The Influence of Temperature and Gas Flow Rate on the Formation CaCO$_3$ Vaterite Phase

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Abstract. CaCO$_3$ powder is much needed in the industry. CaCO$_3$ vaterite phase is widely used as raw material in the pharmaceutical and cosmetic industries. PCC can be synthesized from natural limestone. Indonesia has abundant limestone reserves and has a very high purity$^{1}$. In this study, the synthesis of CaCO$_3$ powder was carried out at 29 °C and 40 °C by carbonation method without and by using gas bubble breakers. Characterization of CaCO$_3$ with SEM and XRD shows the formation of calcite and vaterite phases. The formation of the vaterite phase CaCO$_3$ is very sensitive in the changes of temperature and CO$_2$ gas flow rate. The formation of a vaterite phase without a gas bubble breaker is increased linearly. In contrast to the gas bubble breaker the formation of vaterite is saturated after a CO$_2$ gas flow rate of 2.3 lt/min.

1. Introduction
CaCO$_3$ is polymorphic because it has three different types of crystal phases, aragonite, calcite and vaterite. Calcite with rhombic morphology is the most stable phase and easy to formed crystalline phase. Vaterite with microsphere morphology is the most unstable phase and the most difficult phase to form. The formation of the vaterite phase is influenced by many parameters, such as pH, temperature, and reactant concentration $[1]$. Calcium carbonate (CaCO$_3$) has been widely used in various industrial fields, such as papers, plastics, coatings, ink, paint and polymer products. Meanwhile, higher and special quality CaCO$_3$ has also been needed for ingredients from cosmetics $[2]$, drug delivery $[3]$, bioactive materials $[4]$, to supplements of nutrition $[5]$. The type of calcium carbonate precipitates is used in the industry. The precipitated CaCO$_3$ (PCC) is generally prepared by precipitation process using CO$_2$, gas bubbling in the solution containing Ca ions, such as Ca(OH)$_2$. The starting materials Ca(OH)$_2$ may potentially be a limestone as natural resources with calcium content of around 98% $[6]$. PCC with varying morphology are generally synthesized from CaCl$_2$ solutions, either by mixing methods or by carbonation. Indonesia has an abundant source of limestone. CaCO$_3$ powder is synthesized from natural limestone. In our previous study, the PCC has successfully been prepared from limestone employing a facile method of carbonation, resulting in CaCO$_3$ with various phases and unique morphology $[7]$. In this work, we have succeeded in synthesizing CaCO$_3$ vaterite and calcite phases by carbonation method. The Ca(OH)$_2$ precipitating reaction with CO$_2$ gas is carried out with and without gas bubble breakers with different CO$_2$ gas flow rates at 29 °C and 40 °C.
2. Material and Methods

2.1. Materials
The limestone from a quarry in Tuban (East Java, Indonesia) has a 98% calcite content, as the starting material, was calcined for 5 hours at 900 °C. 40 gram of calcined products dissolved into 20 liters of demineralized water for 20 hours. Furthermore a clear Ca(OH)$_2$ solution will be used for the synthesis of CaCO$_3$ powder.

2.2. Synthesis procedure
The synthesis of 1 liter of Ca(OH)$_2$ solution was carried out at 29 °C and 40 °C with 3 steps:

- Step 1: CO$_2$ gas is flowed through 0.4 cm diameter pipe into Ca(OH)$_2$ solution and the solution is stirred at 200 rpm rotation rate.
- Step 2: CO$_2$ gas is flowed through 0.4 cm diameter pipe at which the end of the pipe is subjected to a gas bubble breaker and inserted into a stirred Ca(OH)$_2$ solution at a rate of 200 rpm rotation.
- Step 3: CO$_2$ gas is flowed through 0.4 cm diameter pipe which at the end of the pipe is given a gas bubble breaker and inserted into solution of Ca(OH)$_2$ which is stirred at high rotation rate.

2.3. Characterization
The powder diffraction patterns were recorded using XRD (Philips X’Pert MPD system, monochromated Cu-Kα radiation), employing record in the diffraction angle (2θ) range of 20° – 70°. The morphology of powder was observed using SEM (FEI Inspect S50, at the acceleration voltage of 15 kV), by dropping the particle suspension on a glass slide, drying overnight, then sputtering with gold-palladium in a vacuum evaporator (Emitech SC7620 sputter cooter).

