PRODUCTION OF PRECIPITATED CALCIUM CARBONATE PARTICLES WITH DIFFERENT MORPHOLOGIES FROM DOLOMITE ORE IN THE PRESENCE OF VARIOUS HYDROXIDE ADDITIVES

Mahmut ALTINER, Mehmet YILDIRIM

Mining Engineering Dept., Faculty of Engineering and Architecture, Cukurova University, Adana, 01330, Turkey
maltiner@cu.edu.tr

Abstract: The aim of this study was to produce precipitated calcium carbonate (PCC) with different morphologies from dolomite ore ($CaMg(CO_3)_2$) by means of leaching and carbonation method. The optimal experimental conditions determined in our previous study for the leaching process was conducted. During the leaching process, CO_2 released was stored in a lab scale gasometer for the use in the carbonation test. The carbonation test was performed in the presence of Mg^{2+}, Na^+ or NH_4^+ ions added as $[OH]^-$ additives. XRD, SEM, FT-IR, brightness and particle size analysis were conducted to determine properties of the PCC. It was determined that the morphology, crystallite and particle size distribution properties of PCC were influenced by the OH^- additives. The PCC containing pure aragonite or calcite crystals were produced successfully, depending on the experimental conditions. The necessary carbonation time decreased with the increase of CO_2. It was understood from the uniformity coefficient values that the homogeneity of PCC produced in the presence of NH_4^+ was lower compared to PCC produced in the presence of Mg^{2+} and Na^+. Furthermore, the Mg/Ca ratio in the solution indicated which morphology of PCC could be produced.

Keywords: carbonation, CO_2 storage, calcite, aragonite, eco-friendly

Introduction

Researches in the fields of chemistry and material science have led to the development of inorganic materials that possess properties that cannot be found in natural materials (Sommerdijk and Gijsbertus, 2008). One of these inorganic materials is precipitated calcium carbonate (PCC) that its importance increases day-by-day in the scientific and industrial applications due to its non-toxicity properties on the human body. PCC has superior advantages compared to ground calcium carbonate (GCC) as the chemical composition, polymorph properties of GCC are unchangeable, and its usage area is

limited in industrial applications. PCC can be produced with different polymorphs (calcite, aragonite, vaterite, calcium carbonate monohydrate, calcium carbonate hexahydrate and amorphous material) and desired properties, depending on the production conditions. The most stable polymorph at ambient temperature and pressure is rhombohedral calcite crystal, whereas the less stable polymorph is aragonite and the even less stable polymorph is hexagonal vaterite crystal. Rhombohedral calcite crystals are produced in the absence of templates or additives in the solution at ambient temperature. However, specific production conditions are required to produce pure aragonite or vaterite crystals in comparison with the calcite production. The Mg/Ca ratio, CO_2 flow rate and reaction temperature must be controlled for the synthesis of aragonite crystals (Mann et al., 1990; Ota et al., 1995; Meldrum and Hydeb 2001; Hu and Deng 2004; Thriveni et al., 2015). In order to produce pure vaterite crystals, aspartic acid, glycine, trichloroacetic acid, hydroxyethylidene-1 or 1-phosphonic acid should be used (Dupont et al., 1997; Kasuga et al., 2003; Tong et al., 2004; Hou and Feng, 2005; Hou and Feng, 2006; Shivkumara et al., 2006; Mori et al., 2009). PCC is a useful material for many industrial applications such as plastic, pigment, rubber, paper, paint, coating, drug delivery, biomedical, biosensor, pharmacy, medicine and cosmetic and so on (Boyjoo et al., 2014). The morphology, particle size, brightness and surface properties of PCC influence on its usage area. For example, hollow or porous spherical PCC particles are used as a drug carrier (Ueno et al., 2005; Zhao et al., 2006; Fujiwara et al., 2008; Baumler and Georgieva, 2010). The abrasiveness property of toothpaste is adjusted easily through the aragonite addition (Pickles, 2005). Moreover, the increase of aragonite content in the paper improves the brightness, opacity, strength and printability properties (Katayama et al., 1991).

