Growth Rate of Tiny Calcite Crystal just Nucleated in Supersaturated Solution with Unstable Intermediate by Addition of Sodium Chloride Crystal

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Precipitation of calcite by reacting aqueous solutions of calcium chloride and sodium carbonate was studied in a well-mixed semi-batch crystallizer. In this study, a calcium carbonate intermediate precipitated first and quickly transformed into calcite upon the addition of sodium chloride. As long as the intermediate remained present in the slurry, the calcite crystals kept growing. The slurry was sampled at appropriate time intervals, and a change in crystal size distribution of the calcite crystals was observed. From these data, a crystal growth rate of calcite was obtained and it was turned out that the growth rate of the tiny calcite crystals were fast just after their nucleation and then gradually decreased during growth until their size became 7 microns, when the growth rate became constant. The growth rate of the calcite crystals below 7 microns was correlated with their size. Also, the concentration of the calcium ions in the slurry and an amount of intermediate were measured for all samples, and the supersaturation was found to be constant. The mechanism of crystal growth and nucleation of calcite by transformation from the intermediate upon the addition of sodium chloride crystal was discussed and a new model of them was proposed.

1 Introduction

Precipitation generally takes place through a chemical reaction. In some cases, an intermediate crystallizes first and then transforms into the final crystal. In such a case, the behavior of an intermediate affects the precipitation, and control of the transformation of the intermediate offers an attractive way for the production of the tiny well faceted crystals. The authors have studied the precipitation of calcite by reacting aqueous solutions of calcium ions and carbonate ions, as a model system. In this reaction, a calcium carbonate intermediate turned out to transform easily into calcite by adding an inorganic substance like sodium chloride or by mechanical energy generated by collision with solid particles, and these calcite nuclei grow out to become regular shaped crystals in an agitated [1,2] slurry of calcium carbonate intermediate. The growth rate of relatively large calcite crystals was measured as a function of the supersaturation that is created by the solubility of the calcium carbonate intermediate, which is higher than the calcite solubility. But when the same growth rate is used to estimate the growth of the tiny calcite just after nucleation, a far too long nucleation time of calcite is needed for a correct modeling of the experimental data. Therefore, in this study, the crystal growth rate of tiny calcite crystals just after their nucleation is studied, and a mechanism for their nucleation and growth will be proposed.

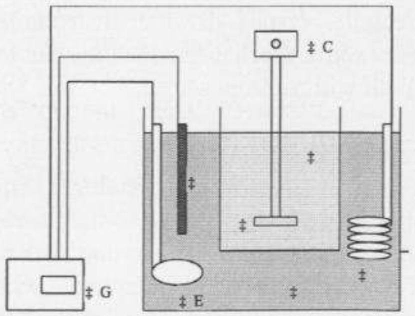
2 Experimental

A well-mixed type of batch crystallizer shown in figure 1 was used. One liter of sodium carbonate solution of a selected concentration was placed in the two-liter vessel and was agitated with a 4-bladed impeller. The temperature of the solution was maintained at 298K, and then a stoichiometric amount of calcium chloride solution was added into it rapidly at a time. The total volume of the solution was 1100ml. A measured amount of sodium chloride crystals was added the calcium

Table 1 Experimental condition

		Run No						
		1	2	3	4	5	6	7
Conc. of Na_2CO_3 solution	[mol/1000ml]	0.05	0.01	0.02	0.05	0.08	0.10	0.05
Conc. of $CaCl_2$ solution	[mol/100ml]	0.05	0.01	0.02	0.05	0.08	0.10	0.05
Amount of added NaCl crystals	[mol]	0.01	0.20	0.20	0.20	0.20	0.20	0.20
Agitational speed	[rpm]	300	300	300	300	300	300	600

