

The Simple Method of Synthesizing Calcite and Aragonite from Indonesian Limestone

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ABSTRACT: Precipitated CaCO_3 (PCC) with calcite and aragonite phases have been successfully synthesized using natural limestone. Synthesis of PCC was carried out by the simple method of carbonation using slurry $\text{Ca}(\text{OH})_2$ with a variation of CO_2 gas flow rate at room temperature and variation of temperatures at a constant CO_2 gas flow rate. The raw material used is a very high purity Madura Island limestone. The PCC product was characterized by X-Ray Diffraction (XRD), Fourier Transform Infra-Red (FT-IR), and Scanning Electron Microscope (SEM). PCC on CO_2 gas flow variation produced the same phase, calcite with the characteristic of $2\theta = 29.23^\circ$ (104), rhombohedral cubic morphology, and a wavenumber of 712 cm^{-1} as displayed from the FTIR spectra. The mixture of aragonite and calcite phase was observed in PCC products with temperature variations of $60 - 90^\circ\text{C}$. The characteristic aragonite was observed at $2\theta = 26.2^\circ$ with needle-like morphology. The highest fraction of aragonite was at the temperature of 60°C at 71.35%.

KEYWORDS: Electron microscopy; Aragonite; Needle-like; Crystal morphology; Calcite.

INTRODUCTION

In recent years, the synthesis of precipitated CaCO_3 has received more attention in obtaining three basic phases, which are calcite, aragonite, and vaterite. Since it is widely used in various industries as a filler in paper, rubber, and plastic material [1-6, 43], CaCO_3 is also used as a sorbent to reduce SO_2 emissions [44, 45]. The three polymorphs of CaCO_3 have different characteristics. Calcite polymorphism is thermodynamically more stable [1-3, 7] and most widely used in industry [3], whereas aragonite and vaterite are metastable [1-3, 7].

The synthesis of PCC has been carried out by many

researchers, including those who have successfully obtained the calcite phase [5, 6, 8-17], the aragonite phase [18 – 27], calcite and vaterite phase [2, 7, 28, 29], calcite and aragonite phase [30, 43], vaterite phase [32] and all three of the combined phases [1, 33]. The majority of research on the synthesis of precipitated CaCO_3 still uses commercial chemicals and only a scarce amount of researchers have used natural raw materials such as limestone [5, 10, 27, 29, 34]. Out of the researchers who have succeeded in obtaining the aragonite phase on average using commercial chemicals [18-26, 41], only

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Dagaonkar et. al [35] who have used dolomite powder, and Arifin, et. al [34] were the sole group of researchers who used calcite-based limestone. Thus it is necessary to conduct further studies regarding the synthesis of PCC from limestone.

The most widely used PCC synthesis method is the carbonation method as this method is simple, low cost has higher purity, and results in higher products [3]. Researchers who have previously used the carbonation method are Han, et. al using $\text{CaCl}_2 + \text{NH}_4\text{OH}$ flowed with $\text{CO}_2 + \text{N}_2$ [2], Arifin, et. al using dolomite + HCl flowing with CO_2 [10], Thriveni, et. al using $\text{Ca}(\text{OH})_2$ flowed by CO_2 in a closed-loop reactor [12], Ahn, et. al using $\text{Ca}(\text{OH})_2 + \text{MgCl}_2$ flowing with CO_2 [18, 20], Park, et. al using $\text{Ca}(\text{OH})_2 + \text{MgCl}_2$ flowing with CO_2 [23], Ramakhrisna, et. al using dolomite + MgCl_2 in the flow of CO_2 [27], Altiner using $\text{Ca}(\text{OH})_2$ flowing with CO_2 using a microbubble generator [31], Arifin, et. al using $\text{Ca}(\text{OH})_2$ flowing CO_2 [34], and Dagaonkar, et. al using $\text{Ca}(\text{OH})_2$ flowing CO_2 in an inert environment [35].

