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# A Brief review of Aragonite Precipitated Calcium Carbonate (PCC) Synthesis Methods and Its Applications

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**Abstract** – This article provides an exclusive overview of the synthesized aragonite precipitated calcium carbonate and its applications in various fields. The last decade has seen a steady increase in the number of publications describing the synthesis, characterization and applications of calcium carbonate morphologies. Mainly, two kinds of processes have been developed for the synthesis of aragonite precipitated calcium carbonate under controlled temperature, concentrations and aging, and the final product is single-phase needle-like aragonite precipitated calcium carbonate formed. This review is mainly focused on the history of developed methods for synthesizing aragonite PCC, crystal growth mechanisms and carbonation kinetics. Carbonation is an economic, simple and ecofriendly process. Aragonite PCC is a new kind of functional filler in the paper and plastic industries, nowadays; aragonite PCC synthesis is the most exciting and important industrial application due to numerous attractive properties. This paper describes the aragonite PCC synthetic approaches and discusses some properties and applications.

Key words: Calcium carbonate, Aragonite, Carbonation, Solution process, Synthesis

## 1. Introduction

Calcium carbonate ($CaCO_3$), as one of the most abundant biominerals, has attracted considerable attention not only as an important building material in organisms but also a widely used filler in paints, plastics, rubber, and paper [1-3]. Calcium carbonate crystallization has been widely studied for decades, receiving both scientific and industrial interest. The properties and applications of $CaCO_3$ depend on the morphology, polymorph, particle size, and chemical purity of the crystals. In general, $CaCO_3$ has been divided into three different anhydrous polymorphs: calcite, aragonite, and vaterite with rhombohedral, needle-like and hexagonal structures, respectively, as shown in Fig. 1. Calcite form is the most stable and abundant material in the earth's crust and aragonite form is metastable under ambient temperatures and high pressures [4,5], whereas vaterite is the least stable phase since it slowly recrystallizes to become calcite in contact with water. These forms of calcium carbonate can be prepared by carbonation process with suitable conditions [6].

Aragonite is the main ingredient of nacre and mollusk shells. The most common structure of aragonite is rod-like [7-9]. Other aragonite morphologies, such as multilayered [10], pseudo hexagonal [11], needle-like [12], and dendrite-like [7], have also been successfully fabricated. A constant composition environment is developed for calcium carbonate polymorphs and studied the various factors which affects the formation of polymorphs [13]. In recent years, more efforts have been devoted to understand how the organic additives affect the crystal polymorph and structural features.

Aragonite's crystal lattice differs from that of calcite, which results in different crystals having needle shape and its physical properties depend on the needles' aspect ratio (length to width ratio) within a range of 3:1 and 15:1, based on which it can exhibit either acicular aragonite or needle/spindle-shaped aragonite. Aragonite has a specific gravity of 2.95, whereas calcite has 2.71. The orthorhombic-shaped and denser aragonite tends to be more adherent to heat transfer surfaces than the hexagonal-shaped calcite [14,15]. Needle-like aragonite was obtained exclusively in U-rich layers and re-crystallized [16]. Aragonite can now be manufactured in crystal sizes up to needle lengths of greater than 50 μm. The larger size of aragonite can be used as a filter aid in cosmetics, as filler, and as a replacement, for mineral powders. The control of the crystal shape and morphology of $CaCO_3$ is important for industrial application. Most of the studies reveal that the properties of aragonite, such as the size and morphology, are strongly dependent on the preparation methods and the respective conditions.

The main purpose of this review is to provide a detailed investigation of the methods related to synthesis of aragonite PCC, the factors involved for the formation of aragonite and its wide range of advantageous applications in the paper industry, rubber industry and recently in the automotive industry (car bumpers) as filler for polyolefin and polypropylene resins.

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‡ This article is dedicated to Prof. Choon Han on the occasion of his retirement from Kwangwoon University.

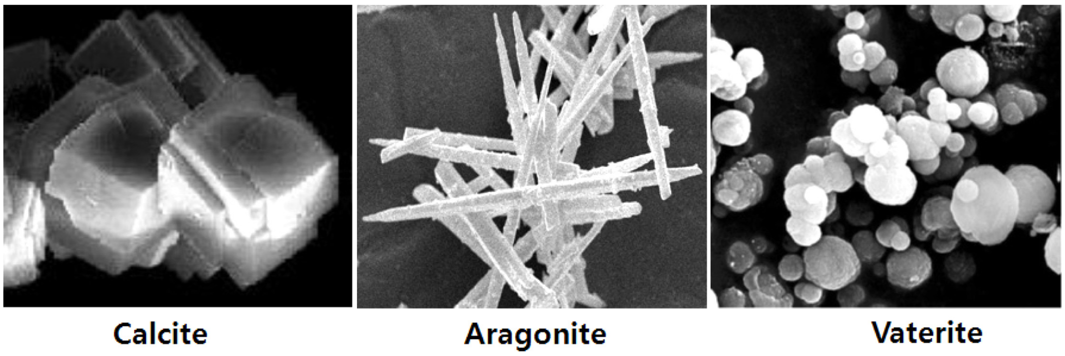
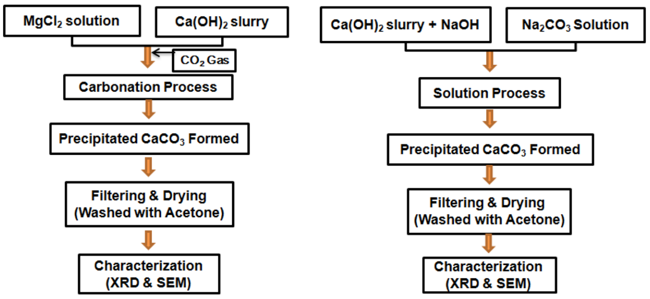


**Fig. 1.** $CaCO_3$ **polymorphs (Source: Modified figure adapted from reference-4).**

## 2. Developing Methods for Aragonite Synthesis

Generally, aragonite is synthesized by two methods: carbonation process [17-20], and solution process [21,22], as shown in Fig. 2. Among which, carbonation is being widely used because of its industrial importance. Extensive research has been done based on synthesis of calcium carbonate for many decades in water systems. Many researchers have developed a number of methods for the production of aragonite [23-39]. To overcome the drawbacks of the above existing chemical methods, they developed a novel process for production of aragonite PCC in the presence of active agent. In this process, which possesses reacting aqueous calcium hydroxide slurry with a gas selected from carbon dioxide, conditions such as temperature, pH range and high shear mixing speeds such that the desired product is obtained.