This paper was focused on the production of PCC with various morphologies from dolomite sample via leaching-carbonation method in the presence of different $[OH]^-$ additives. The leaching test was performed at the optimal conditions that were determined in our previous work (Altiner et al., 2016). During the leaching process, CO_2 gas released was stored for the use in the carbonation process. In the carbonation process, the influences of additives ($Mg(OH)_2$, NaOH and NH_4OH) and CO_2 flow rates on the morphology and particle size distribution properties of PCC produced were investigated and discussed.

Experimental

Materials

The dolomite sample used in this study was collected from Aydincik/Mersin Province in Turkey. The sample was composed of 22.84% MgO, 32.37% CaO, 0.42 Fe_2O_3%, 44.63 CO_2%. All chemical used in this study (HCl, $Mg(OH)_2$, NaOH, NH_4OH) were analytical grade and the pure water was used.

Method

Figure 1 shows the flowsheet of the overall production process which mainly divides into leaching & CO_2 storage, purification of the leachate solution and carbonation stages. All stages were explained in the following sections.

Leaching and CO_2 storage

At first, the sample was leached with the HCl acid. The experimental conditions determined in our previous study are as follows: 50 g of the sample sized below 2.80 mm was added to 150 cm^3 of HCl solution and stirred at 150 rpm. The reaction time, solid/liquid ratio, and acid/dolomite ratio were 16 min, 25% and 4.50, respectively. The leaching experiments were performed at room temperature (Altiner et al., 2016). The representative chemical reaction is given in Equation 1:

$$CaMg(CO_3)_2 + 4HCl + H_2O \rightarrow CaCl_2 + MgCl_2 + 3H_2O + 2CO_2(\uparrow) \ . \qquad (1)$$
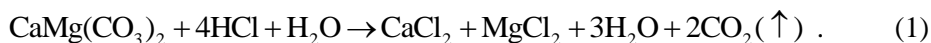
Carbon dioxide released during the leaching test was stored in a lab scale gasometer, and pressured by the compressor in order to use in the carbonation test. After the leaching test, the insoluble content (SiO_2) was removed from the solution. However, iron (Fe) as impurity dissolved together with calcium (Ca) and magnesium (Mg) ions. The solution pH was therefore increased up to 7.00 with the adding of different OH^- additives, and Fe was precipitated in hydroxide form. The solution purified was obtained after the solid/liquid separation.
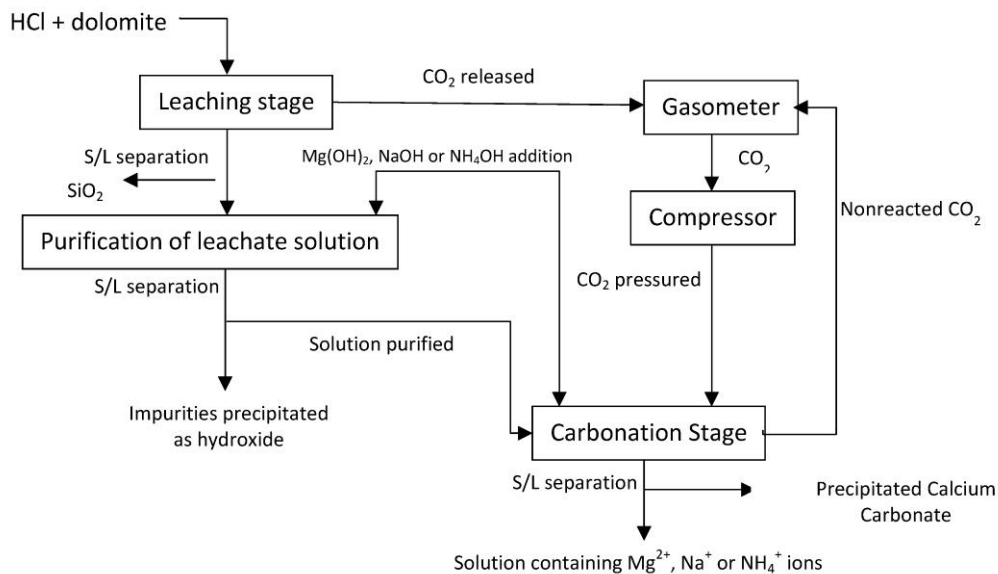