The aim of this research was to investigate the effects of both constant and varied gas flow rates on the varied synthesis temperatures of 60, 75, and 90°C. The constant gas flow rate was set at 8 liters/min, whereas the varied gas flow rates were set at 2, 4, 6, 8, and 10 liters/ min. The synthesis was carried out using the simple carbonation method with a bubble breaker.

EXPERIMENTAL SECTION

Preparation of slurry $\text{Ca}(\text{OH})_2$

The raw materials used were limestone obtained from a quarry in Pamekasan (Madura Island, Indonesia) [36]. The limestone was calcined at 850°C for 6 hours. Lime (CaO) was dissolved in distilled water and precipitated for 24 hours. $\text{Ca}(\text{OH})_2$ solution was prepared with a concentration of 1 M. CO_2 gas was purchased from UD. Wonokoyo, Indonesia. The synthesis method used is the carbonation process.

Synthesis of PCC with CO_2 gas flow rate variation

The CO_2 gas flowed to a solution of $\text{Ca}(\text{OH})_2$ with differences in flow rates of 2, 4, 6, 8, and 10 L/min using bubble breakers with a diameter 1.97 mm, with the reaction carried out at room temperature. The reaction was stopped when a constant pH was acquired. The precipitate was filtered using filter paper and dried at 105°C for 3 h. in the oven.

Synthesis of PCC with variation temperature

The CO_2 gas was controlled at a flow rate of 8 L/min. The temperature variations used were 60, 75, and 90°C. During the carbonation process, the $\text{Ca}(\text{OH})_2$ solution was stirred continuously using a magnetic stirrer at 300 rpm. The reaction was terminated when a constant pH was reached. Subsequently, the precipitate was filtered using filter paper and dried at 105°C for 3 hours in the oven.

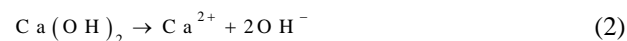
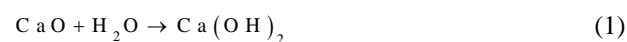
Characterization

The crystalline phase of PCC formed was characterized by X-ray diffraction (XRD) X-Pert MPD with Cu-K α radiation ($\lambda = 1,5406 \text{ \AA}$) and scanned from 10° to 60°. The FT-IR spectra were taken in the range of 500 – 4000 cm^{-1} using Thermo Scientific Nicolet iS10. As for the morphological investigation of PCC, it was analyzed by Scanning Electron Microscope (SEM) FEI Inspect S50 X'pertPRO PANalytical.

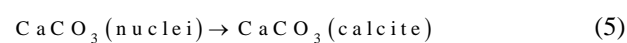
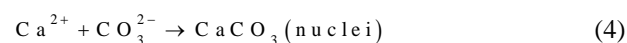
RESULTS AND DISCUSSION

Reaction Mechanism

The reaction for producing a $\text{Ca}(\text{OH})_2$ solution conformed by the following equation:



When CO_2 is flowed into solution of $\text{Ca}(\text{OH})_2$, the reaction of the carbonation process is as follows [2, 12, 27, 31]:



When the solution reached equilibrium, calcite was formed from the growth of CaCO_3 crystals (nuclei) [12]. Calcite was the most stable phase among the 3 polymorphs. Whereas aragonite was affected by the temperature during the reaction [18, 20] and vaterite was influenced by the rate of flowing CO_2 [2] and stirring speed [42].