Amorphous calcium carbonate synthesis of by carbonation process was reported in 1996; in this mechanism is involved the calcium hydroxide suspension into $CO_2$ [40]. Ahn et al. [41,42] reported that the synthesis of aragonite by carbonation process has no relation with the pH value; only the molar ratio of $MgCl_2/Ca(OH)_2$ is required such that the concentration of $Mg^{+2}$ ion appropriate range (0.1~0.26 mol/L) and the $Ca^{+2}$ ion concentration is below (0.25 mol/lit), which is most suitable for the formation of needle-like aragonite as shown in Fig. 3 and Fig. 4. This shows the XRD results corresponding to the experimental conditions in Table 1, at the reaction temperature of 80 °C, if the concentration more than that the calcite will appear. In 2004 was reported the synthesis of calcium carbonate by carbonation reaction of $Ca(OH)_2$ slurry with $CO_2$ gas at 80 °C monophasic calcite crystals phase was obtained; however with increasing the addition of $MgCl_2$, calcite phase gradually decreased while aragonite crystal phase increased, due to the $Mg^{2+}$ ions substituted to $Ca^{2+}$ ions site of calcite lattice and forming magnesium calcite; it led to distorted calcite structure and the aragonite crystal growth was formed [43]. Similarly, $Na^+$ ions also were substituted into $Ca^{2+}$ ions site, then disturbed the growth of calcite, and while proceeding the crystal growth in a cer-



**(a). Carbonation process** **(b). Solution process**

**Fig. 2.** $CaCO_3$ **synthesis processes: (a) Carbonation process, (b) Solution process (Source: Modified figure adapted from reference-19, 21).**

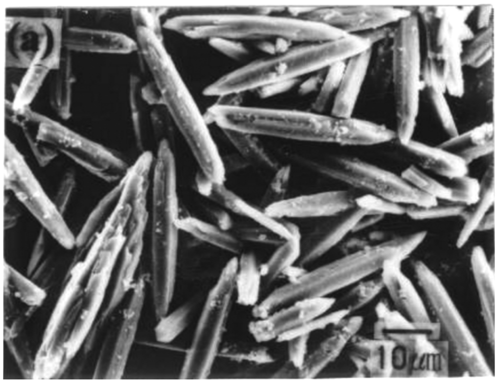


**Fig. 3. SEM photographs of aragonite for the conditions in Table-1, batch 4 (Source: Modified figure adapted from reference-42).**

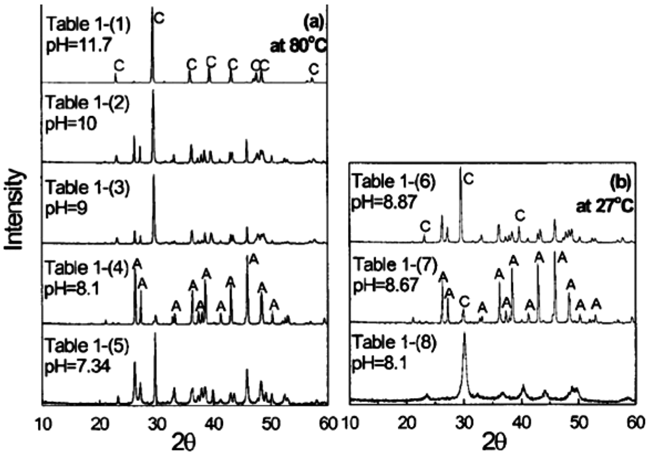


**Fig. 4. XRD results of precipitates at the reaction temperature of (a) 80 °C and (b) room temperature for the experimental condition in Table-1 (Source: Modified figure adapted from reference-42).**

**Table 1. Experimental conditions and ion concentrations, when the amount of $Ca(OH)_2$ is fixed to 0.2 mol (Source: Adapted from reference-42)**

| Batch No. | T (°C) | pH | Starting Materials (mol/L) | | Ion Concentration (mol/L) | |
|---|---|---|---|---|---|---|
| | | | $Ca(OH)_2$ | $MgCl_2$ | Ca | Mg |
| 1 | 80 | 11.7 | 0.2 | 0 | 0.015 | 0 |
| 2 | 80 | 10.0 | 0.2 | 0.15 | 0.150 | 0.00016 |
| 3 | 80 | 9.0 | 0.2 | 0.17 | 0.140 | 0.005 |
| 4 | 80 | 8.1 | 0.2 | 0.4 | 0.162 | 0.255 |
| 5 | 80 | 7.3 | 0.2 | 0.8 | 0.170 | 0.502 |
| 6 | 27 | 8.9 | 0.2 | 0.4 | 0.144 | 0.189 |
| 7 | 27 | 8.7 | 0.2 | 0.8 | 0.146 | 0.585 |
| 8 | 27 | 8.1 | 0.2 | 1.36 | 0.140 | 1.160 |

tain direction and promoting the formation of aragonite [44]. Aragonite forms crystals having a length/width ratio (aspect ratio) in the range between >1:1 and 100:1 (in particular of the length/width ratio-10), where the aragonite forms long, thin needles. Therefore, aragonite having high aspect ratio may be denoted as needle shaped crystals [45]. The effect of aluminum ions contained in $3CaO\text{-}Al_2O_3\cdot 6H_2O$ enhanced the formation of aragonite synthesis by carbonation process [46].

