Preparation of Needle like Aragonite Precipitated Calcium Carbonate (PCC) from Dolomite by Carbonation Method

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ABSTRACT

In this paper, we have developed a simple, new and economical carbonation method to synthesize a pure form of aragonite needles using dolomite raw materials. The obtained aragonite Precipitated Calcium Carbonate (PCC) was characterized by XRD and SEM, for the measurement of morphology, particle size, and aspect ratio (ratio of length to diameter of the particles). The synthesis of aragonite PCC involves two steps. At first, after calcinated dolomite fine powder was dissolved in water for hydration, the hydrated solution was mixed with aqueous solution of magnesium chloride at 80°C, and then CO₂ was bubbled into the suspension for 3 h to produce aragonite PCC. Finally, aragonite type precipitated calcium carbonate can be synthesized from natural dolomite via a simple carbonation process, yielding product with average particle size of 30-40 μm.

Key words : *Precipitated calcium carbonate (PCC), Carbonation, Dolomite, Aspect ratio*

1. Introduction

Precipitated Calcium carbonate (PCC) is a chemical industrial product that is extensively used in industries such as plastics, rubber, paint, printing ink, weaving, toothpaste, make-up, and food.^{1,2)} It has three polymorphs, calcite, aragonite, and vaterite, which have trigonal, orthorhombic/needle, and hexagonal crystal systems, respectively. Different polymorphs of CaCO₃ can have different functions as additives. Needle like aragonite has a reinforcing effect on rubber and plastics; spherical CaCO₃ has a significant impact on the brightness and transparency of ink.³⁾ Therefore, controlling the structure and morphology of CaCO₃ is an important subject for research and development scientists. Many approaches have been studied to control the phases and morphologies of PCC to meet the demands of practical applications.⁴⁻⁶⁾

Synthesis of PCC has mostly been performed using good quality carbonate rocks with a high percentage of CaCO₃.⁷⁾ However, some common carbonate rocks contain dolomite as the prominent rock forming mineral.⁸⁾ Although there are numerous dolomite mines present worldwide, synthesis of PCC using dolomite has not yet been reported. Dolomite is composed of CaMg(CO₃)₂⁹⁾ and is a valuable source of PCC nanoparticles after Ca and Mg components are separated from it. In this study, calcium is easily extracted from natural dolomite and needle-like aragonite CaCO₃ is successfully

prepared via a simple carbonization process. The effects of carbonization time, temperature, and CO₂ flow rate on the aragonite crystal morphology are explored. The experimental conditions used to prepare needle-like aragonite CaCO₃ are discussed.

2. Experimental Procedure

The starting materials, MgCl₂ with 95% purity (Junsei Company, Japan), Dolomite powder (Gangwon-do, South Korea), and pure CO₂ gas were supplied by Jeil Gas Company, South Korea.

In this study we used dolomite powder from Gangwon-do in South Korea as the raw material; powder was calcined at 800°C for 12 h in a shaft kiln. The mineral phase content of the calcined dolomite powder was calculated and found to be 47.22% CaO, 41.6% MgO, 17.2% Ca(OH)₂, and 2.5% CaCO₃.

The calcined raw materials were mechanically grinded for 1 h until the particle size was less than 100 μm. This dolomite fine powder was processed to hydration with distilled water at 80°C for 1 h and filtered with 200 mesh; then, the solution was washed three times with distilled water and filtered with 325 mesh; filtrate was collected and dried at 80°C for 12 h. The main chemical composition of the dried dolomite powder was as follows: 55.9% Ca(OH)₂, 34.2% MgO, and 2.2% Mg(OH)₂. The chemical reaction mechanism in water can be described in equation (2).

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After hydration and filtering processes, calcium carbonate was synthesized by a carbonation method in which gaseous CO_2 was injected into a Ca^{2+} ion solution to precipitate calcium carbonate. In this process, 32 g/L of calcium-rich dolomite dried powder was added to 0.6M magnesium chloride solution and gaseous CO_2 was injected into a suspension of MgCl_2 - Ca^{2+} rich dolomite powder at pH-8, as shown in Fig. 1. The carbonation reaction started from the hydration of carbon dioxide and the ionization of calcium hydroxide, as shown in Equations (5) and (6). The calcium and carbonate ions reacted together to form a calcium carbonate precipitate. The effects of carbonization temperature, reaction time, and carbon dioxide flow rate on the morphology of the resulting product were investigated.

