

Control of Crystal Size and Morphology of Calcium Carbonate Crystal Polymorphism

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Abstract

Calcium carbonate, the main component of lime, has been widely used in industry due to its stability and economy. Calcium carbonate has three types of crystalline polymorphism, calcite, aragonite and vaterite, each with different properties. Therefore, the control of crystal polymorphism is required for industrial applications. In addition, the control of crystal size and shape is similarly required for different applications. In this study, the effect of SrCO₃ on the size control of fine aragonite-type calcium carbonate crystals by uniform urea precipitation and the effect of SrCO₃ addition was investigated by adding solid strontium carbonate and dissolved strontium carbonate. The addition of solid strontium carbonate affected the crystal polymorphism and size of the calcium carbonate produced, depending on the properties of the solid particles and the amount of SrCO₃ added. Experiments on the addition of dissolved SrCO₃ showed that the supersaturation formation rate could be controlled to control the crystal polymorphism.

Keywords

CaCO₃, Aragonite, SrCO₃, Crystal Polymorphism, Size Control

1. Introduction

Limestone is one of the few mineral resources that are self-sufficient in the country, and veins of limestone, the raw material of limestone, are scattered throughout the country. Calcium carbonate (CaCO₃), the main component of limestone, has good stability and economy and is widely used industrially in rubber, plastics, paints, and paper-making. The industrially used CaCO₃ is classified into two types: ground calcium carbonate (GCC), which is made by finely

grinding natural lime, and precipitated calcium carbonate (PCC), which is produced through chemical synthesis. GCC is produced by the crushing and classifying process and has irregular particle size and shape, while PCC is mainly produced by the lime milk coal oxidation method, in which calcium carbonate is precipitated by blowing CO₂ into calcium hydroxide slurry. Other methods of PCC include the sodium carbonate lime method and the calcium nitrate-ammonium carbonate method. Calcium carbonate has three crystalline polymorphs: calcite, aragonite, and vaterite [1] [2] [3].

Thermodynamically, calcite is the most stable, and calcite is the main component of limestone. Aragonite is stable at room temperature and pressure, but it is easily transferred to calcite when heat or pressure is applied. For this reason, calcite transferred from aragonite is often found in fossils. Vaterite is the most unstable and easily transfers to aragonite and calcite under ambient temperature and pressure. Thus, it is desirable to control the crystal polymorphism of calcium carbonate according to the application because it shows different physical properties depending on the crystal polymorphism.

Therefore, the control of crystal polymorphism by various methods has been studied [4]-[9]. The polymorphism of calcium carbonate crystal is also affected by the additives [6] [7]. For example, it has been reported that the addition of metal ions to the reaction system stabilizes aragonite by Ni²⁺ addition, Mg²⁺ promotes the transition to calcite, and Fe³⁺ stabilizes the satellite [8]. In addition, calcium carbonate polymorphism is affected by the polymorphism present in the reaction system. When calcium bicarbonate saturated solution contains a small amount of calcite, the product is 100% calcite, and when a small amount of aragonite is present, only aragonite is obtained. In industrial applications, it is also desirable to control the size and morphology of the crystals according to the application. For example, fine crystals of CaCO₃ and crystals with large specific surface areas have the effect of increasing the strength of rubber and the glossiness of paper when added. In the past, most of the PCC used calcite, but recently, columnar aragonite has been attracting attention as a paper coating pigment. Columnar calcium aragonite has good dispersibility in water. In addition, it has good flowability in a high particle density slurry state, improves the whiteness and opacity of coated paper, and shows good printing characteristics due to its good lubrication of the coated paper surface.

The purpose of the study was to control particle size of fine aragonite-type calcium carbonate crystals by uniform urea precipitation and to clarify the effect of SrCO₃ addition. Furthermore, the effect of SrCO₃ addition was investigated in detail by using two kinds of SrCO₃, one is solid SrCO₃ and another is dissolved SrCO₃.