The formation of precipitated calcium carbonate (PCC) in pure ethanol as the solvent was possible without leaving $Ca(OH)_2$ as reactants; among them calcite was first precipitated from the carbonation in bulk solution as in the pure water, while the aragonite and vaterite might have been synthesized via local carbonation occurring in the surface of the $Ca(OH)_2$ grain following the bulk carbonation in the solution. It shows the possibility of formation of PCC in pure ethanol not as small additives, but as the main solvent to precipitate a variety of $CaCO_3$ via carbonation reaction [47]. The formation behavior of precipitated calcium carbonate polymorphs was investigated in three different super saturation levels, because the most easily adjustable and influential variable determining supersaturation is the ion concentration of the major reactants $Ca^{2+}$ and $CO_3^{2-}$, the supersaturation can be adjusted by changing the ion concentration of these two ions. At high supersaturation, vaterite was mainly synthesized even though some calcite was mixed. It was realized that vaterite was mainly synthesized in the lowest region of nucleation energy, that is, the highest nucleation rate among three polymorphs. Secondly, at medium supersaturation, calcite was formed primarily. This result is because that supersaturation in this reaction system was lowered together with a lowered nucleation rate, and the free energy for stable nucleation finally passed over the range of free energy for nucleation of the vaterite. Lastly, at low supersaturation, aragonite predominated. At this point, the addition of NaOH to adjust supersaturation lowered the solubility of $Ca(OH)_2$, a main reactant by common ion effect. The addition of NaOH reduced $Ca^{2+}$ ion concentration in the solution. As the reaction continued, the formation yield of aragonite was increased, whereas that of calcite decreased continually. It is considered that lower supersaturation at the early stage of reaction and sufficient aging time would be necessary to obtain single phase aragonite [48].

A higher formation of aragonite yield of above 98% was obtained by the adding of the $Mg^{2+}$ ion in a 0.2 M $Ca(OH)_2$ - 0.6M $MgCl_2$ - $CO_2$ system at 80 °C. The particle size and aspect ratio increased at a high temperature, a low flow rate of $CO_2$ gas, and a high concentration of $Ca(OH)_2$ slurry. Small-sized aragonite was obtained at a low temperature. The increase in crystal size with the decrease in the $CO_2$ gas flow rate can be explained by the decrease in the nucleation rate, in addition to the increase in the crystal growth rate resulting from the decrease in the dissolution rate to $CO_3^{2-}$ ion [49-51].

### 2-1. Aragonite Synthesis Mechanism:

Generally, calcium carbonate was synthesized by carbonation reaction and the reaction mechanism in water can be described as follows:

$$CO_2 + H_2O \rightarrow H_2CO_3 \rightarrow H^+ + HCO_3^- \rightarrow 2H^+ + CO_3^{2-} \quad (1)$$

$$Ca(OH)_2 \rightarrow Ca^{2+} + 2OH^- \quad (2)$$

$$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3 \quad (3)$$

Overall reaction;

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O \quad (4)$$

The carbonation reaction starts from hydration of carbon dioxide and ionization of calcium hydroxide such as shown in Eqs. (1) and (2). Ionized calcium and carbon dioxide reacted together and calcium carbonate was precipitated.

However in the solution process ($CaCl_2\text{-}Na_2CO_3$, $CaCl_2\text{-}(NH_4)_2CO_3$, $CaCl_2\text{-}K_2CO_3$ system), carbonation reactions can be suggested (as shown in Eqs. (5) and (6))

$$CaCl_2 + Na_2CO_3 \rightarrow CaCO_3 + 2NaCl \quad (5)$$

$$CaCl_2 + (NH_4)_2CO_3 \rightarrow CaCO_3 + 2NH_4Cl \quad (6)$$

$$CaCl_2 + K_2CO_3 \rightarrow CaCO_3 + 2KCl \quad (7)$$

Scanning electron microscope (SEM) and X-ray diffraction (XRD) were used to characterize the morphology and the crystal structure of aragonite.

## 3. Experimental Parameters Affecting on Formation of Aragonite PCC

For a long time, aragonite precipitated calcium carbonate products have been recognized as both performance additives and functional fillers. Calcium carbonates are the major engineered filler, used in plastics, with more than half of the total mineral consumption. Polymorph, morphology and size of precipitated calcium carbonate particles are influenced by several parameters such as temperature, pH, degree of supersaturation, ion concentration and presence of additives. Aragonite precipitated calcium carbonates provide a broad spectrum of sizing and physical attributes required for functional filler in plastic applications.

### 3-1. Effect of Particle Size and Shape

A method was studied of controlling sizes of aragonite type precipitated calcium carbonate comprising the steps of manufacturing various sized calcium hydroxide through the hydration reaction of CaO, which is caustic lime, while changing the solid-liquid ratio of caustic lime and the initial reaction temperature to 10~80 °C stabilizing calcium hydroxide by adding the aqueous solution of sodium carbonate while stirring the suspension in the above stabilizing step; and drying the above suspension of calcium carbonate [22].

As the $Mg^{2+}$ ion concentration increases, the aspect ratio also increases until it attains the concentration range of 71~75 mol% and thereafter decreases. This implies that when the ratio of Mg to Ca exceeds 2.5:1, the growth of aragonite crystals is inhibited in the plane of the *c*-axis as well as in the plane perpendicular to the *c*-axis. It was even seen that when the ratio of Mg to Ca is < 2.5:1, $Mg^{2+}$ ions promoted the growth of the major axis of the needle-like crystals through a selective side-poisoning mechanism. However, when the ratio was above 2.5:1, the selective side-poisoning mechanism was no longer effective, which increased the relative growth of the minor axis increases, consequently decreased the aspect ratio of aragonite.

To investigate the effect of $Mg^{2+}$ ions on the shape of needle-like calcium carbonate, the morphological characteristics of aragonite were determined at various $MgCl_2$ concentrations (33~88 mol%). At a Mg/Ca ratio of 1:2 (33 mol% $MgCl_2$), minute PCC particles were formed, whereas when the Mg/Ca ratio was 3:2-5:1 (60~84 mol% $MgCl_2$), perfectly formed needle-like aragonite crystals were produced; on the other hand, when the ratio was above 5:1 (84 mol% $MgCl_2$), pyramid-shaped aragonite crystals were produced. In particular, when the Mg/Ca ratio was 7.3:1 (88 mol% $MgCl_2$), pyramid-shaped aragonite crystals predominated. From these results it was inferred that a tight constraint on $Mg^{2+}$ ion concentration can control the morphologies of aragonite crystals [52].