Reaction mechanism:

Supersaturation (S_I) of the solution with respect to calcium carbonate,

$$S_I = \frac{(Ca^{2+})(CO_3^{2-})}{K_{sp}} > 1 \quad (10)$$

where (Ca^{2+}) and (CO_3^{2-}) are the activities of calcium and carbonate ions in the solution, respectively, and K_{sp} is the

thermodynamic solubility of the aragonite product.

During the carbonation process experiments, metastable crystalline forms of CaCO_3 such as aragonite and vaterite were not identified in the X-ray diffraction spectra.

3. Results and Discussion

3.1 Effect of temperature

Temperature is one of the key determining factors of the formation of aragonite. The first experimental measurement of the temperature coefficient was found on the basis of the inorganic precipitation of aragonite or aragonite-calcite mixture from sea water in a temperature range of 0°C–80°C.¹⁰⁾ Temperature and aging time affected the formation of polymorphs. Although the stability of the aragonite growth units superimposed on each nucleus is lower than that of calcite because the competition of calcite growth units is smaller, the nucleation of aragonite has priority. Once aragonite nucleation starts, because of the small size of the nuclei, the driving force of nuclei disappearance is less than the minimum driving force of nuclei growth, so the nuclei can grow.^{11–12)} Because aragonite is metastable, a certain number of dislocations can be produced during the crystal growth process; these dislocations are able to reduce the force field and reduce the free energy of the system.^{13–14)}

Some results show that aragonite can be synthesized at room temperature by applying the Kitano method to a supersaturated solution of calcium bicarbonate in the presence of additives or self-assembled monolayers^{15–19)}; synthesis has even been achieved at slightly elevated temperatures.²⁰⁾ Uniform needle like aragonite particles with a mean length of 45 μm and aspect ratio of ~ 10 were obtained after 3hr of aging in a mixed solution containing 0.25 mol dm^{-3} CaCl_2 and 0.75 mol dm^{-3} urea at 90°C by homogeneous precipitation process without pH adjustment.²¹⁾

The effect of temperature on carbonation in the synthesis of CaCO_3 product from dolomite was investigated by bubbling CO_2 gas with a concentration of 40% through the CaCl_2 - NH_4Cl reaction system for 0.5 h at 25°C, 40°C, 60°C, and 80°C; the CaCO_3 was isolated after aging time of 12 h. When the carbonization temperature was 80°C, the content of the product was aragonite 56.96%, calcite 31.56%, and vaterite 11.49%. This shows that an increased carbonization temperature is not conducive to the formation of aragonite.²²⁾ Many researchers have investigated the dependency of temperature on the formation of aragonite PCC and aragonite whiskers.^{23–29)}

Aragonite is a thermodynamically metastable crystalline phase. It can easily transform into the stable calcite crystal phase in aqueous solution. However, the present work reveals needle like aragonite synthesis via the combining of gaseous CO_2 that is injected into an aqueous mixture solu-

Fig. 1. Aragonite synthesis from dolomite by carbonation method.

Fig. 2. XRD analysis of needle shaped aragonite at different carbonation temperatures (60, 70, and 80°C).

tion of Dolomite and $MgCl_2$ solutions at different temperatures (60, 70, and 80°C). The aragonite formation increased as the carbonization temperature increased up to 80°C; needle like aragonite is formed at 80°C in a 50 cc carbon dioxide flow rate, which can be clearly observed in the XRD analysis results shown in Fig. 2 and Fig. 3, which show the morphology of aragonite needles obtained by scanning electron microscopy.

3.2 Effect of reaction time:

Many reports have attempted to analyze the different time effects on the carbonation process; Ge et al.²²⁾ reported that when the carbonization time was 0.5 h, calcite and vaterite were obtained. However, the calcite phase transformed into aragonite and vaterite when the carbonization time was extended to 1 - 1.5 h. When the carbonization time was extended to 2 h, pure aragonite was synthesized and the aragonite content gradually increased, the vaterite content first increased and then decreased, and the calcite content decreased with increasing carbonization time. When

Fig. 4. XRD analysis of aragonite needles at different carbonation time durations (2, 2.5, and 3 h).

the carbonization time reached 3 h, the aragonite content was 81.35%, calcite was 4.56%, and vaterite was 14.09%. Extending the carbonization time aids the formation of aragonite. After aging for 3 h, characteristic diffraction peaks of aragonite appeared in the system. As the aging time lengthened further, the intensities of the aragonite diffraction peaks increased. It can be concluded that the longer aging time increased the content of aragonite in the carbonation process.