Fig. 1. Flowsheet for PCC production from dolomite ore

When NaOH or NH$_4$OH was used in order to increase the solution alkalinity, the amounts of Ca and Mg in the solution were 2.00, 1.90 mol/dm^3. However, 200 cm^3 of the solution was poured into the pure water (1300 cm^3) and the initial concentrations of Ca and Mg were 0.26, 0.24 mol/dm^3 prior to the carbonation test. The Mg/Ca ratio in the solution was determined as 0.92. When Mg(OH)$_2$ was used to increase the solution alkalinity, the amount of Mg in the solution was determined as 12.45 mol/dm^3. The initial concentrations of Ca and Mg were 0.26 and 1.66 mol/dm^3. The Mg/Ca ratio in the solution was 6.42.

Preparation and characterization of PCC

The carbonation experiments to produce PCC were performed in a 2.5 dm^3 stainless steel carbonation reactor, equipped with the teflon coated mechanical stirrer. Equation 2 shows the representative carbonation reaction

$$CaCl_2 + MgCl_2 + X + CO_2 \rightarrow CaCO_3 (\downarrow) + aMgCl_2 + bCl + H_2O \qquad (2)$$
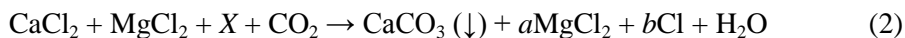
where X is Mg(OH)$_2$, NaOH or NH$_4$OH, a is amount of MgCl$_2$ and b represents NH$_4^+$ or Na$^+$. Different OH$^-$ sources such as (Mg(OH)$_2$, NaOH and NH$_4$OH) were added to 1500 cm^3 Ca-Mg rich solution in order to increase of the solution alkalinity, and the initial solution pH was 10.50. All carbonation test were performed at ambient temperature except for Mg(OH)$_2$ used as [OH]$^-$ resource as it is understood from the preliminary experiments that the ionization degree of Mg(OH)$_2$ was lower and the reaction took a long time. Therefore, the solution was heated to 40°C when Mg(OH)$_2$ was used in the carbonation test. Furthermore, the stirring speed was 750 rpm for each carbonation test. CO$_2$ adjusted with different flow rates (3.00, 6.00 and 9.00 dm^3/min) was bubbled into the solution in the bottom of the carbonation reactor, and non-reacted CO$_2$ was stored in the lab scale gasometer to re-use in the carbonation est. The time needed for the completion of the reaction was variable due to the CO$_2$ flow rates. For that reason, during the carbonation test the solution pH was monitored by a pH meter (WTW 3310). When the solution pH was 7.40, CO$_2$ flow was switched off and the reaction was completed. The solution was filtered through a 0.45 µm filter and the precipitates were dried at 105°C for 4 h. The chemical composition of precipitate was determined using standardless X-ray fluorescence (XRF, Panalytical MiniPal4) equipment and wet chemical method. The total carbon content of precipitate was determined using CS 200 carbon/sulfur analyzer. The morphological property of PCC was examined via Rigaku X-ray diffractometer (XRD) equipped with CuKα radiation with the 2θ range of 15–80°, with a step size of 0.02. The diffraction data was evaluated by means of PDXL software program for the mineral identification. The surface morphology of precipitate was characterized using scanning electron microscope (SEM, Zeiss Supra 55). The particle size distribution of precipitate was determined using Malvern Mastersizer (Hydro 2000MU). FT-IR spectrum curve of precipitate was obtained using Thermo-Scientific Nicolet IS10 equipment. The brightness value of precipitate was determined with the help of Konica Minolta CM-5

equipment. The amount of aragonite crystal in the PCC was further calculated using Equation 3, given below (Wada et al., 1993):

$$x = \frac{3.90 \cdot S_a}{S_c + 3.90 \cdot S_a} \tag{3}$$

where x is the calculated fraction of aragonite; S_c and S_a are the integrated intensities of X-ray diffraction spectra characteristic of calcite ($d_{(104)} = 0.33035$ nm, $2\,h = 29.404\,j$) and aragonite ($d_{(111)} = 0.3396$ nm, $2\,h = 26.213\,j$).