Characteristics of nucleation and crystal growth of aragonite PCC in $Ca(OH)_2$-$MgCl_2$-$CO_2$ system via carbonation process were studied. In this process, same aragonite is used as a seed for crystal growth of aragonite. Aragonite, with an aspect ratio ranging from 5~27 and diameter from 3~24 μm, respectively, was grown at a reaction temperature of 80 °C and $CO_2$ flow rate of 50 ml/min. The synthesized aragonite seed is shown in Fig. 5(a), and it was grown up via three step carbonation process, as shown in Fig. 5(b), (c) and (d). The added aragonite seed was used for nuclei in the system and by which aragonite crystal growth was developed. Because aragonite nucleation rate is faster in this supersaturated condition, crystal growth rate could be slower. Also, aragonite secondary nuclei could be expected to grow on continuing reaction. Fig. 5 and Fig. 6 show the changes in the concentration in calcium hydroxide slurry via three step carbonation process; the particle size and the aspect ratio of the synthesized aragonite were increased gradually. Subsequently from the results, it was concluded that the particle size and the aspect ratio of the synthesized aragonite increased under the high temperature and concentration of calcium hydroxide slurry [53].

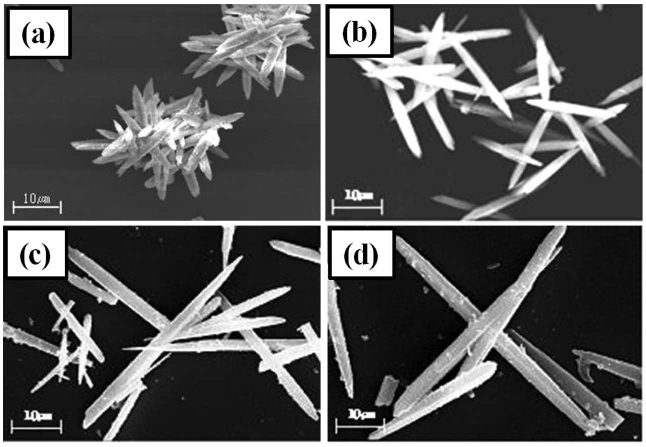


Fig. 5. SEM images of crystal growth aragonite by three step carbonations; (a) seed aragonite (b) 1st carbonation aragonite, (c) 2nd carbonation aragonite, (d) 3rd carbonation aragonite (Source: Modified figure adapted from reference-53).

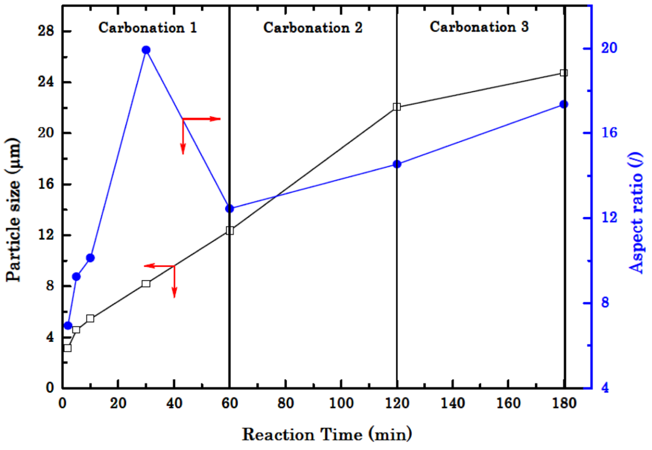


Fig. 6. Change of the growing aragonite particle size and aspect ratio by three steps carbonation (Source: Modified figure adapted from reference-53).

The effects of various factors such as i) effects of surfactants and additives, ii) effect of $CO_2$ flow rate, iii) effect of pH level, iv) effect of temperature during carbonation, and v) effect of initial concentration, on the particle size of precipitated calcium carbonate formed in a wet carbonation process were investigated experimentally. Finally, it was concluded that the particle size depends on $CO_2$ bubble size, $CO_2$ concentration and decreases with these two factors, at higher temperatures (80 °C) particle size will be increased.

### 3-2. Effect of temperature

Temperature is one of the key determining factors in the formation of aragonite. The first experimental measurement of this temperature coefficient was found on the basis of inorganic precipitation of aragonite or an aragonite-calcite mixture from sea water in a temperature range 0~80 °C [54]. Phase equilibrium studies of calcite-aragonite were determined as a function of temperature in the range of 25 to 80 °C at high pressure. The data was obtained from the equilibrium curve of polymorphs calcite and aragonite. The electrical resistance of aqueous solutions was measured for each formed crystal at high temperatures and pressures, respectively [55].

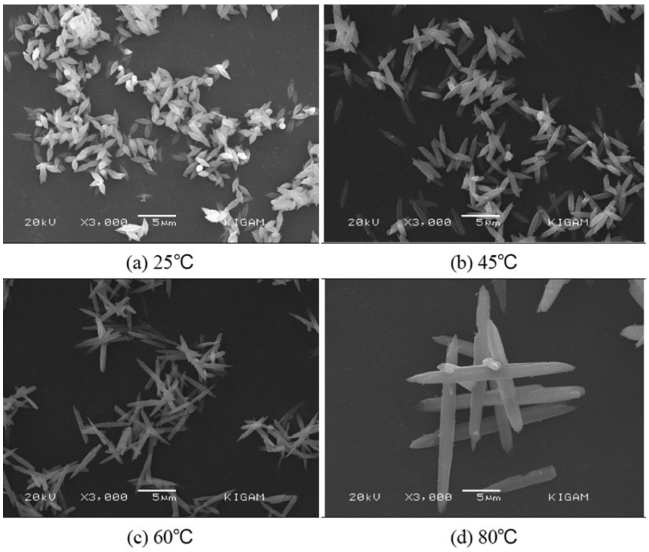
A hydrothermal hot processing technique was developed to solidify aragonite type of calcium carbonate at lower temperatures, and therefore its application as solid material was increased [56]. Temperatures and aging time were affected on the formation of polymorphs. Calcium carbonate in direct precipitation method was prepared by using calcium nitrate and sodium carbonate without controlling the solution pH the composition, and high fraction aragonite was isolated at temperature above 50 °C with digestion time 0.1 h [57].

