Journal of Metals, Materials and Minerals, Vol.19 No.2 pp.67-72, 2009.

Crystal Habit of $CaCO_3$ Under Different Carbonation Methods

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Abstract

The saturated solutions of $Ca(OH)_2$ were carbonated by CO_2 in air under static and turbulent conditions. The saturation state of starting solution and carbonation methods had effect on the crystal habit. The phase of $CaCO_3$ precipitated from saturated solution is calcite. No metastable phase of $CaCO_3$ was found.

Key words: Calcium carbonate, Carbonation, Precipitation, Crystal habit

Introduction

Calcium carbonate ($CaCO_3$) is commonly found as mineral and in living organisms. This compound has 3 polymorphs, i.e., calcite, aragonite and vaterite. However, amorphous $CaCO_3$ was also found in some living organisms.(1, 2) Phases and crystal habit of calcium carbonate are governed by various parameters. This is important for biomineralization processes and for the industry. The synthesis of calcium carbonate is mostly done by the carbonation process, i.e., flowing CO_2 through $Ca(OH)_2$ solution, and the precipitation from Ca-salt. Many research works had reported the effect of parameters, e.g., the concentration of the starting material and additive.(3- 7) From our previous work, we prepared $CaCO_3$ from precipitation of $CaCl_2$.(8) We found that a very low concentration of starting materials, all 3 polymorphs of $CaCO_3$ were found at the onset of the precipitation before they transformed into the most stable phase, calcite.

The purpose of this work is to study the crystal habit and phase formation of $CaCO_3$ prepared from carbonation of saturated $Ca(OH)_2$ solution.

Materials and Experimental Procedures

Experimental procedure

$Ca(OH)_2$, analytical reagent (96%, UNIVAR) was used as starting material. The saturated $Ca(OH)_2$ solution was prepared by mixing $Ca(OH)_2$ in distilled water, stirred for 1 min and filtered with filter paper in order to acquire a clear saturated solution. S-0.01 and S-0.2 are the saturated solutions prepared from mixing calcium hydroxide (0.01 mol and 0.2 mol) before filtration, respectively. The saturated solution was freshly prepared before every carbonation test. The carbonation tests were run at room temperature.

The carbonation methods of saturated solution by CO_2 in air were carried out by 2 methods: static surface carbonation and air bubbling carbonation. Under static surface carbonation, the solution was kept in the glass vessel and covered with a bigger glass vessel to protect the solution from any particulates in the air. Carbonation occurred directly at the surface of the solution and formed a thin layer of $CaCO_3$. The thin layer on the surface of the solution was collected by very thin glass sheet after different carbonation times and the surface of the thin layer was dried immediately by small pieces of filter paper before drying in the oven at 110°C at least for 24 hours before further characterizations. Air bubbling carbonation was carried out by air bubbling in the saturated solution through a glass tube which has an inner diameter of 4 mm. Then the solution was stirred at various carbonation times. The flow rate of air bubbling was 2 l/min. After carbonation, the saturated solution was turbid and turned into a suspension. A small amount of the suspension was taken out at various carbonation times and dropped

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on very thin glass sheet and left for 1 min. After this procedure, it was dried with small pieces of filter paper before drying in the oven at 110°C at least for 24 hours before further characterizations. In some carbonation tests, the air bubbling was stopped for different carbonation times. The white precipitation was washed and dried in the oven at 110°C at least for 24 hours.

The thin layer on glass sheets from both carbonation methods and white precipitates from air bubbling carbonation were investigated by SEM (JEOL JSM-6480) to observe the crystal habit. Phases of samples were characterized by XRD (Bruker D8, Cu K_{α})

Results and Discussion

Static Surface Carbonation

Saturated clear $Ca(OH)_2$ solutions started to form a very thin layer at the surface within a few minutes. We observed that there was a white zone in the solution around the surface and the thin layer was formed at the surface. This confirms the direct carbonation between Ca^{2+} in the solution and CO_2 in air. When this thin layer was left on the surface for a few days, it turned into a hard white crust.