Powder diffraction of CaCO_3

Powder X-Ray Diffraction patterns displayed in Fig. 1 exhibited a crystalline phase of CaCO_3 from the carbonation

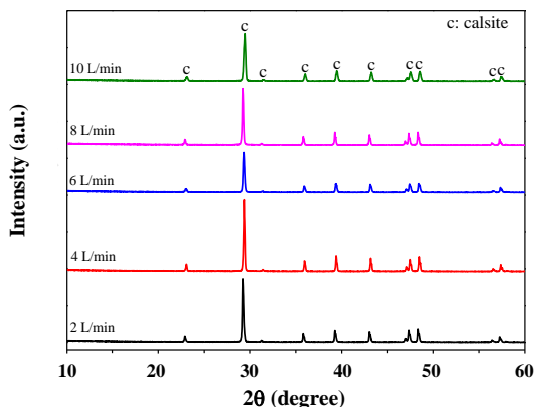


Fig. 1: XRD patterns of PCC powder with a variation of CO_2 gas flow rate variation.

process in varied CO_2 gas flow rates. The main peak of calcite was identified by the characteristic at 2θ of 29.23° (104), which matched the results from the previously reported experiments [2, 12, 34, 37]. The calcite phase was rhombohedral with lattice parameters of $a = 4.9910 \text{ \AA}$ and $c = 17.0680 \text{ \AA}$, in accordance with JCPDS: 96-600-9668. Fig. 2 displays the XRD patterns of the synthesized CaCO_3 at temperature variations of 60° , 75° , and 90°C . The presence of both aragonite and calcite was strongly indicated by the diffraction peaks at 2θ of 26.2° (111) [18-27] and 29.4° (104), respectively. The aragonite phase was orthorhombic with lattice parameters of $a = 4.9566 \text{ \AA}$, $b = 7.9808 \text{ \AA}$, and $c = 5.7464 \text{ \AA}$, in accordance with JCPDS:96-901-5894.

The crystal size of PCC was calculated using the Scherrer equation. The crystal size distributions of PCC in the varied CO_2 gas flow rate are shown in Fig. 3, whereas the average crystal size as a function of CO_2 gas flow rate is presented in Fig. 4. Based on Fig. 3, it is shown that at the CO_2 gas flow rate of 4 L/min, the PCC has the most extensive range and average crystal size. On the contrary, the lowest average crystal size was obtained at the CO_2 gas flow rate of 10 L/min with an average crystal size of 71 nm, as indicated in Fig. 4.

Aragonite and calcite fractions were calculated by implementing the equation used by Park *et al.* equation [23], as illustrated in Fig. 5. The highest percentage of aragonite fraction was obtained at 60°C . At 75°C the percentage of aragonite fraction decreased, and it experienced a slight increase at 90°C . The aragonite fraction was found to be the most abundant at 60°C , which matched the aragonite phase [38] as a result of aragonite being easy to grow

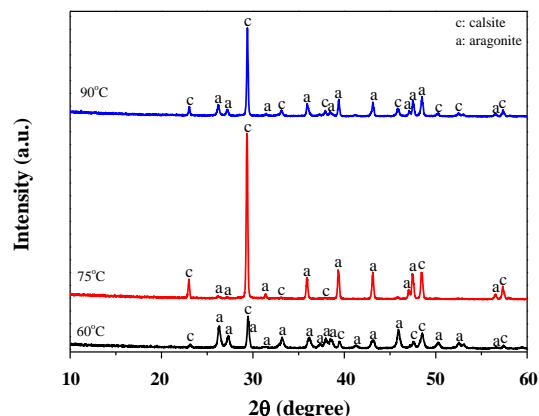


Fig. 2: XRD patterns of PCC powder with temperature variation.

at low temperatures and pressures. Previous researchers have made aragonite at 80°C with $\text{Ca}(\text{OH})_2 + \text{MgCl}_2$ and CO_2 gas flow rate of $100 \text{ cm}^3/\text{min}$. The addition of MgCl_2 was intended as an inhibitor of calcite growth [20]. Meanwhile, in this study, the synthesis of aragonite only used a solution of $\text{Ca}(\text{OH})_2$ with a CO_2 gas flow rate of 8 L/min, at temperatures of 60°C , 75°C , and 90°C , and a stirring speed of 300 rpm.