Aragonite was synthesized by co-precipitation of $Sr^{2+}$ and soluble calcium salts over 3~100 °C [58,59]. Aragonite was precipitated below 30 °C through slowly decomposing the mixed solution of calcium bicarbonate and $Mg^{2+}$ [60]. It was for the first time that aragonite was synthesized by the direct precipitation method at 70 °C [61].

Some results show that aragonite is synthesized at room temperatures by applying Kitano method from a supersaturated solution of calcium bicarbonate in the presence of additives or self-assembled monolayers [62-64], and some are even achieved at slightly elevated temperatures [65]. Uniform needle-like aragonite particles with a mean length of 45 μm and aspect ratio of ~10 were obtained, at 3 h. 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 [66].

Many researchers have investigated the dependency of temperature on the formation of aragonite PCC and aragonite whiskers [13,18,67-69]. Different types of aragonite crystals were synthesized by combining aqueous solution of $CaCl_2$ and $Na_2CO_3$ under ambient reaction conditions. A plausible mechanism was proposed for the formation of aragonites based on the phase transformation behavior during the synthesis. This preparation technique involved double decomposition of aqueous solutions of $CaCl_2$ and $Na_2CO_3$ at room temperature without any use of additives or crystal habit modifier, which leads to the formation of aragonite with different shapes. From the result, two reaction parameters showed significant effect on the morphology of aragonite phase: (i) concentration of reagents and (ii) temperature of the reaction. These aragonite crystals were found to be stable in solid states for a long time [70]. Similarly, 0.1M solutions of $CaCl_2$ and $Na_2CO_3$ were simultaneously injected into a glass reactor containing 10 mL of double-distilled water at 50 °C temperature for 1 h 30 min reaction time for the synthesis of nano aragonite whiskers [71].

The phase and morphology were found to be affected by various factors for calcium carbonate preparation by bubbling method. Aragonite was prepared by bubbling $CO_2/N_2$ mixed gas into a $CaCl_2$ solution at 60 °C. While the effect of the several factors was studied, the parameters like initial $CaCl_2$ concentration, flow rate and temperature showed profound impact, whereas the effects of the bubbling time and stirring rate were found to be minor on the phase and morphology of PCC. Aragonite was coordinated to nine oxygen atoms to the calcium atoms, which might be probably accounting for an increase in effective radii of the calcium atoms at high temperature [72].



(a) 25°C (b) 45°C (c) 60°C (d) 80°C

**Fig. 7. SEM of aragonite at various temperatures (Source: Modified figure adapted from reference-49).**

Generally, high temperatures favor the formation of aragonite, and the formation yield of above 98% aragonite was obtained by adding the $Mg^{2+}$ ion in a 0.2 M $Ca(OH)_2$-0.6M $MgCl_2$-$CO_2$ system at 80 °C. From Fig. 7, it was observed that temperature affects the formation of aragonite. In the presence of $Mg^{2+}$ ion, though aragonite was formed at temperature between 25 °C and 80 °C, but a part of that, two more phases, calcite and aragonite, were also being found during the synthesis. In addition, the aspect ratio of aragonite was also increased along with an increase in temperature [49-51].

PCC was obtained by three processes: calcination, hydration and carbonation. Few studies were reported on the synthesis of aragonite by hydration process. Particle size of the calcium hydroxide is affected by hydration in aragonite synthesis. The effect of hydration condition like temperature, in particular on the synthesis characteristics of calcium hydroxide and aragonite PCC, was studied, and results showed that the particle size of calcium hydroxide changes with variations in the initial hydration temperature. A higher initial temperature results in a larger particle size of the calcium hydroxide. The particle size and yield of aragonite also increased when calcium hydroxide was created at relatively high temperatures. The water/solid ratio or total amount of the hydration time had no effect on the manufacturing process of aragonite (Fig. 8) [73].

Calcium carbonate was crystallized from calcium bicarbonate solutions by applying microwave radiations on the basis of hydration

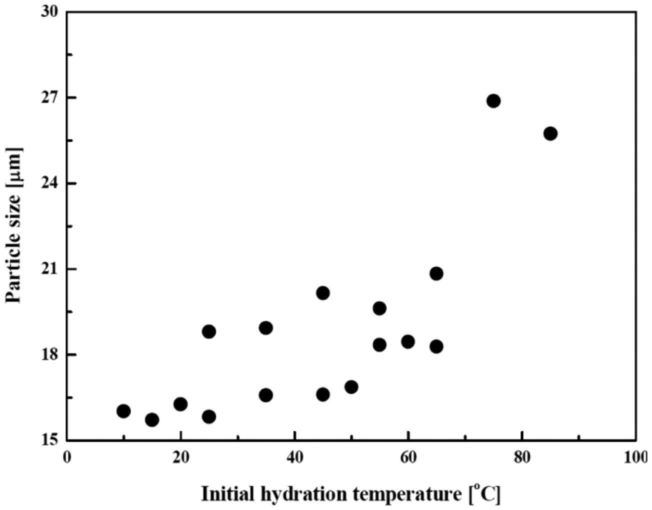


**Fig. 8. Variation of the particle size of PCC as a function of initial hydration temperature (Source: Modified figure adapted from reference-73).**

process. At short microwave exposure time, flower-like vaterite was formed and at higher exposures 99% metastable aragonite was achieved. At lower degree of supersaturation, the size of the needle like aragonite crystals does not depend on microwave radiation exposure times [74].

### 3-3. Effect of pH

The pH of the reaction solution is an important factor in the formation of desired phase of aragonite. Pure aragonite was obtained at pH 10, when the pH value was greater than 12 and calcite was obtained [75]. From the parametric variation study on synthesis of aragonite, it was concluded that the pH <11 and the temperatures (~7 °C) suppressed the formation of aragonite and calcite, but nearly pure aragonite was obtained at 58 °C for a pH < 10 [13]. Highly oriented aragonite particles were found in the nacre layers of mollusk shell, and recently aragonite rods were also obtained at pH ranging from 1.5~6.9 without bio or organic macromolecules [76].