2. Experimental

2.1. CaCO₃ Crystallization Experiments in the Presence of Solid SrCO₃

The crystallization tank with a 500 mL interference plate contained 200 mL of 1

mol/L aqueous urea solution and a 300 mL beaker contained 200 mL of 0.4 mol/L aqueous $\text{Ca}(\text{NO}_3)_2$ solution, and the two solutions were heated; when the temperature reached 80°C , the aqueous solution was added to the aqueous urea solution in the crystallization tank, where SrCO_3 was added simultaneously. The amount of SrCO_3 added was advanced at 2.95×10^{-3} , 7.38×10^{-3} , 2.95×10^{-2} , 7.38×10^{-2} and 2.95×10^{-1} (g/100 mL). Three types of SrCO_3 with different particle sizes were used for the addition.

The mixture was kept at 80°C and stirred at 300 rpm for 4 h with a stirring blade, and the resulting crystals were filtered, washed and dried and shown in **Figure 1**. The average grain size and aragonite content of the obtained crystals were evaluated. The average size was determined from the size distribution measured by optical microscope images. Aragonite content was calculated using calibration curve after PXRD measurement of the product crystals. In addition, elemental analysis was performed by EDX.

2.2. CaCO_3 Crystallization Experiments in the Presence of Dissolved SrCO_3

The CaCO_3 crystallization experiments during the addition of solid SrCO_3 were a process involving the dissolution of SrCO_3 . Therefore, the effect of solid SrCO_3 was avoided and CaCO_3 was prepared by adding dissolved SrCO_3 and its effect was investigated. SrCO_3 , 2.3 g (0.022 mol) was added to 50 mL of 1 M HNO_3 solution to prepare dissolved SrCO_3 . 150 mL of 1 mol/L aqueous urea solution was heated in a 500 mL crystallizer with a 500 mL interfering plate. 200 mL of 0.4 mol/L aqueous $\text{Ca}(\text{NO}_3)_2$ solution and 50 mL of dissolved SrCO_3 solution were heated to 80°C . When the temperature reached 80°C , three aqueous solutions were mixed in the crystallizer, at which time $\text{Ca}(\text{NO}_3)_2$ and dissolved SrCO_3 were added at six different rates. The mixture was kept at 80°C and stirred at 300 rpm with a stirring blade, and the crystals obtained in a total of 4 hours were filtered, washed and dried and shown in **Figure 1**.

[Reaction crystallization of CaCO_3]

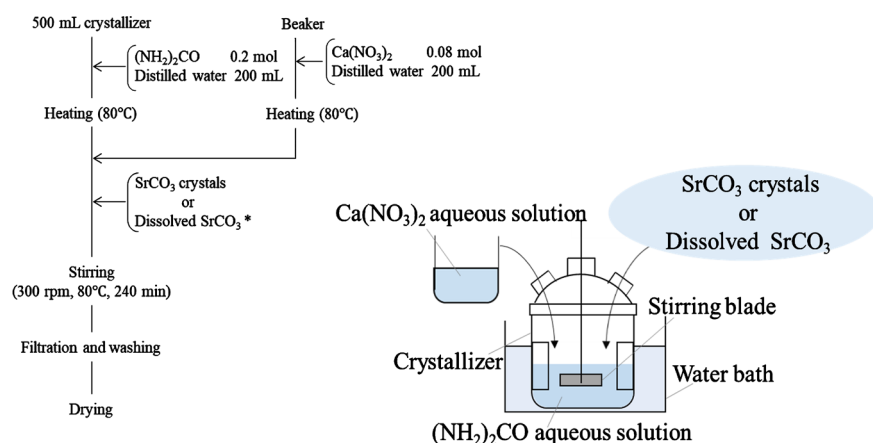


Figure 1. Schematic diagram of experimental setup.