carbonate intermediate slurry 15 seconds after the calcium chloride solution was added. Two samples were withdrawn at several different time intervals after the sodium chloride crystals were added. One of the samples was diluted by the addition of a measured amount of ion exchanged water to dissolve the suspended intermediate, and was filtered through a 1.0 micron membrane filter. The other was filtered through a 0.45 micron membrane filter without dilution to determine the concentration of the calcium ions. Subsequently, the concentration of the calcium ions in the filtrate was analyzed by chelatometric titration. The slurry obtained by reaction of both solutions was continued to be agitated for thirty minutes after the calcium chloride solution was added, and was then filtered through a 1.0 micron membrane filter to separate the final crystals. Microscopic and SEM photographs of the crystals separated from their mother liquor were taken and their size distributions were measured. The precipitated crystal was also analyzed by X-ray diffraction. The experimental conditions are shown in Table.1.



crystallizer
impeller
thermostat sensor
cooler
thermostat bath
motor
heater
thermostat controller

Figure 1 Schematic diagram of experimental apparatus

3. Results and discussion

3.1 Size Distribution of calcite transformed from intermediate

In our experiments in this study, cloudy calcium carbonate intermediates as reported by Ogino [3] developed just after the addition of the calcium chloride solution to the agitated sodium carbonate solution, which gradually transformed into vaterite and calcite. When however, sodium chloride crystals were added to the viscous slurry of suspended intermediate, fine calcite crystals suddenly appeared and quickly grew larger. An example of a SEM photograph of the crystals sampled 30 minutes after the addition of sodium chloride crystal in test run No 1, is shown in figure 2. As shown in this photo, the precipitated calcite had a relatively uniform size distribution of regular shaped crystals and a deformed bad shape crystal was scarcely observed in it. That calcite precipitated in the experiment was confirmed not only by the shape of the transformed crystals on the photographs but also by X-ray analysis.

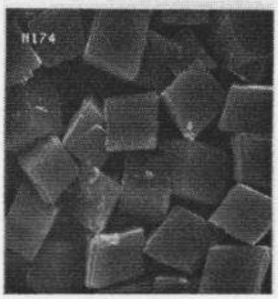


Figure 2 SEM photograph of precipitated calcite obtained from run No 1

A size distribution change of calcite measured from microscopic photos is shown in figure 3. The plots in the figure were obtained from the crystals sampled as particular time intervals of 1.0 to 30 min. and the size

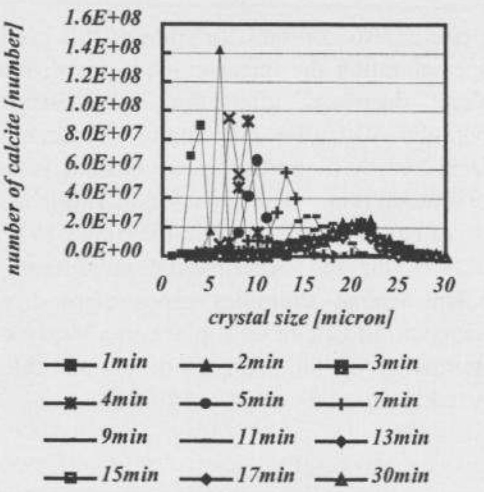


Figure 3 Crystal size distribution obtained from run No 1

distribution is relatively narrow at shorter sampling times after nucleation took place. The vertical axis of the figure represents the number of calcite crystals a particular size and was calculated by equation (1).

$$N_i(L_i) = \frac{W_t}{\int_0^{\infty} n(L_i)L_i^3 dL} \cdot \int_{L_i-1}^{L_i} n(L_i)dL \qquad (1)$$

Here, n (L_i) is an observed number of crystals of size L_i, and W_t is the total amount of precipitated calcite estimated from the difference between the measured calcium ion concentration in the solution filtered after dissolution of the calcium carbonate intermediate and the one in a feed solution.

