



Original Research Paper

Production and characterization of synthetic aragonite prepared from dolomite by eco-friendly leaching–carbonation process



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ABSTRACT

Dolomite is an alternative material for producing precipitated calcium carbonate (PCC) particles, which have widespread industrial applications depending on their morphology and particle sizes. These properties are readily controlled by the production conditions such as reaction time, temperature, stirring speed, and CO₂ flow rate. In this paper, we investigate the influences of these experimental conditions on the production of synthetic aragonite crystals from dolomite using a leaching carbonation process. The proposed process is believed to be more eco-friendly than other methods suggested in the literature because the CO₂ released from the dolomite during the leaching stage is stored for use in the carbonation stage. The experimental results indicate that the morphology of the produced PCC is influenced not only by the reaction time and temperature, but also the stirring speed and CO₂ flow rate. The required reaction time decreases with an increase in the CO₂ flow rates. However, calcite forms along with the aragonite crystals at higher CO₂ flow rates. We successfully synthesized pure aragonite crystals in the reaction temperature range of 40–70 °C at a fixed CO₂ flow rate of 3.00 l/min, and at a stirring speed of 750 rpm. The *d*₉₀ values of the aragonite crystals at various temperatures ranged from 18.47 to 25.99 μm. We fit the experimental results by a single-term exponential model.

Additionally, we obtained a Mg-rich solution and CO₂ gas as by-products, which are in high demand.

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1. Introduction

Precipitated calcium carbonate (PCC) is an important resource used in many industrial applications. It is generally preferred over titanium dioxide (TiO₂) [1], and is used as a filler material in the coatings, paint, and plastic sectors due to its rheological and whiteness properties. It contributes to an increase in mechanical and hardness properties of polyvinyl chloride (PVC) [2,3]. Moreover, the energy required for the production of plastic is reduced in a curing process using PCC [4]. It is used as a drug carrier in the biomedical industry due to its non-toxicity in the human body. Hollow spherical PCC particles are also preferred in the biomedical industry [5]. It can be used as a paper filler in place of kaolin and talc in order to increase the light dispersion property in paper, thereby increasing paper's opacity, water resistance, and whiteness [5,6]. Furthermore, PCC is used as an enzyme immobilization matrix or catalyst in the food industry, as well as to capture CO₂ at high temperatures [7–9].

Three polymorphs –calcite, aragonite, and vaterite– can be synthesized using different production conditions. These different polymorphs have allowed PCC to have different functions when used as an additive. For example, dispersion is better in paint when PCC-containing rhombohedral calcite crystals are added [10], whereas PCC-containing needle-like aragonite crystals demonstrate better performance than calcite as a filler material in the paper and plastic industries [11–13]. In addition, aragonite is a more useful additive in the biomedical industry due to its higher density [14,15].

It is well known that calcite is the stable and least soluble polymorph at ambient conditions, whereas aragonite and vaterite minerals are metastable and more soluble in water than calcite [16]. The stabilization of CaCO₃ polymorph is important for industrial production and the metastable phase can be stabilised by decreasing its surface free energy [17–19].

PCC-containing pure calcite crystal is produced through a simple gas–solid–liquid carbonation process [20–22], which is simpler than that for synthesizing pure aragonite. The morphology of PCC is influenced by organic and inorganic additives as Sr, Ba, Pb, and Mg ions [23]. Researchers have found that Mg is the most effective ion and the molar ratio of Mg/Ca is an important parameter for

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producing aragonite crystals in the carbonation process [6,24–33]. PCC-containing crystallite aggregates form, rather than single crystals due to the alteration of the nucleation and growth processes of the calcite crystal [32–35]. Furthermore, the growth rate of the calcite in the solution decreases in the presence of Mg ions [24–26]. Park et al. [6] revealed that the amount of aragonite crystals in PCC increase as the Mg content is increased. The Mg/Ca ratio must be higher than 2 to obtain needle-like aragonite crystals. However, the aspect ratio of aragonite decreases with an increase in the Mg/Ca ratio. Similar results have been obtained by Hu et al. [23]. Likewise, Thriveni et al. [31] found that the aspect ratio of aragonite crystals increased with an increase in the reaction temperature. In addition, the Mg/Ca ratio required for aragonite synthesis decreases to 2.50 from 6 as the reaction temperature increases to 50 °C from 30 °C [27].

Although the production of PCC from good quality limestone rocks has been carried out in industrial areas, many studies have been conducted to prepare PCC from dolomite using two different processes consisting of several stages [36–40]. The process suggested by Mantilaka et al. [38,39] is divided into three stages comprising calcination, dissolution in sucrose, and carbonation. The researchers dissolved calcined dolomite in sucrose solution to obtain a calcium succrate solution. PCC nanocomposites were then prepared from the calcium succrate solution. Mustafa et al. [40] produced pure aragonite crystals from dolomite by a leach-precipitation-pyrohydrolysis process. In these studies, the authors obtained MgO [38,39] or Mg-rich solution [36,40] as by-products that can be used in many areas. It is clear that the carbonation process influences the morphology of PCC.