3. Results and Discussion

3.1. Effect of Adding SrCO₃

Crystallization experiments were conducted under a total of 15 conditions using 0.3 μm, 30 μm, and 100 μm solid SrCO₃, with the addition of 2.95×10^{-3} , 7.38×10^{-3} , 2.95×10^{-2} , 7.38×10^{-2} and 2.95×10^{-1} (g/100 mL). Optical microscopic images of crystallized CaCO₃ are shown in **Figure 2**. Columnar crystals were obtained. As the amount of strontium carbonate was increased and the particle size of strontium carbonate was decreased, the size of the crystals became smaller. Under the present conditions, the SrCO₃ crystals are completely dissolved in the solution when 0.00295 and 0.00738 (g/100mL) are added to the solution. However, above 0.0295 g/100mL, the added SrCO₃ crystals were not completely dissolved and crystallized in suspension.

Figure 3 shows the average grain size in the longitudinal direction of the obtained columnar crystals. In the figure, the case of 100 μm SrCO₃ addition is shown in green, 30 μm in blue and 0.3 μm in red. Regardless of the average particle size of the added SrCO₃, the particle size tended to decrease as the amount of solid SrCO₃ added increased. The coefficient of variation (CV) of the crystals obtained under these conditions was in the range of 0.3 - 0.5. This may be due to the fact that heterogeneous nucleation occurred with the increase in the number of crystals in the solution due to the increase in the amount of adding. Furthermore, the use of smaller particle sizes of added SrCO₃ resulted in finer aragonite crystals when the amount of addition was equal. This may be due to the nucleation induced by the increase in the specific surface area of the solid SrCO₃ in contact with the solution.

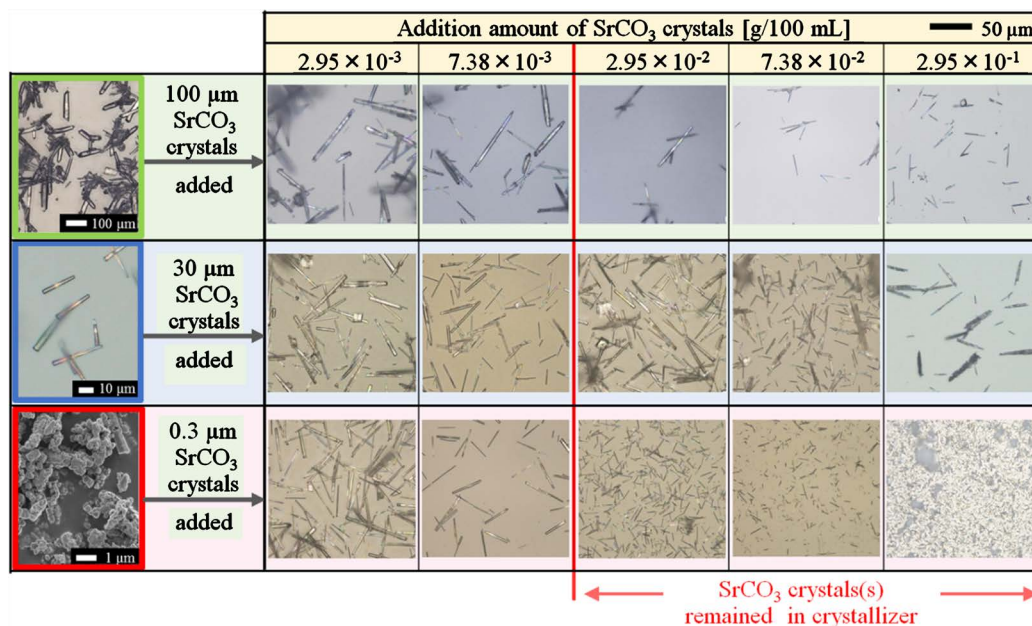


Figure 2. Optical micrographs and SEM images of SrCO₃ crystals (100 μm, 30 μm, 0.3 μm) and CaCO₃ produced by adding various amounts of SrCO₃ crystals.