3. Results and Discussion

3.1. Effect of gas bubble breakers and stirring speed
The process of formation of carbonate ions from CO$_2$ gas occurs in the layer between the liquid-gas interface [8]. In the case of carbonation in Ca(OH)$_2$ solution, this layer is in the gas bubble wall while in the solution. The total surface area of the bubbles in the liquid is inversely proportional to its volume. If the surface area increases, then the number of carbonate ions formed per unit time become more. This opinion can be an explanation of why the use of bubble breakers can accelerate the carbonation process.

The results of the previous study [7] suggest that the dissolved CaCO$_3$ mass reaches the optimum conditions occurring at ph 7 - 8. The time required for the solution to reach pH 7-8 at different flow rates is shown in Figure 1.
Figure 1. The time required for the solution to reach pH 7-8 at different CO$_2$ gas flow rates: (a) step 1 (b) step 2 (c) step 3

Next will be discussed saturation at flow rate above 2.35 lt/min (Figure 1). Factors affecting CO$_2$ gas absorption rate in solution are reaction rate, mass transfer, and solution concentration. The types of reactions that occur in this case are chemical and physical reactions. The physical reaction takes place when CO$_2$ with a diffused gas phase into the solution produces dissolved CO$_2$. While chemical reactions occur in the formation of various species of ions to the formation of CaCO$_3$, this chemical reaction takes place much shorter than the physical reaction. Thus, the saturation state of Figure 1b may be due to the low rate of solubility of the CO$_2$ gas and not due to the slow reaction of ion formation.

Rapid carbonation time is generated in synthesis using step 3 (Figure 1c). The increase of CO$_2$ gas flow rate can be explained from three aspects: the size of the gas bubble, the process of mass transfer of CaCO$_3$ from the bubble surface, and the chance of collision between the reactant particles.

The bubble size is determined from the buoyant force equilibrium against surface tension and bubble adhesive style with nozzle (bubble breaking pores). Stirring at high rotation gives an external force that contributes negatively to the last two forces, consequently bubbles can break away from nozzles with relatively smaller sizes (compared to step 2). As mentioned earlier, a small size of gas bubble can increases the total surface area of the liquid-gas interface.

The next reason is due to mass transfer of CaCO$_3$ as a reaction product. In chemical reactions, the higher concentration of the reactant the faster the reaction occurs, on the contrary, the product concentration will slow down the reaction rate. If the reaction of carbonic ion formation occurs in the liquid-gas interface then the reaction of CaCO$_3$ molecule formation also occurs in this area. In low agitation, the CaCO$_3$ (solid) molecule does not immediately leave the liquid-gas interface area. This, of course, slows down the formation of other CaCO$_3$ molecules. With high stirring, the CaCO$_3$ molecule will leave the liquid-gas interface area rapidly, so that the reactions to the gas bubble wall remain normal.

The last allegation is viewed from the aspect of chance of collision between reactant ions. The use of a blender is intended to force the reaction medium to move faster. The non-smooth wall structure of the tubes causes the fluid (reaction medium) to move turbulently. Although it does not increase the ionic energy significantly, it can increase the chance of collision rate accumulation which contributes to the increase of reaction rate.
3.2. Effect of variation of carbonation rate
The first treatment was performed to find the optimum synthesis temperature for the formation of vaterite. This is done by varying the solution temperature at 29 °C and 40 °C. Synthesis was carried out in standard solution with 200 rpm stirring and flow rate of 2.3 lt/min.

Based on XRD pattern formed calcite and vaterite phase. At both temperatures a slight increase in the vaterite fraction is characterized by a decrease in calcite peak height 104 in the angle 2θ = 29°. Further data processing showed changes in vaterite fraction from 43 wt% at 29 °C to 50 wt% at 40 °C. The results of this observation are consistent with the results of the study [9], although carried out with different materials and methods. Thus, the optimum temperature for the highest vaterite synthesis is 40 °C. The heavy fraction of vaterite refinement results with MAUD software is shown in Figure 3.

![Figure 2](image)

**Figure 2.** The XRD spectra of samples synthesized at temperature (a) 29 °C (b) 40 °C.

![Figure 3](image)

**Figure 3.** The resulting vaterite weight fraction at CO₂ gas flow rate and different carbonation: (a) T= 29 °C step 1  (b) T= 40 °C step 1  (c) T=29 °C step 2  (d) T= 40 °C step 2  (e) T= 29 °C step 3  (f) T=40 °C step 3

According to Figure 3d, the vaterite fraction is saturated at a fraction of about 57 wt% weight fraction, as well as its carbonation rate is also saturated. The vaterite fraction at different step with CO₂ gas flow rate of 2.3 lt/min at 40 °C showed significant difference, 11 wt%, 53 wt%, and 65 wt%
respectively. From this data it is known that the increase of vaterite weight fraction is agree with the rate of carbonation process.