The present study attempts to analyze the different time effects on the carbonation process. In this process we observed needle like aragonite synthesis via a combining of gaseous CO_2 that was injected into the aqueous mixture solution of dolomite and $MgCl_2$ solution for different time durations of 2, 2.5, and 3 h at constant temperature. We obtained aragonite needles after 3 h reaction time via a carbonation process; this was confirmed by XRD results (Fig. 4) and scanning electron microscopy (SEM) images (Fig. 5), which show the morphology of the aragonite needles.

Fig. 3. Effect of different carbonation temperatures on the morphology of aragonite needles, determined by scanning electron microscopy: (a) 60°C, (b) 70°C, and (c) 80°C.

Fig. 5. Effect of different carbonation time durations on the morphology of aragonite needles, determined by scanning electron microscopy (a) 2 h, (b) 2.5 h, and (c) 3 h.

3.3 Effect of carbon dioxide (CO₂) flow rate:

The driving force for CaCO₃ precipitation is supersaturation, determined by the product of the ionic concentration of calcium and carbonate ions. Precipitation involves four steps: (i) dissolution of Ca(OH)₂, (ii) mass transfer between the CO₂ phase and the water phase and the formation of carbonate ions, (iii) chemical reaction, and (iv) crystal growth that is relatively highly absorbed in water with respect to other similar compounds.³⁰⁾

This process can be explained as resulting from the electrostatic forces of water molecules, which can polarize CO₂ molecules, increasing their ability to penetrate the water phase. On the other hand, the reagent CO₂ must enter the phase containing the Ca²⁺ ions, and the mass transport resistance is therefore also a very important parameter. The resistance of CO₂ to penetrating through water can be stated in terms of viscosity. Compressed CO₂ is to some extent more viscous than atmospheric CO₂, but still considerably less viscous than water. After CO₂ is absorbed in water it hydrates to form CO₂(aq) or carbonic acid (H₂CO₃) (Eq. 13); for the most part, H₂CO₃ subsequently yields bicarbonate ions (HCO₃⁻) (Eq. 14) and carbonate ions (CO₃²⁻) (Eq. 15). These transformations are fast but only about 1% of the absorbed CO₂ is transformed into carbonate ions. *K*₄, *K*₅, and *K*₆ are the equilibrium constants and *k*₄ and *k*₅ are the velocity constants (s⁻¹) at 298K.³¹⁾

The carbonation process was carried out in an open vessel; we investigated different CO₂ gas flow rates in a range of 40 mL/min to 100 mL/min at 80°C. However, after a certain limit, increasing the flow rate no longer had any effect; this was due to the higher mobility of CO₂ molecules with respect to water, resulting in CO₂ bypassing the solution. A 50 mL/min CO₂ gas flow rate was suitable for the unreacted calcium hydroxide crystals to become embedded and for another calcium carbonate polymorphic phase to appear; these results can be clearly observed in the results of the XRD analysis at different CO₂ flow rates, as shown in Fig. 6 and Fig. 7, which provide scanning electron microscopy (SEM) images of needle shaped aragonite calcium carbonate at different CO₂ flow rates.

4. Conclusions

The production of precipitated calcium carbonate, PCC, by a carbonation process of slaked lime was performed in a bench-scale glass reactor. The carbonation process was

Fig. 6. XRD analysis of aragonite needles at different CO₂ flow rates (40, 50, 70 and 100 ml/min).

Fig. 7. Effect of different CO₂ flow rates on the morphology of aragonite needles by scanning electron microscopy: (a) 40 ml/min, (b) 50 ml/min, (c) 70 ml/min, and (d) 100 ml/min.

demonstrated with the chosen range of process parameters (temperature, CO₂ gas flow rates, and reaction time); calcite particles/crystals with different characteristic morphologies (needle like aragonite) were produced. Needle-like aragonite was synthesized from dolomite via a simple carbonization procedure. Aragonite needles with width of 3 μm and length 40 μm were formed by feeding 50 ml/sec CO₂ gas into MgCl₂+Ca(OH)₂ solution from dolomite at 80°C for 3 h carbonation process without any additives. The morphology of the CaCO₃ is sensitive to the carbonization time, the CO₂ flow rate, and the carbonization temperature. Increasing the reaction time and the temperature of the carbonization process promotes the formation of CaCO₃ with needle like morphology.

This study demonstrated that the temperature and the CO₂ gas flow rates have significant effects on the average particle size, precipitation, and the morphology of calcium carbonate crystals. Needle shaped aragonite crystals having strong potential for industrial applications, including as

filler in plastics and papermaking, can be synthesized by a carbonation process with optimized conditions.

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