Figure 4 shows the aragonite content in relation to the amount of strontium carbonate added. The addition of $0.3 \mu\text{m}$ SrCO_3 (red markers) resulted in higher aragonite content at all doses. When $30 \mu\text{m}$ and $100 \mu\text{m}$ SrCO_3 was used (blue and green markers), the calcite content increased and the aragonite content decreased with increasing amounts of SrCO_3 added (blue and green markers). The presence of small diameter strontium carbonate solids inhibited the formation of calcite and also allowed the refinement of aragonite.

Figure 5 shows the SEM and optical microscope images of CaCO_3 crystallized with $2.95 \times 10^{-1} \text{ g}/100 \text{ mL}$ of SrCO_3 . **Figure 5(a)** is an SEM image of the crystals obtained without the addition of strontium carbonate. The average particle size was $62.8 \mu\text{m}$ and the coefficient of variation (CV) was 0.38. **Figures 5(b)-(d)** show that the addition of $0.3 \mu\text{m}$, $30 \mu\text{m}$, and $100 \mu\text{m}$ solid SrCO_3 decreased the particle size of aragonite along with the decrease of strontium carbonate particle size, along with this average particle size. Furthermore, in **Figure 5(b)**, cubic

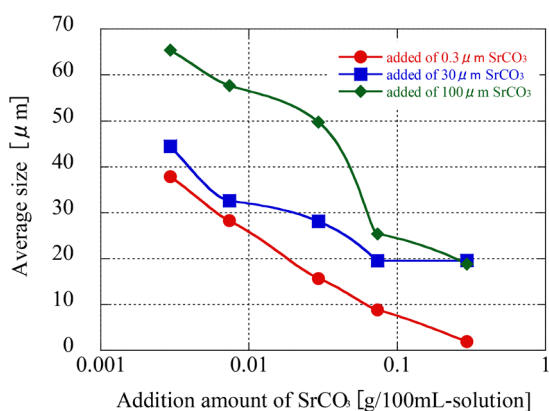


Figure 3. Addition amount of SrCO_3 crystals [g/100mL-solution] vs. size of aragonite [μm].

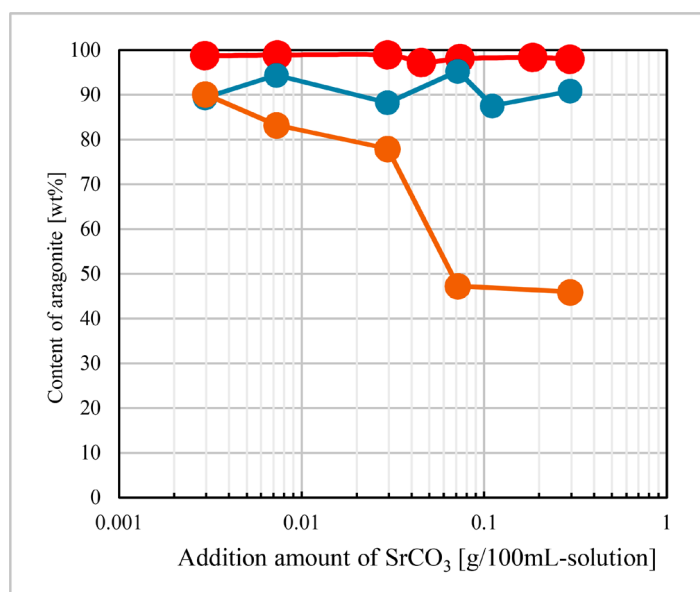


Figure 4. Addition amount of SrCO_3 crystals [g/100mL] vs. aragonite content [wt%].

particles were also observed, which also confirmed the formation of calcite.

3.2. Elemental Analysis of CaCO_3 after Crystallization

Elemental analysis of CaCO_3 crystals obtained with 0.295 g/100mL of SrCO_3 crystals with the average grain size of 30 μm and 100 μm was performed by EDX mapping (Figure 6). In Figure 6, Ca is shown in red and Sr is shown in green, indicating that CaCO_3 is formed around solid SrCO_3 . Furthermore, there is a difference in the crystal polymorphism of CaCO_3 preferentially crystallized from the SrCO_3 surface when the average particle size of the added SrCO_3 is 30 μm and 100 μm in solid SrCO_3 . Columnar aragonite was frequently observed in the 30 μm grain size of added SrCO_3 , whereas cubic calcite was predominantly observed in the 100 μm grain size. When 0.3 μm SrCO_3 was added, CaCO_3 crystallization from the SrCO_3 crystal surface could not actually be observed, but aragonite was inferred to be crystallized from the 0.3 μm SrCO_3 surface.