FT-IR Spectra of CaCO_3

FT-IR spectra of precipitated CaCO_3 are shown in Fig. 6. As exhibited in Fig. 6, samples prepared with varied CO_2 flow rates revealed characteristic bands of calcite [$1, 7, 12, 39, 40$] at 871 cm^{-1} and 712 cm^{-1} . Whereas by referring to Fig. 7, for samples at $T = 60^\circ\text{C}$, the characteristic bands of aragonite are seen at 712 cm^{-1} in in-plane bending mode (ν_4), in out-of plane bending mode (ν_2) at 853 cm^{-1} , in symmetric stretching (ν_1) at 1082 cm^{-1} , and in asymmetric stretching (ν_3) mode at 1447 cm^{-1} [1]. At $T = 75^\circ\text{C}$, the identified functional group of CaCO_3 was the aragonite band characteristic, sighted at 712 cm^{-1} . Whereas at 871 cm^{-1} and 1393 cm^{-1} , the functional group of calcite was identified as the specific band characteristic. At $T = 90^\circ\text{C}$, an aragonite band characteristic was detected at 712 cm^{-1} and 1082 cm^{-1} . At the same temperature of $T = 90^\circ\text{C}$, a calcite characteristic band was also observed at 872 and 1409 cm^{-1} . This result is in accordance with the XRD measurements.

Morphology of CaCO_3

The morphology of CaCO_3 product was observed by scanning electron microscope. Fig. 8 shows the SEM

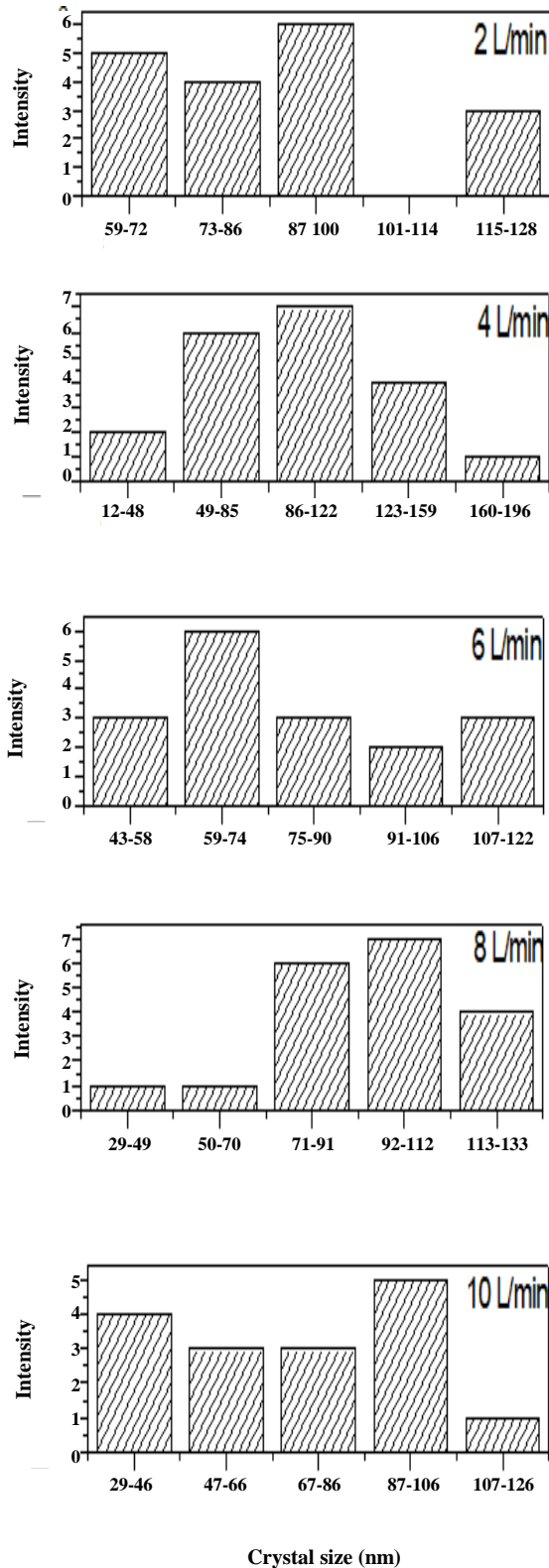


Fig. 3: Crystal size distributions of PCC on variations in the flow rate of CO₂ gas.