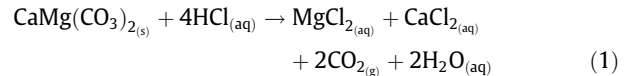
In this study, we performed a leaching-carbonation process to prepare pure aragonite crystals from dolomite collected from the Mersin/Aydincik region in Turkey. The method we adopted here differs from that of previous studies [36–40] since the required CO₂ gas was not purchased but was provided from the dolomite. The CO₂ released during the leaching process was stored in a laboratory scale gasometer for use in the carbonation stage. As such, this method can be classified as more eco-friendly. We obtained two times more CO₂ gas with a high purity than was needed. We investigated in detail the influences of reaction time, temperature, stirring speed, and CO₂ flow rate on the properties of the PCC.

2. Experimental procedure

The sample used in this study, taken from the Mersin/Aydincik region in Turkey, was composed of 19.84% MgO, 31.37% CaO, 48.30% CO₂, and 0.49% impurities (Fe₂O₃ and SiO₂). The experimental process, as shown in Fig. 1, comprises five stages, including leaching, gas storage, solid/liquid separation and purification, gas

pressurization, and carbonation. These five experimental stages are explained below:

1. Leaching stage: In our previous study, we determined the optimal experimental parameters for the dissolution of dolomite [41]. In our current study, the experimental conditions were as follows: we crushed the sample to particles smaller than 2.80 mm using a jaw crusher. Next, we leached 50 g of the sample with 150 mL of 1.21-M HCl (acid/dolomite molar ratio: 4.50) solution stirred at 150 rpm by a Teflon-coated mechanical stirrer at room temperature for 16 min. The chemical reaction between dolomite and HCl is given in Eq. (1).



2. Gas storage stage: We stored the CO₂ released during the leaching stage in a lab scale gas holder tank for use in the carbonation stage. Using a Servomex CO₂ analyzer, we determined the purity of the CO₂ to be 99.50%.
3. Separation and purification stage: To produce highly pure PCC, the purification of the leachate solution was necessary prior to the carbonation stage. At first, the insoluble impurity (SiO₂) was removed via the solid/liquid separation. Thereafter, the impurities in the leachate solution were precipitated as the hydroxide form by adding Mg(OH)₂ that leads to the increase the solution pH and removed via the solid/liquid separation. Thus, the purified solution was prepared for the carbonation stage.
4. Gas pressurization stage: In preparation for the carbonation stage, we pressurized the CO₂ from the gas holder using a gas compressor.
5. Carbonation stage: After the leaching and purification stages, we bubbled the CO₂ gas into a Ca-Mg-rich solution in the bottom of the carbonation reactor to selectively precipitate Ca ions as PCC. During the carbonation test, we stored non-reacted CO₂ in a lab scale gas holder for re-use in the carbonation test. In these tests, we kept the initial Ca concentration in the solution constant and the total volume of the solution was 1500 mL. The amounts of Ca and Mg in the purified solution were 10.67 g/l and 41.09 g/l, respectively. The experimental parameters, including reaction time, temperature, stirring speed, and CO₂ flow rate, differed in each experiment. We monitored the solution pH during carbonation, and in the subsequent carbonation test we kept constant the optimal experimental values obtained in the previous experiments. We conducted each carbonation test twice in order to decrease the possibility of experimental error. We used the average value of these experimental results to determine the recovery of the precipitated Ca ions as PCC. When the reaction was complete, we filtered the solution and

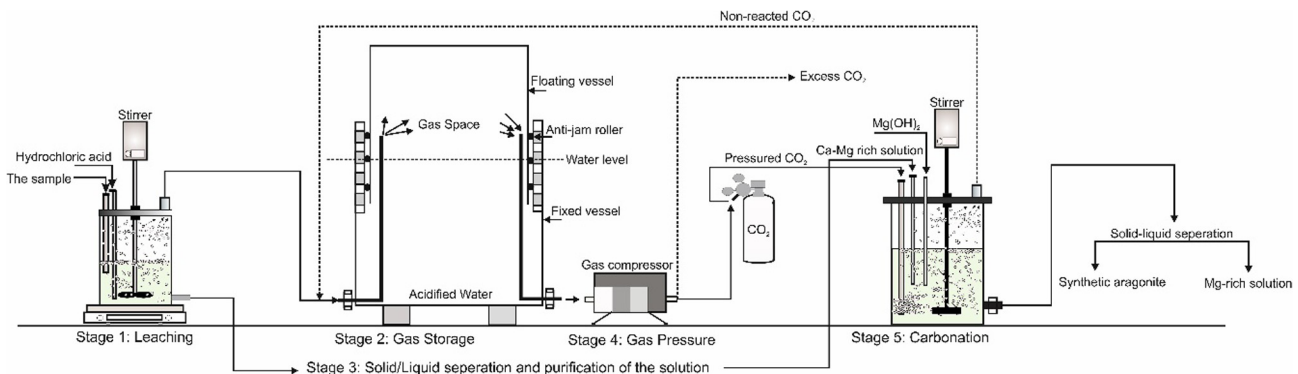


Fig. 1. Flow sheet of the production of precipitated calcium carbonate (PCC) from dolomite ore.

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