### 3-4. Effect of ion concentration

During the synthesis the aragonite content increased with an increase in the $Mg^{2+}$ ion concentration. The formation of $CaCO_3.H_2O$ is also favored, when the ratio of $Mg^{2+}/Ca^{2+}$ is higher than 2.5 [77]. Aragonite formation is through precipitation of calcium carbonate monohydrate in presence of $Mg^{2+}$ ion because of surface energy of a small particle [78].

The effects of seven different divalent cations on nucleation, growth and transformation of $CaCO_3$ polymorphs were investigated using a double diffusion technique. The presence of the cationic impurities like $Fe^{3+}$, $Mg^{2+}$, $Ni^{2+}$, $Co^{2+}$, $Zn^{2+}$ and $Cu^{2+}$ in the reaction medium favored the formation of aragonite, whereas the presence of $Cd^{2+}$ ions did not show any significant effect [79-81].

The effects of the divalent cations like $Fe^{2+}$, $Cu^{2+}$, $Zn^{2+}$, $Mg^{2+}$, $Sr^{2+}$ and $Ba^{2+}$ on the growth and dissolution rates of calcite and aragonite, respectively, were studied. Broadly, these results can be interpreted by a reversible adsorption of the impurity ions at kinks sites according to the Langmuir-Volmer model. Ions of the transition metals showed a stronger inhibition rather than earth alkaline ions; moreover, ions like $Mg^{2+}$ and $Fe^{2+}$ had no influence on the growth and dissolution of aragonite. Further, $Cu^{2+}$ and $Zn^{2+}$ had a stronger effect on calcite, while $Sr^{2+}$ and $Ba^{2+}$ were more effective on aragonite. These results were used to show consequences for the polymorphic precipitation of $CaCO_3$ [82].

Apart from magnesium ions, the other cations, like $Ni^{2+}$, $Co^{2+}$, $Fe^{2+}$, $Ba^{2+}$ and $Sr^{2+}$, strongly favor the formation of aragonite. The aragonite formation was explained in terms of impurity effect through two mechanisms: Inhibition of growth of the metastable phase (aragonite) by adsorption of impurity cations, and formation of the unstable solid solution of calcite through transformation of aragonite. The effect of aluminum ion on the synthesis of aragonite PCC by carbonation process was studied with changing in its amount of addition, mixing condition and reaction temperature. If molar ratio Ca/Al is >1 then it favored a calcite formation, but if Ca/Al is <1 aragonite formation was decreased. In carbonation process, aragonite and calcite PCC were synthesized from either $3CaO.Al_2O_3.6H_2O$ or $3CaO.Al_2O_3.CaCO_3.11H_2O$ by mixing with $Ca(OH)_2$ and $NaAlO_2$ in aqueous medium. The aluminum ion contained in $3CaO.Al_2O_3.6H_2O$ or $3CaO.Al_2O_3.CaCO_3.11H_2O$ enhanced the formation of aragonite. The pH of the suspension decreased as the reaction temperature increased, and thus the fraction of aragonite phase obtained was found to be the largest one at 80 °C [83].

During the crystal synthesis study, $Mg^{2+}$ ion had a significant role in the formation of aragonite by carbonation reaction of $Ca(OH)_2$ slurry and $CO_2$ gas at 80 °C. Further addition of $MgCl_2$ suppressed the formation of calcite type crystal growth and simultaneously increased the growth rate of aragonite type crystal. From this study, as the amount of $MgCl_2$ was increased, the main peak shifted towards the high angle in of the calcite type, whereas the main peak of aragonite remained unaltered regardless of the increase of the quantity of $MgCl_2$. This indicates that calcium ions were replaced by magnesium ion in calcite crystal lattices, resulting in the formation of magnesium calcite solid solution. Table 2 shows the concentration of calcium, magnesium ions and crystal phase of precipitates with the addition of $MgCl_2$ solution at 80 °C.

For the same concentration of $Mg^{2+}$ and $Ca^{2+}$ ions in the solution, the formation yield of aragonite before to calcite and monophasic aragonite was formed with an excess of $Mg^{2+}$ ion concentration. With addition of $MgCl_2$, the concentration of magnesium ion rapidly increased, whereas the value of pH of the final solution decreased. When calcium ion was larger than magnesium ion, the formation ratio of aragonite was also increased, and then monophasic aragonite was formed [84].

### 3-5. Effect of additives

Effects of many additives including inorganic and organic ones

**Table 2. Changes of pH, Ions Concentrations and crystal phases of each precipitate with addition of $MgCl_2$ solution at 80 °C (Source: Adapted from reference-42)**

| Batch No. | Starting Materials (Mole) | | Ion Concentration (mole/L) | | pH | Phase of Precipitates |
|---|---|---|---|---|---|---|
| | $Ca(OH)_2$ | $MgCl_2$ | $C_{Ca}$ | $C_{Mg}$ | | |
| (a) | 0.2 | 0 | 0.015 | 0 | 11.7 | Calcite |
| (b) | 0.2 | 0.15 | 0.15 | 0.00016 | 10.0 | Calcite > Aragonite |
| (c) | 0.2 | 0.17 | 0.14 | 0.0051 | 9.0 | Calcite > Aragonite |
| (d) | 0.2 | 0.25 | 0.124 | 0.045 | 8.1 | Calcite > Aragonite |
| (e) | 0.2 | 0.4 | 0.124 | 0.155 | 7.8 | Calcite, Aragonite |
| (f) | 0.2 | 0.5 | 0.121 | 0.201 | 7.6 | Calcite < Aragonite |
| (g) | 0.2 | 0.6 | 0.118 | 0.25 | 7.5 | Calcite < Aragonite |
| (h) | 0.2 | 0.8 | 0.118 | 0.45 | 7.3 | Aragonite |

were investigated to obtain polymorphs of aragonite PCC with an optimum size and shape. Magnesium ion is the most common additive to obtain pure aragonite. Many organic additives [17,85,86] and inorganic additives with magnesium-containing compounds [87-90] were studied related to the formation of aragonite PCC. High aspect ratio aragonite micro fibers were prepared by using $CaCl_2$ and $Na_2CO_3$ as starting solutions and the seeding technique was used for crystal growth. These microfibers performed as reinforcement in Portland cement paste matrices were verified [91]. The effect of three additives such as $MgCl_2$, $MnCl_2$, and $KH_2PO_4$ on the formation of aragonite was investigated, and it was seen that under suitable conditions, $Mg^{2+}$ and $Mn^{2+}$ promoted the formation of aragonite, but $KH_2PO_4$ often promoted on calcite only. It was found that the effect of $MnCl_2$ was similar to $MgCl_2$ on the formation of polymorphs [13].