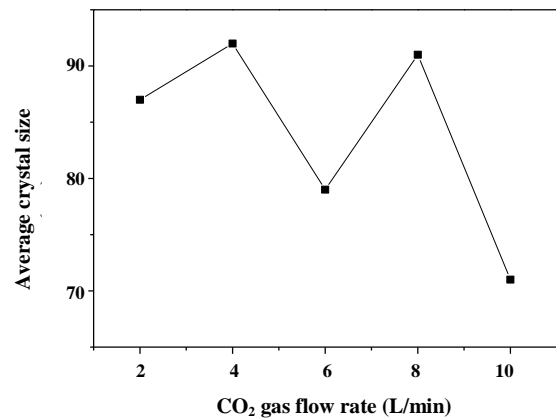


Fig. 4: Average crystal size as a function of CO₂ gas flow rate.

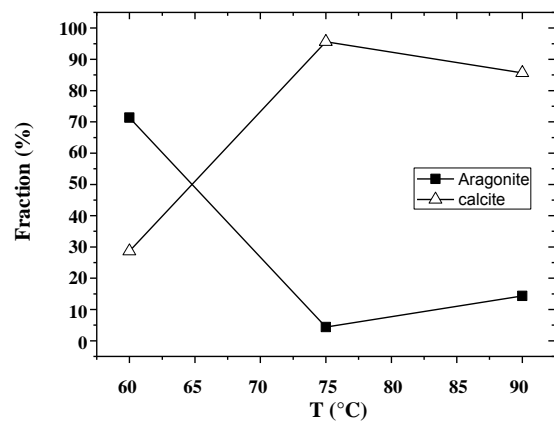


Fig. 5: Aragonite and calcite fractions as a function of temperature.

images of calcite synthesized by different CO₂ gas flow rates. The carbonation process started from the initial pH of 12 and stopped when the pH became constant or when a pH 7 was reached. At different CO₂ gas flow rate variations, the carbonation time decreased as the CO₂ gas flow rate increased. The mechanism of the carbonation reaction can be seen in equations 1 - 5. Based on the SEM images exhibited in Fig. 8a and 8e, calcite was detected to have a cubic rhombohedral structure since it appeared that the particles were clustered and agglomerated. While in accordance with the other three SEM images depicted in Fig. 8b - 8d, it appeared that there was a growth of elongated and irregular cube- and needle-shaped particles. However, clustered and agglomerated morphology was still observed despite the characteristics of calcite being still identified from the XRD and FT-IR results.

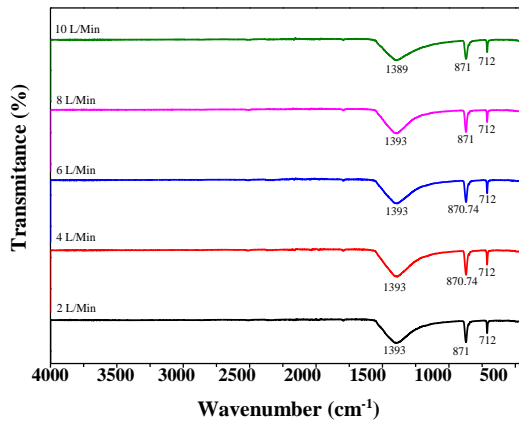


Fig. 6: Spectra of FTIR PCC powder variation of CO_2 gas flow rate.