Characterization with SEM samples synthesized by different steps is shown in Figure 4. The synthesis of CaCO$_3$ in step 1 yields rhombic-shaped particles with a calculated phase composition of 89 wt% (Figure 4a). Figure 4b is a sample synthesized with step 2 with a flow rate of 2.3 lt/min at 40 °C producing particles with rhombic and spheroidal morphology with 47 wt% and 53 wt% compositions. Figure 4c is a sample synthesized with step 3 producing particles dominated by spheroidal vaterite (65 wt%) measuring about 2 μ.

![Figure 4. SEM Photography sample synthesized with different carbonation rates:](image)

(a) Step 1  (b) Step 2  (c) Step 3

The number of particles with the spheroidal morphology of Figure 4b appears dominant although the fraction weighs only 53%. The difference between these two characterizations is the impact of lower density of vaterite particles than calcite. Calcite is a solid particle, whereas vaterite is composed of nano-shaped spheroid aggregations to form a large porous spheroid. In this case, the effect of transformation also needs to be considered because of the difficulty of conditioning a truly objective synthesis treatment. low pH due to excessive carbonation reaction will increase the rate of transformation of vaterite into calcite.

The particle size formed from these three steps also looks varied. This difference is probably due to the stirring rate which disrupts the growth equilibrium of particle size. The next possibility is due to the difference in nucleation rate as the rate of reaction increases. The first possibility is easily denied because the samples in Figures 4a and 4b have different sizes although stirred at the same rate. In Figure 4c, the calcite rhombic particle appears to have an average size greater than that of the surrounding spheroidal particles, this is seen more clearly in Figure 5.

![Figure 5. The calcite crystal growth process of diffused vaterite particles.](image)
This situation is certainly interesting to explain further related to the process of crystal growth. One of the mechanisms of crystal growth is through the diffusion of soluble particles onto the surface of more stable particles, the porous area and its unstable thermodynamic properties, the vaterite acts as a soluble particle. Figure 5 shows some vaterite particles attached to the calcite rhombic surface. Vaterite will transform gradually until it blends into a calcite particle with a larger size. This mechanism is consistent with the results of experiment.

Two other mechanisms of CaCO$_3$ crystal growth were also observed in this study. The first mechanism occurs due to the aggregation of some stable crystalline particles to form new particles of a larger size [8], the visualization can be observed in Figure 5. The next mechanism is the gradual increase of crystal size due to the oriented aggregation of ions, molecules, or nanocrystals at surface of substrate [11].

3.3. Condition of vaterite and calcite formation
Synthesis with step 1 at a flow rate of 1.1 lt/min resulted in the amount of CO$_3^{2-}$ formed in a relatively small amount of time interval. The high [(Ca$^{2+}$) / (CO$_3^{2-}$)] ratio causes the amorphous molecules of CaCO$_3$ to tend to build a rhombohedral calcite structure (Fig. 4a). In the condition of such a reaction medium, the vaterite that had formed would be easy to transform. Conversely, at higher carbonation rates, the amount of CO$_3^{2-}$ which can form within a certain time interval is considerable, so that the vaterite fraction increases, as in the synthesis results with step 2 and step 3.

The next study is the vaterite fraction which can not reach 100%, although it is synthesized with the maximum carbonation rate. This problem is thought to arise when the carbonation process is almost complete pH of the reaction medium begins to decrease as the amount of OH$^-$ starts to decrease. The more dominant bicarbonate ion (HCO$_3^-$) formed at low pH leads to high supersaturation conditions as the requirement for the formation of vaterite is not met. At low pH and supersaturation, vaterite is also more easily dissolved to further transform to calcite. Thus, synthesizing with carbonation methods on fixed volumes without involving additives would be extremely difficult to produce maximum vaterite.

4. Conclusion
Synthesis at low concentrations produces micron-sized particles with rhombic calcite and spheroidal vaterite morphology. Vaterite with spheroid morphology tends to form at high carbonation rates. The maximum weight fraction of the synthesized vaterite CaCO$_3$ micro-sized powders is around 73 wt%, obtained from synthesis step 3 at 40 °C.

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