SrCO_3 has a structure similar to aragonite among the crystal polymorphs of CaCO_3 [1] [2] [3]. Therefore, it is assumed that aragonite is susceptible to crystallization from all aspects of SrCO_3 , which is supported by the SEM images of the products and the high content of aragonite when 0.3 μm and 30 μm SrCO_3 were added. Calcite was preferentially crystallized at 100 μm addition, which was

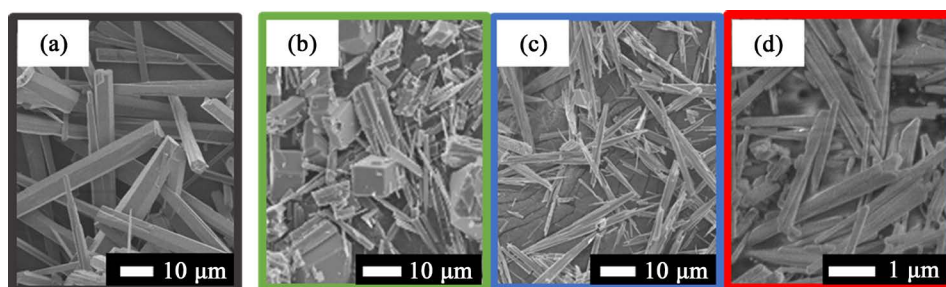


Figure 5. SEM images and optical micrographs of CaCO_3 produced with SrCO_3 crystals of 0.295 g/100mL: (a) without SrCO_3 crystals, (b)-(d) with SrCO_3 crystals (100 μm , 30 μm , 0.3 μm).

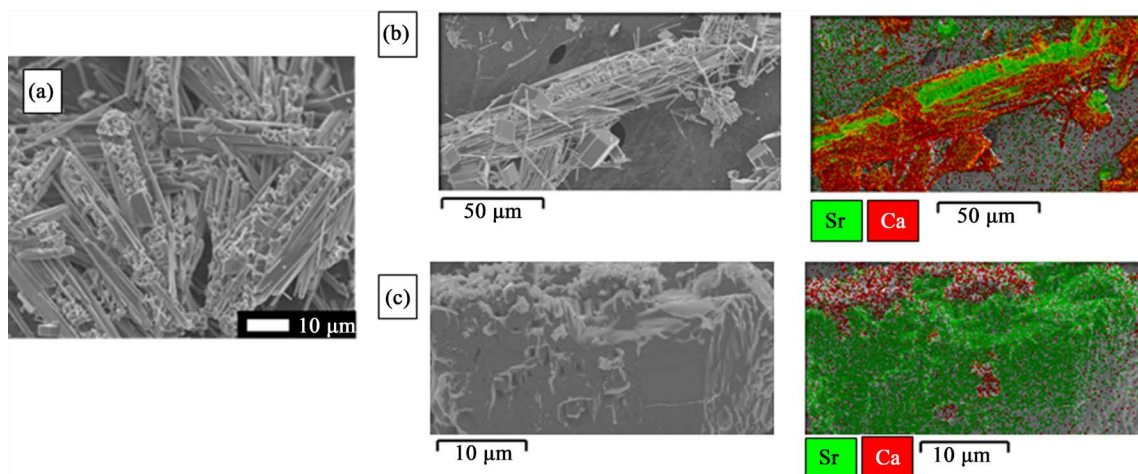


Figure 6. EDX mapping data of CaCO_3 produced with 30 μm SrCO_3 crystals ((a), (b)), with 100 μm SrCO_3 crystals (c) at 0.295 g/100mL. Green; Sr, red: Ca.

attributed to the effect of the (220) plane found on the SrCO_3 side, based on the crystal structure and crystal plane of SrCO_3 [9].