As shown in the plots of the estimated number of calcite crystals in figure 3, the number of crystals of a dominant size decreased gradually during growth of the suspended calcite, although the total number of the calcite crystals remains almost constant except for an initial period just after nucleation of calcite. The crystal size distribution in figure 3 widens during growth of the crystals, and these changes of size distribution are assumed to come from growth rate dispersion. But the total number of calcite nuclei is impossible to be accurately established due to the difficulties in estimating the total amount of precipitated calcite just after nucleation. The size distribution of the calcite sampled after 17 min. of operation, is almost the same as that of the calcite obtained after 30 min. operation, and from these experimental results, contact nucleation is supposed not to take place in this study.

3.2 Crystal growth rate of calcite

The mean crystal sizes of the calcite sampled from slurry as particular time intervals were estimated from crystal size distributions as shown in figure 3. Values calculated for run number 1 are plotted against the sampling times in figure 4.

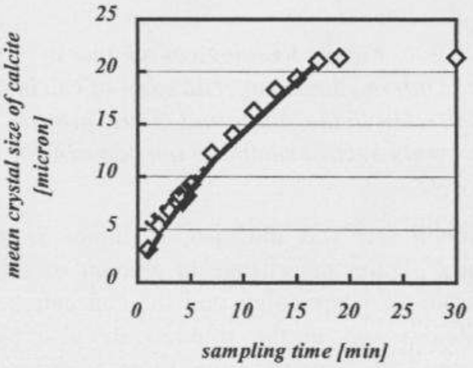


Figure 4 Change of mean crystal size of calcite obtained from run No 1

As shown in this figure, the mean crystal size rapidly increases after the start of the operation and the slope of the curve gradually decreases to approach a constant value, as the growth of calcite continues. The crystal growth rate of calcite was calculated from the difference between adjacent crystal mean sizes and the time needed for growth from a size L_1 till L_2, by equation (2).

$$\left(\frac{dL}{dt}\right)_{t=\frac{t_1+t_2}{2}} = \frac{L_2 - L_1}{t_2 - t_1} \qquad (2)$$

Here, t and L are sampling time and crystal size, and subscripts 1, and 2 show distinction of a sampling. A calculated crystal growth rate is plotted against the corresponding time when a

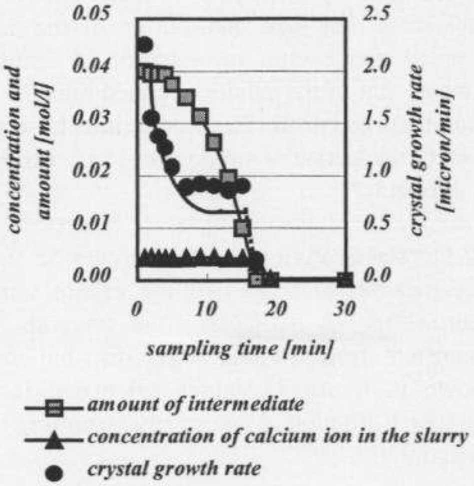


Figure 5 Change of amount of intermediate, concentration of calcium ion in the slurry and crystal growth rate against sampling time on run No 1

growth rate was obtained, in figure 5. In the same figure, the change in amount of calcium carbonate intermediate and the concentration of calcium ions in the solution are also plotted against the sampling time. From comparison of these lines, it follows that after the nucleation of calcite, the concentration of the calcium ions in solution remains constant as long as the calcium carbonate intermediate is present in the agitated slurry. This concentration is higher than the saturated calcium ion concentration in the solution in which calcite is suspended. The equilibrium calcium ion concentration is almost negligible in comparison with the equilibrium concentration of the calcium carbonate intermediate. Therefore, the concentration of the calcium ions in solution in figure 5 is considered to responsible for the supersaturation, which causes the nucleation and growth of calcite. In other words as long as the intermediate is present in the slurry, the difference between its solubility and that of the stable calcite creates the driving force for the conversion of the intermediate into calcite. Since the calcium ion concentration remains constant as the solubility level of the intermediate, until this intermediate becomes exhausted, the driving force for the growth of calcite is also constant. In spite of this constant supersaturation the linear crystal growth rate of calcite decreases after the initial stage of operation, just after nucleation of calcite took place, and then approaches a constant value of 0.9 micron/min. The changes in mean crystal size of calcite precipitated in the runs 2 to 6 (see Table 1 for the experimental conditions) are shown against sampling times elapsed since nucleation of calcite took place in a slurry of an intermediate in the presence of sodium chloride crystal in figure 6.