Results and Discussion

Reaction Time and Chemical Composition Examination

It is obvious that the CO_2 flow rate influenced on the carbonation time needed. An increase in the CO_2 flow rate leds to the decrease of reaction time (Han et al., 2005). The necessary reaction time was 7 min at 9.00 dm^3/min, whereas the time needed to be was 11 min at 3.00 dm^3/min. It was understood from the results given in Table 1 that the purity of PCC was quite high. The amount of MgO identified as an impurity in PCC was in the range of 0.13–0.51%.

Table 1. Chemical composition of PCC produced under different experimental conditions

Flow rate (dm^3/min)	Additive: Mg(OH)$_2$				Additive: NaOH				Additive: NH$_4$OH			
	CaO* (%)	CO$_2$[x] (%)	CaCO$_3$ (%)	MgO[+] (%)	CaO* (%)	CO$_2$[x] (%)	CaCO$_3$ (%)	MgO[+] (%)	CaO* (%)	CO$_2$[x] (%)	CaCO$_3$ (%)	MgO[+] (%)
3.00	55.72	44.01	99.73	0.27	55.70	44.18	99.78	0.12	55.22	44.51	99.73	0.27
6.00	55.65	44.12	99.77	0.22	55.55	44.02	99.57	0.42	55.20	44.36	99.56	0.44
9.00	55.85	44.02	99.87	0.13	55.82	44.01	99.83	0.17	55.60	44.26	99.86	0.14

[+] amount of MgO was determined via standardless XRF
[*] amount of CaO was determined via wet chemical analysis
[x] amount of total carbon was determined via CS200 carbon/sulfur analyzer

XRD Examination

When Mg(OH)$_2$ was added to the solution, the Mg/Ca ratio of the solution increased to 6.42. This ratio indicates that the precipitate is composed of aragonite crystals as the Mg/Ca ratio is higher than that of the Mg/Ca ratio suggested in the literature for the production of synthetic aragonite (Berner 1975; Reddy and Nancollas 1976; Lahann 1978; Mann et al., 1990; Kato 2000; Meldrum and Hydeb, 2001; Hu and Deng, 2004; Park et al., 2008; Santos et al., 2012). Thus, we predicted that the PCC was composed of aragonite crystals according to the previous studies. Figure 2 shows the XRD graphics of PCC produced at various CO_2 flow rates. XRD analyses given in Fig. 2a confirm that the aragonite crystals can be produced in the presence of Mg^{2+}. The CO_2 flow rate should be 3.00 dm^3/min for the production of pure aragonite crystals. However, higher CO_2 flow rates tend to favor calcite crystals together with aragonite