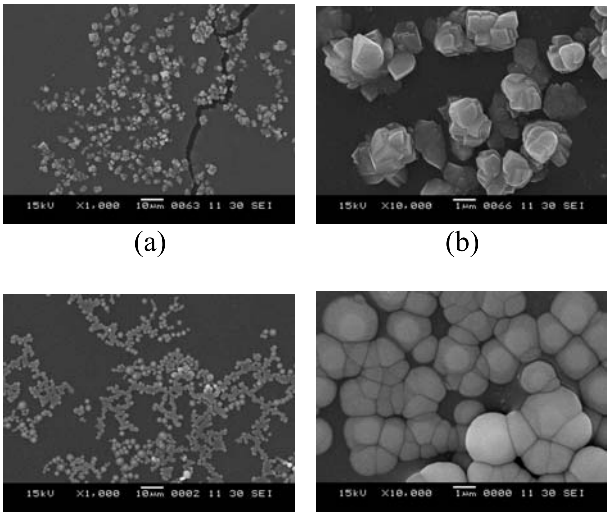

(a) (b) (c) (d)

Figure 1. Thin layers after carbonation at 5 min from S-0.01 (a, b) and S-0.2 (c, d)

After static surface carbonation at 5 min, the thin layers from S-0.01 and S-0.2 showed the different patterns (Figure 1). The layer from S-0.01 showed the tiny separated particles, while the layer from S-0.2 gave the connected globular. The layers had grown as carbonation time increased in different patterns for both saturated solutions (Figure 2). However, we found spherulite crystals in S-0.2 (Figure 2(d)).

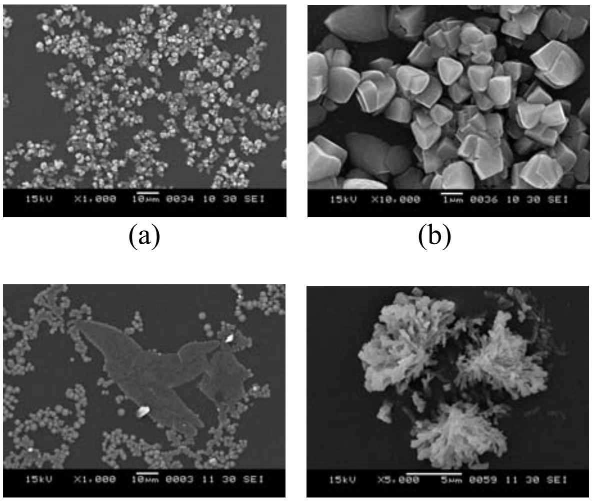

(a) (b) (c) (d)

Figure 2. Thin layers after carbonation at 10 min from S-0.01 (a, b) and S-0.2 (c, d)

The shape of layer from S-0.2 in Figure 1 looks amorphous. However, the XRD pattern of the layer from S-0.2 after 5 min carbonation reveals that the connected globular is calcite (Figure 3).

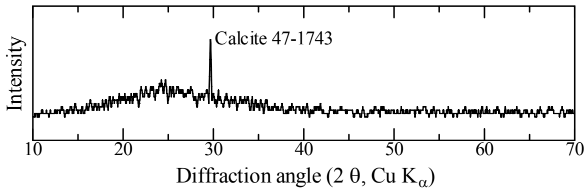


Figure 3. XRD pattern of carbonated layer of S-0.2 at 5 min

The spherulite in S-0.2 grew as carbonation time increased and showed that it was composed of tiny calcite crystals (Figure 4)

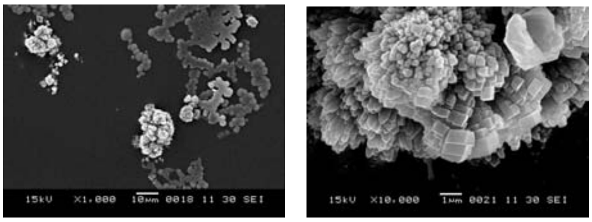

(a) (b)

Figure 4. Thin layer from S-0.2 after 30 min of carbonation. The white particles in (a) were enlarged and showed the tiny calcite crystals in (b)

The crystal on layers from S-0.01 grew as carbonation time increased and did not change the habit as shown in Figure 5 (a) and (b) But the crystal on layers from S-0.2 showed some interesting features (Figure 5 (e), (f)). The phase of the carbonated layers from both saturated solutions, S-0.01 and S-0.2, are calcite (Figure 6).