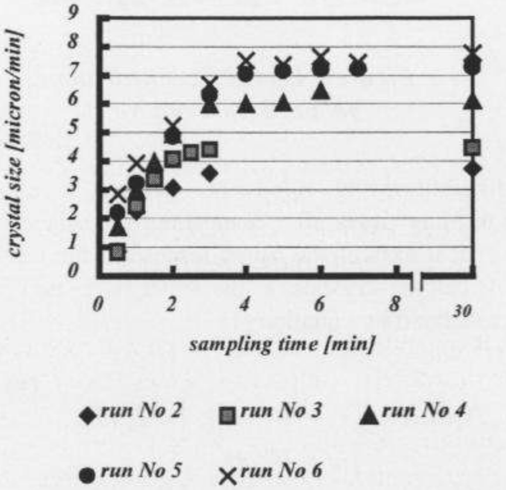


Figure 6 Change of crystal size of calcite precipitated in tests' runs 2 to 6

In these runs, the concentrations of calcium and carbonate ions in the solution were 0.01 to 0.10 mol/1100ml and similar results as presented in figure 5 were obtained. Therefore, when the linear crystal growth rates of calcite are plotted against the mean crystal size of calcite for the range of crystal growth rates measured, a relatively good correlation was obtained in a semi logarithmic diagram as shown in figure 7. In general, the mechanism of crystal growth is considered to be composed two different steps, a diffusion step of growth components through the boundary layer around the growing crystals and a surface integration step. The effect of the stirrer speed on the crystal growth rate was neglected for the 300 and 600 rpm values as shown in figure 7, since the effect on the diffusion step is

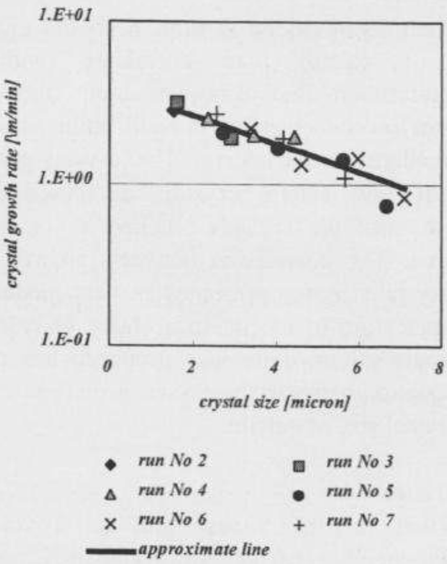


Figure 7 Semi logarimic diagram in which indicated the correlation between mean crystal size of calcite and crystal growth rate

not considered to have any crystal growth rate as is the case for most sparingly soluble salts. The crystal growth rate of fine crystals just after nucleation is faster than that of the further grown crystals and this phenomenon is considered to be due to active growth spots on the crystal surface. Therefore, when the growth rate of tiny crystals is assumed to be fast due to active points developed during their nucleation and these active points are also assumed to decrease during crystal growth, the following equations can be proposed to described the decrease of crystal growth rate observed in this study.

$$\frac{dL}{dt} = \alpha m \qquad (3)$$

$$\frac{dm}{dL} = -\beta m \qquad (4)$$

Therefore, equation (5) is obtained.

$$\frac{dL}{dt} = \gamma \exp(-\beta L) \qquad (5)$$

Here, m is the surface density of active points on the growing crystal surface, and , , and are constants. When equation (5) is applied to correlate the points in figure 7, equation (6) is obtained, independent of the suspension density of the intermediate.

$$\frac{dL}{dt} = 3.9 \exp(-0.2L)$$

$$(0.7<L<7.0 \text{ micron}) \qquad (6)$$

In this study, the decrease of the crystal growth rate of calcite is correlated with the crystal size by equation (6) for the range of 0.7 to 7.0 microns, while the growth rate was almost constant for crystals larger than 7.0 microns when the calcium carbonate intermediate coexisted in a slurry of growing calcite. For calcite crystals with a size below less 0.7 microns, the crystal growth rate could not be observed.