The effect of additives on crystal growth rate of aragonite PCC in $Ca(OH)_2$-$MgCl_2$-$CO_2$ system by a carbonation process was studied. Concentration of $Ca(OH)_2$ slurry, temperature, and the $CO_2$ gas flow rate influenced the particle sizes and aspect ratios. The particle size and aspect ratio increased under the synthetic conditions of a high temperature, a low $CO_2$ gas flow rate and at high concentration of $Ca(OH)_2$, whereas the particle size of aragonite decreased with a decrease in the reaction temperature [73].

Calcium carbonate precipitated in presence of additives such as PDDA, CTAB, and EDTA. Among these, EDTA showed a prominent effect on particle morphology and functionality of these additives and it was sensitive to temperature variations. At 30 °C, the additives showed limited effects on the morphogenesis of $CaCO_3$, but at higher temperature (~90 °C), these additives showed an effect on the particle morphology as well as on the aspect ratio of $CaCO_3$ crystals, which resulted on the suppression of formation of aragonite. The sequence of pH adjustment appeared to be a critical factor for the additive functionality [92] .

An optical flow-cell assay was developed for simultaneous measurement of calcite and aragonite growth, under conditions of constant concentrations of constituent ions and growth-modifying additives. By using this assay, both l-citrate and d,l-isocitrate, selectively inhibited the growth of aragonite crystal seeds, and no effect was found on calcite growth rates at super saturations between 2.5±0.4 [93].

While studying the influences of organic additives on the formation of aragonite, it was observed that phthalic acid had the most marked effect, followed by malate, citrate, and glucose. The order of their effect is in accordance with the order of the association constants for complex formation with calcium ions. The presence of organic additives in the mother liquor or growth solution influences the crystallinity and shape of the aragonite crystals, whereas the presence of citrate ions in mother solution decreases the crystallinity of aragonite. In a similar way, the citrate or malate ions in the mother solution favor the formation of rod-shaped aragonite crystals and granular calcite crystals, while phthalic acid in the solution results in the formation of rhombohedral aragonite microrods [94].

For the first time, sodium stearate was used as an organic additive, and hydrophobic lamellar aragonite particles were obtained successfully. These results revealed that sodium stearate plays an important role in determining the structure and morphology of the sample [95].

An alternating current was applied for the formation of calcium carbonate polymorphs on a porous membrane. Under this circumstance, the rate of ion migration was significantly accelerated since large amount of calcium carbonate polymorphs such as calcite, aragonite and vaterite was formed on this membrane in the absence of chemical additives. The proposed electrochemical approach was found to be leading multiple biomineralization on organic or inorganic hybrid materials [96].

Aragonite PCC micro-rods synthesized in presence of iminodiacetic acid at a lower temperature are similar to aragonite, those obtained at 75 °C without an organic additive. The studies related the stereochemical relationship between calcium ions and the arrangement around ions bound to the carboxyl groups of iminodi-acetic acid was suggested as a potential factor in the oriented nucleation and selectivity for formation of aragonite PCC micro rods [97].

Needle-like aragonite from calcium chloride and sparingly soluble magnesium carbonate aqueous solutions showed that optimum amount of magnesium ion addition is required to increase the aragonite fraction. But addition of excess $MgCl_2$ may decrease slightly the aspect ratio. Authors have developed a method for synthesis of needle-like aragonite by a reversible solution reaction from limestone in presence of $MgCl_2$ without calcinations [98,99]. Monodisperse aragonite microspheres were prepared successfully with diameters ranging from 5 to 15 μm by carbonating a calcium acetate aqueous solution with high $CO_2$ pressure with respective conditions of high pressure of 40 bar, temperature of 80 °C and 60 minutes of reaction time. From these, needlelike aragonite was prepared by self-organizing into a microsphere superstructure [100].

### 3-6. Effect of organic solvents

Calcium carbonate was precipitated in the presence of organic solvents and water in the cetyl tri methylammonium bromide (CTAB) at 80 °C. Even though the test was carried out in various organic solvents such as glycol, glyceryl, glycol-methyl ether, glycol-ethyl ether, formaldehyde and acetaldehyde, but pure aragonite with unusual morphologies could only be produced in the presence of glycol, glycerine, glycol-methyl ether at 80 °C. Consequently, it has been deduced that at high temp 80 °C the amphiphilic property of organic solvent is a key factor to influence the crystal forms and morphologies of $CaCO_3$ particles and favors the forming aragonite [101].

The dissolution and surface reactions between calcite and aragonite in presence of L-Glutamic and L-Aspartic acid solutions were compared. In this investigation we observed that the surface reactions of calcite and aragonites were quite different in amino acid solutions. Calcite was dissolved in amino acid solutions easily, whereas the adsorption of Ca-carboxylate salt limited the dissolution behavior. Aragonite did not dissolve in amino acid solutions like calcite and no adsorption of Ca-carboxylate salt appeared on its surface. For the lateral surface of needle-like aragonite its charge balance was hardly kept during the dissolution [102].

### 3-7. Effect of supersaturation

In general, supersaturation is another main factor affecting the formation behavior of PCC polymorphs and supersaturation in precipitation reaction depends on the ion concentration of the reactants present in the solution. Supersaturation is controlled in aragonite synthesis by applying sparingly soluble calcium sulfate as reactants. Readily soluble calcium sulfate salts were used as reactants in the synthesis of PCC. The counterions of the salt influenced the growth kinetics of PCC and morphology of particles. Chrysanthemum or needle-like aragonite can be synthesized from calcium sulfate and sodium bicarbonate. Low concentration and addition rate of sodium carbonate solutions were favorable to the formation of aragonite. Sodium sulfate promoted the formation of aragonite and decreased crystal size of aragonite, which was due to the decrease of supersaturation and adsorption of sulfate ion [103].