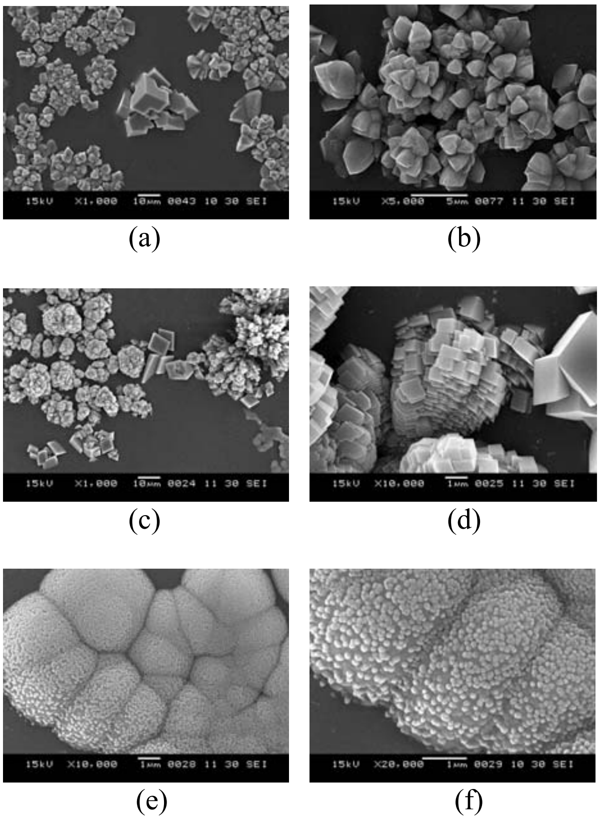

(a) (b)
(c) (d)
(e) (f)

Figure 5. Thin layer from S-0.01 after 1 hour of carbonation (a, b), and thin layer from S-0.2 after 1 hour of carbonation (c-f)

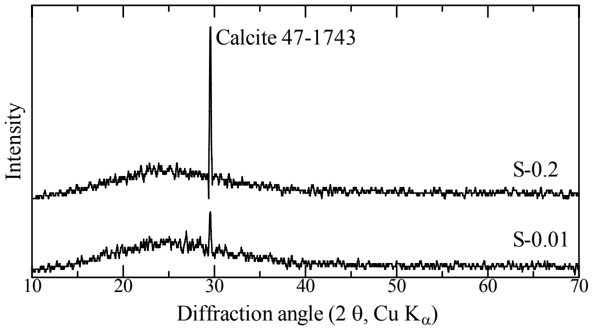


Figure 6. XRD patterns of carbonated layers after 20 min of carbonation

After very long carbonation times, layers from S-0.01 and S-0.2 demonstrated another crystal habit of the calcite (Figure 7)

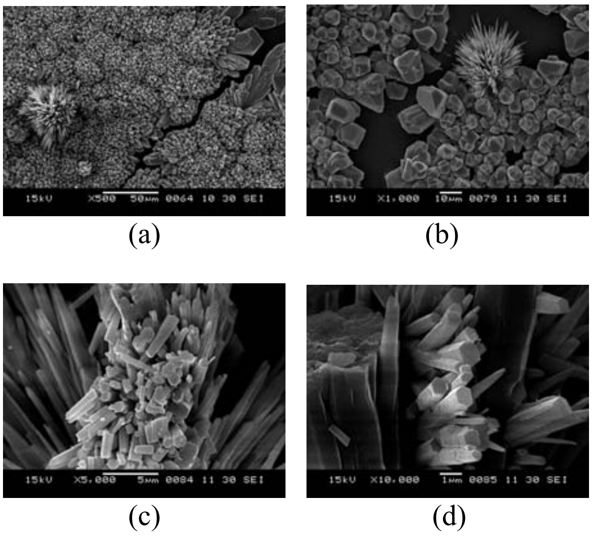
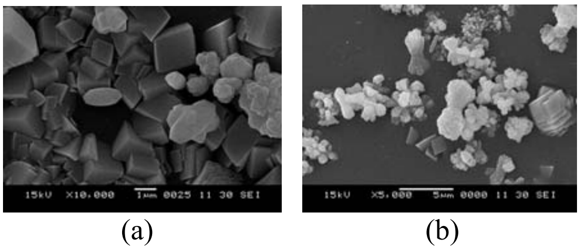

(a) (b)
(c) (d)

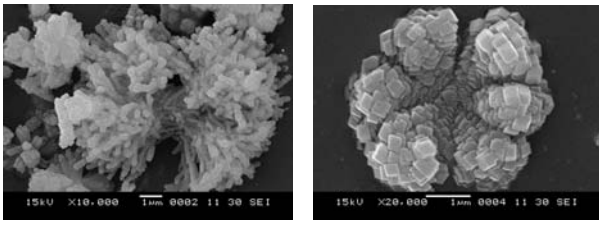
Figure 7. (a) The layer of S-0.2 after 5 days of carbonation and (b) – (d) the layer of S-0.01 after 24 hours of carbonation; the long whiskers show hexagonal shape of calcite crystals.