3.3 The size of calcite nuclei

The size of the calcite nuclei is difficult to observe at present. But when equation (6) is assumed to extend for a crystal size below 0.7 microns and when the addition of sodium chloride is supposed to induce the nucleation of only calcite from the slurry containing the intermediate, the sizes of calcite nuclei were estimated as the value at the nucleation time of plots in figure 6 by use of equation (6). When the sizes of calcite nuclei are plotted against the suspension densities of the calcium carbonate intermediate, the plot in figure 8 is obtained. Here, the suspension density of the intermediate is estimated under the assumption that the total amount of calcium and carbonate ions in the feed solutions minus the observed concentration of both ions in a slurry with the intermediate represents the total amount of intermediate as the time that nucleation of calcite took place.

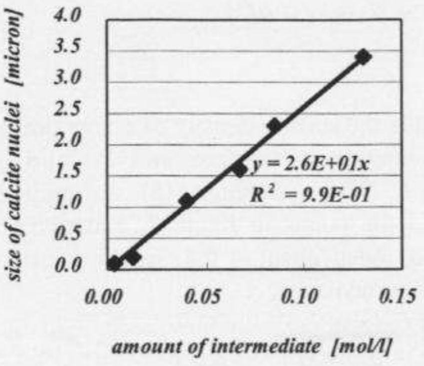


Figure 8 Correlation of amount of intermediate, x, and the size of calcite nuclei, y

Therefore, the correlative equation between the size of calcite nuclei , y, and amount of the intermediate, x, is given by equation (7).

$$y = 26x \qquad (7)$$

To explain this correlation, the nucleation of calcite from a calcium carbonate intermediate by the addition of NaCl crystal is described by a new model. The intermediate is supposed to agglomerate before the addition of the sodium chloride crystal and the agglomerate suddenly transforms into calcite nuclei of the particular size expressed by equation (7) when the sodium chloride is added. The given correlation is considered to be useful to estimate the size of calcite nuclei as an operational condition. When product calcite sizes are considered, equation (7) might be expected to be useful for estimation of an approximate product crystal size.

Conclusions

Precipitation of calcite was studied by reacting aqueous solutions of sodium carbonate and calcium chloride in a semi-batch crystallizer. Changes in crystal size distribution were observed when several samples were taken from fifteen seconds after nucleation of calcite took place by the addition of sodium chloride crystal to a slurry of calcium carbonate intermediate till 30minutes afterwards. From the observed size distributions of calcite in time, a crystal growth rate of calcite was correlated with a supersaturation that was estimated from the calcium ion concentration in equilibrium with the intermediate in the slurry. The crystal growth rate of tiny calcite crystals decreased with growth until the crystals reached a size of 7 microns. The correlation between growth rate and crystal size was presented. A new model for the nucleation of calcite in a slurry of calcium carbonate intermediate was proposed based on the equation between the crystal growth rate and the crystal size of calcite.

Reference

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Nomenclature

L	crystal size [micron]
m	surface density of active points on the growing crystal surface [number / micron^2]
n	population of crystal [number/micron]
N_i	number of crystal [number]
t	elapsed time [min]
W_t	whole amount of a precipitated calcite [micron^3]
x	amount of the intermediate [mol/l]
y	size of calcite nuclei [micron]
	constant [micron^3/min · number]
	constant [1/micron]
	constant [micron/min]