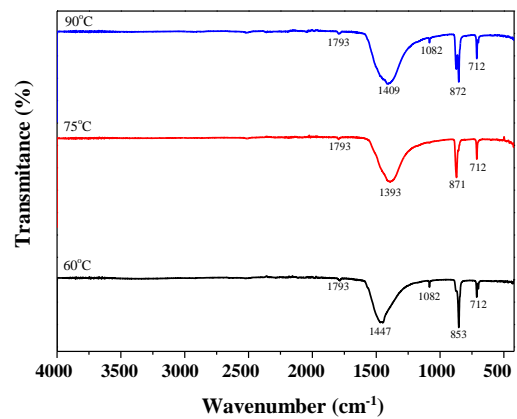


Fig. 7: Spectra of FTIR PCC powder on variation of temperature.

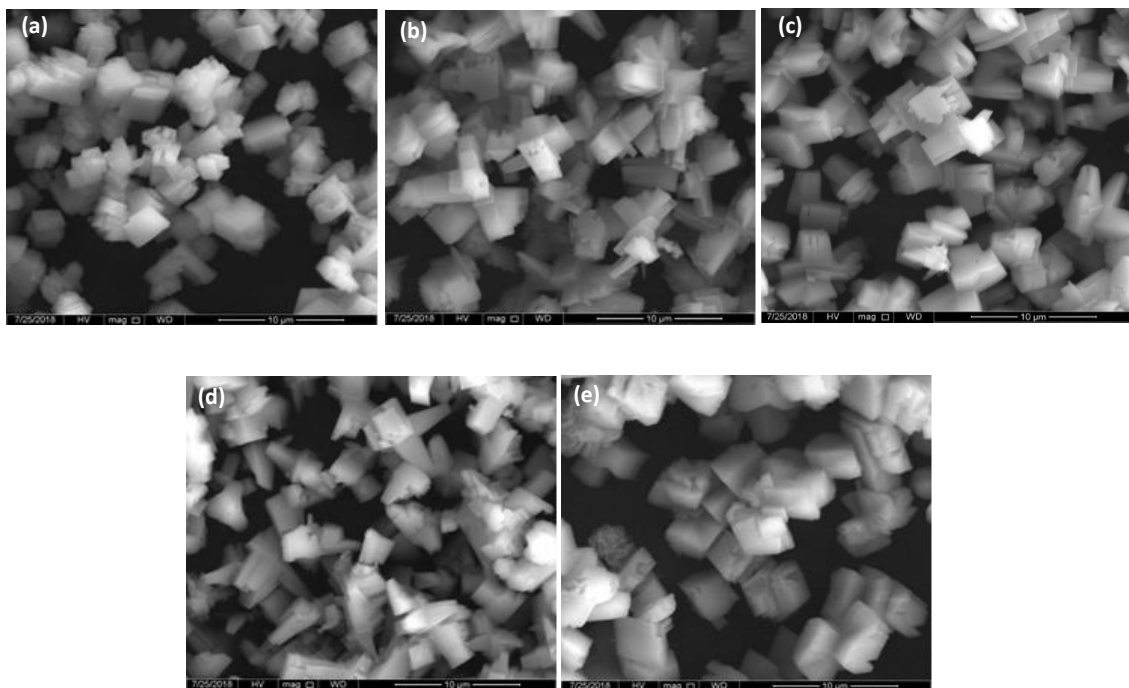


Fig. 8: SEM images of PCC powder synthesized with magnified 10000x (a) 2 L/min, (b) 4 L/min, (c) 6 L/min, (d) 8 L/min and (e) 10 L/min