Air Bubbling Carbonation

The clear saturated solution of S-0.01 and S-0.2 started to get turbid after air bubbling of less than 5 min with stirring action and without stirring action. To test the effect of direct carbonation between atmosphere and solution surface, the clear saturated solution of S-0.2 was stirred vigorously without air bubbling. The solution started to get turbid after stirring of about 50 min. During stirring, formation of a thin carbonated layer on solution surface did not occur. In this work, the maximum carbonation time is 1 hour; therefore, we assume that the diffusion of CO_2 from the atmosphere through the solution surface does not have an effect on this experiment, and $CaCO_3$ in the suspension had formed via the carbonation from CO_2 in air bubbles flowing in the solution.

The precipitates from S-0.01 after 5 min show the rhombohedral crystals of calcite (Figure 8(a)) while S-0.2 resulted in rhombohedral and spherulite at the same carbonation time. Under higher magnification, we found that spherulite was also composed of tiny rhombohedral calcite crystals.

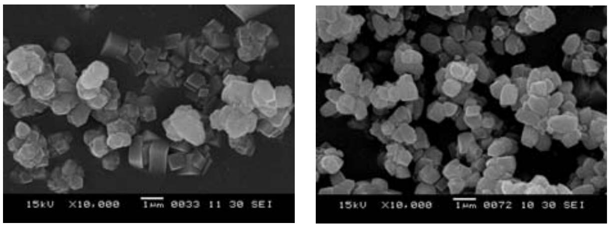

(a) (b)



(c) (d)

Figure 8. (a) The precipitate from S-0.01 and (b) – (d) the precipitate from S-0.2; after 5 min of air bubbling carbonation

As the air bubbling carbonation times were increased, both solutions, S-0.01 and S-0.2, were more turbid and the amounts of precipitate were increased. The crystal habit of precipitates from S-0.01 were not effected by air bubbling carbonation time. The particle size of 1-hour carbonation time is not larger than that of 10-min carbonation time due to the movement of air bubbles, and stirring action dispersed the $CaCO_3$ particles during carbonation and prohibited the crystal growth.

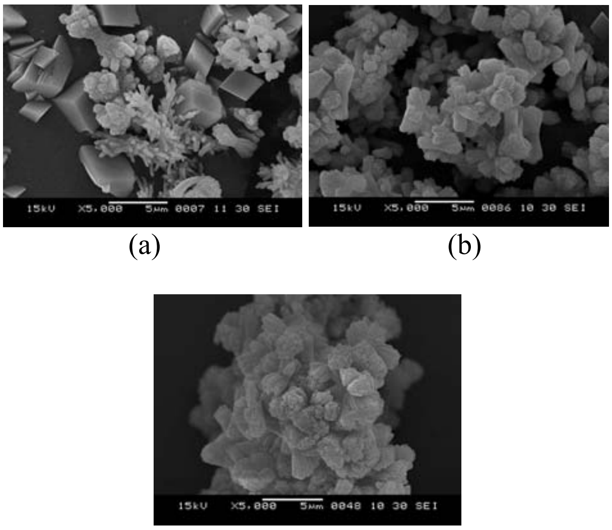


(a) (b)

Figure 9. Precipitate from S-0.01 after air bubbling (a) 10 min and (b) 1 hour

However, the precipitates from S-0.2 at longer air bubbling carbonation time yield both rhombohedral and spherulite shape, and crystal growth occurred after longer carbonation time (Figure 10). This might be the effect of crowded Ca^{2+} in supersaturating solution.

The phase of white precipitates from S-0.01 and S-0.2 after various carbonation times are shown in Figure 11 and 12. The precipitates indicate the main peak of calcite from 5 min carbonation. They also reveal the complete characteristic of calcite at 30 min for both solutions (the XRD patterns are not shown here). Though the spherulite occurred after 30 min and 1 hour of carbonation, the XRD pattern in Figure 12 confirms that all spherulite crystals are also calcite.



(a) (b)

(c)

Figure 10. Precipitates from S-0.2 after (a) 10 min, (b) 30 min and (c) 1 hour of carbonation time

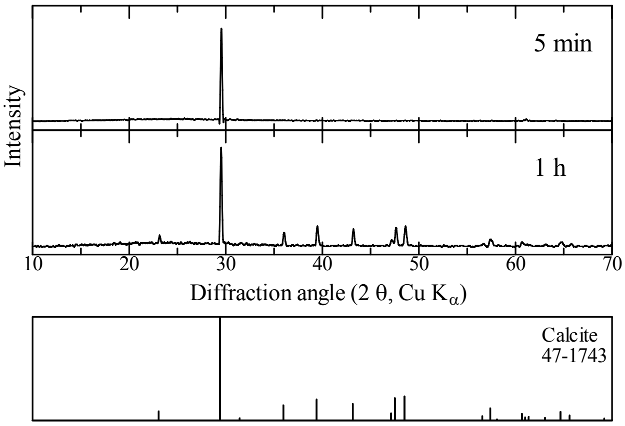


Figure 11. XRD patterns of white particles from S-0.01 after air bubbling carbonation for 5 min and 1 hour

