.58}$.

**ACKNOWLEDGEMENTS**

This research was supported by the National Key Research and Development Program of China (2016YFC0400706),
the Natural Science Foundation of China (Grant No. 51278409), China Postdoctoral Science Foundation (No. 2015M580821), the project of Shaanxi Province Youth Science and Technology Star, and the Research Program of China State Construction Engineering Corporation Ltd (No. CSCEC-2014-Z-32).

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First received 20 April 2016; accepted in revised form 9 September 2016. Available online 30 September 2016