Fig. 9 is a SEM image of the synthesized precipitated CaCO_3 with different temperatures at a constant CO_2 gas flow rate of 8 L/min and stirring speed of 300 rpm during the carbonation process. Fig. 9a shows a more evenly distributed needle-shaped morphology in accordance with the appearance of a dominant phase and rhombohedral cubic particles. The size of the needle-shaped particles is roughly uniform. The morphology of

the CaCO_3 particles shown in Fig. 9b has a dominant cubic rhombohedral shape. The calcite particles appeared to be overlapping and clustered, with a very small number of needle-shaped particles also present. While in Fig. 9c, the morphology of the precipitated CaCO_3 was needle-shaped with a smaller size distribution compared to Fig. 9a and 9b with some rhombohedral cubic particles that were also observed. When viewed from the calculation

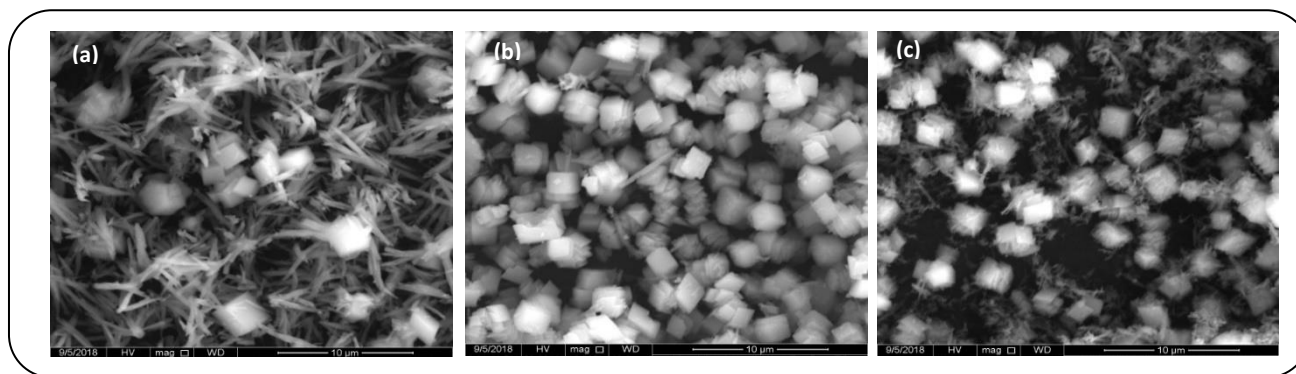


Fig. 9: SEM images of PCC powder synthesized with magnified 10000x (a) 60°C, (b) 75°C and (c) 90°C

Of the aragonite and calcite fractions in Fig. 5, the SEM test results are very similar to each other. The aragonite fraction in Fig. 9a, 9b, and 9c is 71.35%, 4.34%, and 14.36%, respectively. Thus the highest aragonite fraction was found at a temperature of 60°C.

Effect of CO₂ gas flow rate and temperature

The PCC produced in the varied CO₂ gas flow rate did not show any difference in the crystal phase formed since the CO₂ gas flow rate was too fast. Consequently, the crystals formed were the only calcite phase in accordance with the results from XRD, FT-IR, and SEM, as the nature of calcite is the most stable CaCO₃ polymorph. In the previous study, in order to obtain a vaterite phase, a low varied flow rate of below 2 L/min was used [2, 12, 37].

The PCC from temperature variation with constant CO₂ constant gas flow rate produced two phases: calcite and aragonite. Aragonite was mostly formed at 60°C (Fig. 2), while at 75°C and 90°C a small amount of aragonite was formed. Such an occurrence was due to the aragonite instability, which is influenced by temperature [3]. Previous research managed to obtain aragonite using the carbonation method at a temperature between 25 - 80°C [20, 27].

CONCLUSIONS

In conclusion, the synthesis of PCC with natural limestone has been successfully carried out. The calcite phase was very easy to form as it was very stable. Aragonite formation, on the contrary, was influenced by the temperature. Aragonite was formed at a low temperature of 60°C. The calcite formed had a cubic rhombohedral morphology, whereas, for aragonite, the morphology took the form of a needle. The characteristics of calcite and aragonite can also be seen from the results of XRD and FT-IR.

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