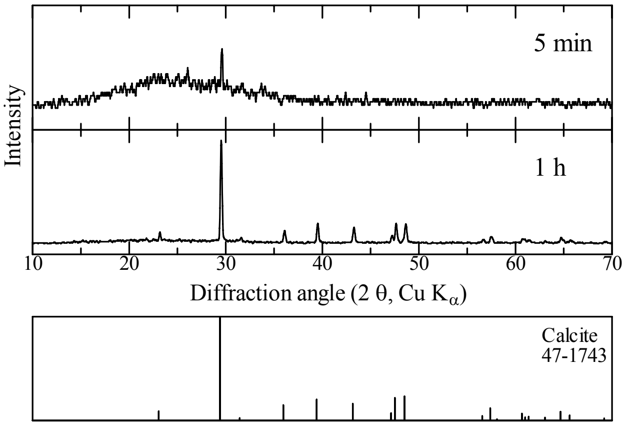


Figure 12. XRD patterns of white particles from S-0.2 after air bubbling carbonation for 5 min and 1 hour

$Ca(OH)_2$ slightly dissolves in water. This finding can be observed from pH change of water after adding $Ca(OH)_2$. Though we prepared $Ca(OH)_2$ solution at a concentration lower than 0.01 mol, $Ca(OH)_2$ particles did not completely dissolve at room temperature. The different crystal habits after the carbonation process confirm that the saturated solution, S-0.01 and S-0.2 contained different amounts of Ca^{2+}. This work clarifies that $Ca(OH)_2$ solution is very sensitive to reaction with CO_2 even at very low concentrations of CO_2 in the air (0.027-0.036 % v/v).(9) In our previous work Mungsawat and Homchuen (2007) we obtained calcite, aragonite, and vaterite at 5 min precipitation process from 0.01 mol $CaCl_2$ solution before aragonite and vaterite transformed into calcite within 2 hours. Though S-0.01 contained less than 0.01 mol of Ca^{2+}, Ca^{2+} in $Ca(OH)_2$ solution was fully saturated. Therefore it tends to form the most stable form of $CaCO_3$ – calcite immediately, and no metastable phase (aragonite and vaterite) was found in 5-min carbonation.

S-0.01 and S-0.2 are saturated Ca^{2+}-containing solutions. However, as seen from the carbonation process of both solutions, $CaCO_3$ shows different crystal habits. The irregular surface structure of calcite in Figure 5(f) is possibly due to the very high concentration of Ca^{2+} from the solution around the fresh crystallized surface created nucleation sites. The spherulite polycrystalline generally occurred under high driving force condition.(1) The supersaturation state of S-0.2 can cause the spherulite polycrystalline as shown in Figures 8 and 10.

Conclusions

The saturated solution from $Ca(OH)_2$ is reactive to a very low amount of CO_2 in the air and formed calcite immediately after crystallization. No metastable phase of $CaCO_3$ was found during crystallization at all. The crystal habit of calcite was affected by the amount of saturated Ca^{2+} ion the solution, carbonation methods (static and turbulent conditions), and carbonation time. The supersaturation state of the starting solution (S-0.2) yielded non-rhombohedral calcite. Under static condition (static surface carbonation), S-0.2 reacted with CO_2 and gave connected globular layer while S-0.01 (normal saturated solution) gave separated tiny calcite. Under turbulent condition (air bubbling carbonation), S-0.01 formed rhombohedral calcite while S-0.2 yielded rhombohedral calcite and spherulitic calcite. The carbonation time had no effect on the crystal habit from S-0.01. But the crystal habit from the carbonation of S-0.2 changed as carbonation time increased. This was probably due to the supersaturated state of the solution, which caused the crowded Ca^{2+} ion at the vicinity of the crystal surface.

Acknowledgements

This research work was financially supported by Ratchadapisek Sompoj Endowment, Chulalongkorn University. Mr. Jeerawat Ariyaprayoon would like to thank the Research Unit of Advanced Ceramics, Department of Materials Science, Faculty of Science, Chulalongkorn University, for financial support during his studies.

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