3.3. The Effect of Dissolved SrCO_3 Addition

The concentration of Ca ions in the initial solution and the rate of addition of the solution were changed and the images of the crystals formed are summarized in **Figure 7**. The crystal polymorphism of the obtained calcium carbonate differed depending on the initial solution and the drop operation. The polymorphism could not be controlled as Ca^{2+} (mol) in the initial solution produced aragonite, calcite, and satellite at ≥ 0.08 , while between 0.08 and 0.06, vaterite, aragonite, and calcite were formed, and at ≤ 0.02 , aragonite, vaterite, and calcite were observed. However, only aragonite-type calcium carbonate with an average particle size of about $40 \mu\text{m}$ could be obtained selectively when Ca^{2+} in the initial solution was 0.02 - 0.06 mol. In the range of 0.02 - 0.06 mol of Ca^{2+} , the aragonite with the largest average particle size was obtained at 0.03 mol of Ca^{2+} in the initial solution. This may be due to the fact that the initial concentration of Ca ions and the rate of addition could be adjusted to the supersaturation level, which promotes the selective formation of aragonite and crystal growth. The dissolved SrCO_3 addition experiments showed that the crystal polymorphism could be controlled by controlling the supersaturation formation rate.

4. Conclusion

In calcium carbonate crystallization using the homogeneous urea precipitation method, the addition of solid strontium carbonate affected the crystal polymorphism and size of the calcium carbonate crystals produced, depending on the characteristics of the solid particles and the amount added. It was found that finer aragonite-type calcium carbonate crystals with a higher content were

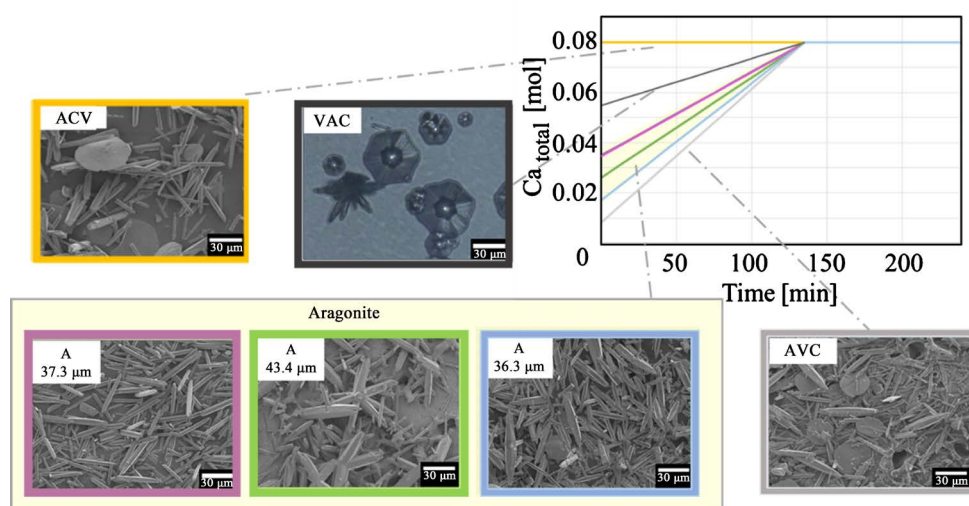


Figure 7. Time [min] vs. Ca_{total} [mol] in crystallizer and SEM images and optical micrograph of CaCO_3 produced with dissolved SrCO_3 .

obtained when SrCO₃ with a smaller average particle size of about 0.3 μm was used. When strontium carbonate was added, the crystal polymorphism of the obtained calcium carbonate differed depending on the initial solution concentration in the crystallizer and the speed of addition. Especially, the selective preparation of aragonite was possible at the initial Ca concentration in the crystallizer in the range of 0.02 - 0.06 mol.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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