In the solution process, the phase and morphology can be constrained more easily by controlling super saturation than in the carbonation process. The range of supersaturation was adjusted to three different levels: high, medium, and low. At high super saturation level, vaterite was formed mixed with calcite. At medium super saturation level calcite was formed primarily, and at low super saturation, aragonite predominated. The addition of NaOH reduced the $Ca^{2+}$ ion concentration in the solution. As the reaction continued, the formation yield of aragonite was increased; at the same time the formation of calcite decreased and then disappeared. It is considered that lower supersaturation at the early stage of reaction and sufficient aging time would be necessary to obtain single phase aragonite. The single phase aragonite was produced by adjusting the $Ca^{2+}$ concentration, at low concentration of $CO_3^{2-}$ (Fig. 9) [104].

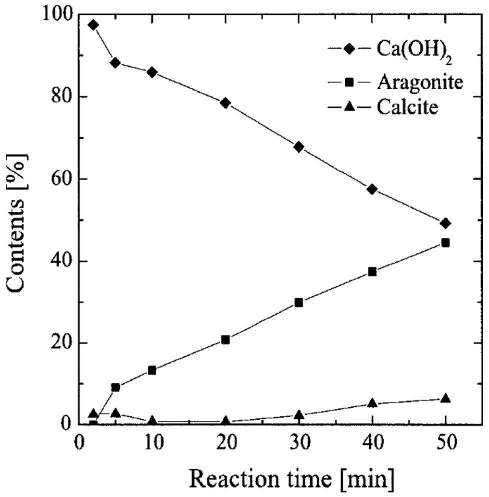


**Fig. 9. Content of each polymorph and residual ca(OH)$_2$ in the reaction (4) as a function reaction time of which both concentration of ca$^{2+}$ and $CO_3^{2-}$ are low, so the supersaturation is low (Source: Modified figure adapted from reference-104).**

## 4. Applications

Aragonite PCC as filler has tremendous importance in various fields. Particularly, acicular type aragonite PCC has very large aspect ratio and is attracting attention as inorganic filler which can enhance impact resistance, oil absorption, strength, whiteness and so on. The usage of aragonite PCC as the filler for rubber, plastic, pigment, paper, thermoplastic and polypropylene resins is expected to increase mechanical and optical properties of the above mentioned polymers. Many reports have been cited relating to the needle-like aragonite phase enhancing the mechanical properties of polymer, rubber and reinforcing materials in the paper industry [105-110].

Generally, addition of filler to printing or writing papers (up to 72% of the total global use of PCC) enhances the opacity, brightness, smoothness, writing suitability, touch, and printability of paper by increasing the dispersion of light [111]. Moreover, it can be readily used as a new advanced functional material in place of existing paper fillers, such as kaolin and talc. Needle-like calcium carbonate used as paper filler provides high bulk, brightness, opacity, wire abrasion resistance by taking a causticization step. In the first step of the causticization process, 10% by weight quick lime having a calcium carbonate is slaked with liquor at the pH range 5.5 to 13.5 with concentration of 20% to 60% to make milk of lime. In a second step, causticization reaction takes place at a green liquor loading rate of 0.02 cc to 0.5 cc (green liquor)/min/g (quick lime) at temperature 20 °C to 105 °C to afford spindle- or needle-like calcium carbonate

[112]. If needle-like aragonite ratio is increased, the paper cost will be decreased. When needle-like aragonite PCC was applied to paper as filler, mechanical properties (tensile strength; *Z*-direction tensile strength and folding endurance) were increased, but at the same time the optical properties were decreased compared to the paper using in commercial PCC (precipitated calcium carbonate) as filler.

Aragonite has a slightly greater average index of refraction than calcite. Hence, aragonite is expected to have higher performance properties as filler in the paper and plastic industries when compared with calcite [113,114]. Aragonite PCC is often used as a filler in rubber, plastic [115], paint, pigment, paper, thermoplastic polypropylene resins. In particular, aragonite PCC, needle-shaped particles with a very high aspect ratio, increases the bending and impact strength of rubber and plastic and hence used as filler in these products. Due to this effect, aragonite PCC is employed in car bumpers and dashboards as filler incorporated into thermoplastic and polypropylene composites [116]. Aragonite whisker was much better than calcite as filler for polyvinyl (PV) or polypropylene (PP) composites, which enhances the tensile strength, impact strength, glass transition temperature and decomposition temperature [67, 117]. The three polymorphs of calcium carbonate were synthesized in the emulsion state at 50 °C and we investigated the physical properties and mechanical properties. While making PP composite with $CaCO_3$ polymorphs, morphology of polymorphs play a significant role on mechanical properties and thermal properties [118].

Aragonite is a good biomedical material [119,120], because it is denser than calcite [121]. Aragonite calcium carbonate combined with calcium phosphate has the biological activities, and these materials may prove to be useful in the biomedical field also. Orthophosphate layer and calcium carbonate whiskers were implanted into the bone defect sites [122].

## 5. Conclusion

This paper provides a detailed investigation relating to several methods for synthesizing needle-like aragonite PCC by carbonation process, solution process and its applications in various fields. Influences of various experimental factors on synthesis of the aragonite were also discussed. In the solution process, controlled supersaturation is to increase the formation of aragonite. Carbonation process is also industrially useful, but in this the process control of crystal phase and morphology is difficult. Basic principles, advantages, and applications of aragonite PCC are comprehensively presented. In addition, during the last two decades calcite as filler has been used to make lightweight vehicles for plastics in the automobile industry. We also want to mention the necessity and importance of aragonite PCC as a new kind of functional filler in the future, not only for the paper industry but also for the automobile industry. The purpose of the present review on the synthesis of new single phase aragonite PCC of needle shape with high aspect ratio by solution process at lower reaction temperatures was compared to existing synthetic methods. Aragonite PCC is cost-effective and uncomplicated manufacturing. The findings of the present study are quite significant in the context of the synthesis of aragonite PCC by carbonation and solution process applying this methodology to other fields such as rubber industry, plastic and automobile industry. Overall, the outlook for acicular aragonite PCC filler is promising. With the expansion of the automobile industry in coming years, the demand for aragonite PCC filler in the plastic industry (bumpers and other parts of the car) is expected to grow tremendously.

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