(Fig. 2. b, c). The amount of the aragonite crystals in the PCC was determined as 19.82%, in rest identified as 81.18% when the CO_2 flow rate was 6.00 dm^3/min, according to the Debye-Scherrer equation (Wada et al., 1993).
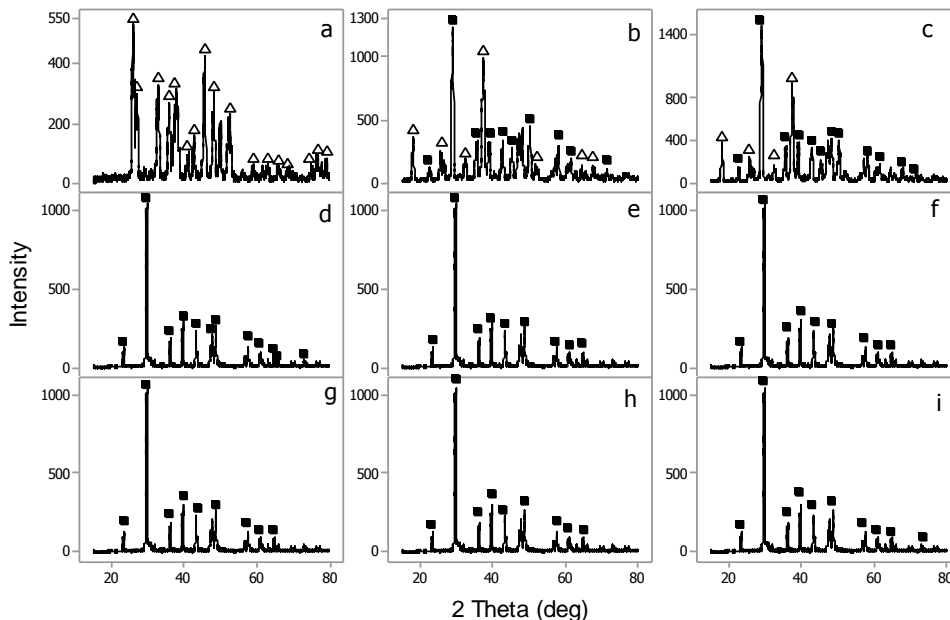

Fig. 2. XRD graphics of PCC produced: a) $Mg(OH)_2$ – 3.00 dm^3/min, b) $Mg(OH)_2$ – 6.00 dm^3/min, c) $Mg(OH)_2$ – 9.00 dm^3min^{-1}, d) NaOH – 3.00 dm^3min^{-1}, e) NaOH – 6.00 dm^3min^{-1}, f) NaOH – 9.00 dm^3min^{-1}, g) NH_4OH – 3.00 dm^3min^{-1}, h) NH_4OH – 6.00 dm^3min^{-1}, i) NH_4OH – 9.00 dm^3min^{-1} (Δ: aragonite, ■: calcite)

Likewise, the ratio of calcite crystals in PCC was 86.77% at the fixed flow rate of 9.00 dm^3/min^{-1}. In the light of these results, it can be said that the CO_2 flow rate was the effective parameter for the production of pure aragonite crystals. With the increase of CO_2 flow rates, calcite crystals together with aragonite were formed. We produced the pure aragonite crystals at higher CO_2 flow rates in comparison with the previous study (Santos et al., 2012). On the contrary, aragonite crystals in the PCC were not produced when the NaOH or NH_4OH were used as the OH^- source due to the fact that the Mg/Ca ratio of the solution was 0.95, which was lower for the aragonite production (Kato, 2000; Santos et al., 2012). Figure 2 d–f shows that PCC produced in the presence of Na^+ was composed of pure calcite crystals. These findings were in good agreement with the literature (Eloneva et al., 2008; De Crom et al., 2015). Moreover, PCC produced in the presence of NH_4^+ was composed of calcite crystals at CO_2 flow rate as shown in Figure 2 g–i, even though previous studies published in elsewhere (Prah et al., 2011; Weiss et al., 2014) indicate that PCC containing pure vaterite crystals was produced due to the presence of NH_4^+ in the solution.

SEM Examination

Figure 3 shows the SEM images of PCC produced in the presence of Mg^{2+} ions. The need-like aragonite crystals prepared in the presence of Mg^{2+} ions in the solution were observed, when CO_2 rate was 3.00 dm^3/min (Fig. 3a). However, the aspect ratio of PCC containing pure aragonite crystals was lower due to the fact that the Mg/Ca ratio in the solution was considerably high (Mg/Ca ratio: 6.42). Similar findings were revealed by the previous studies (Hu and Deng, 2004; Park et al., 2008). Figure 3 b–c shows that the particles containing the mixture of rhombohedral calcite and aragonite crystals were observed at $\geq$ 6.00 dm^3/min in the presence of Mg^{2+}. These results are in good agreement with the XRD examination.
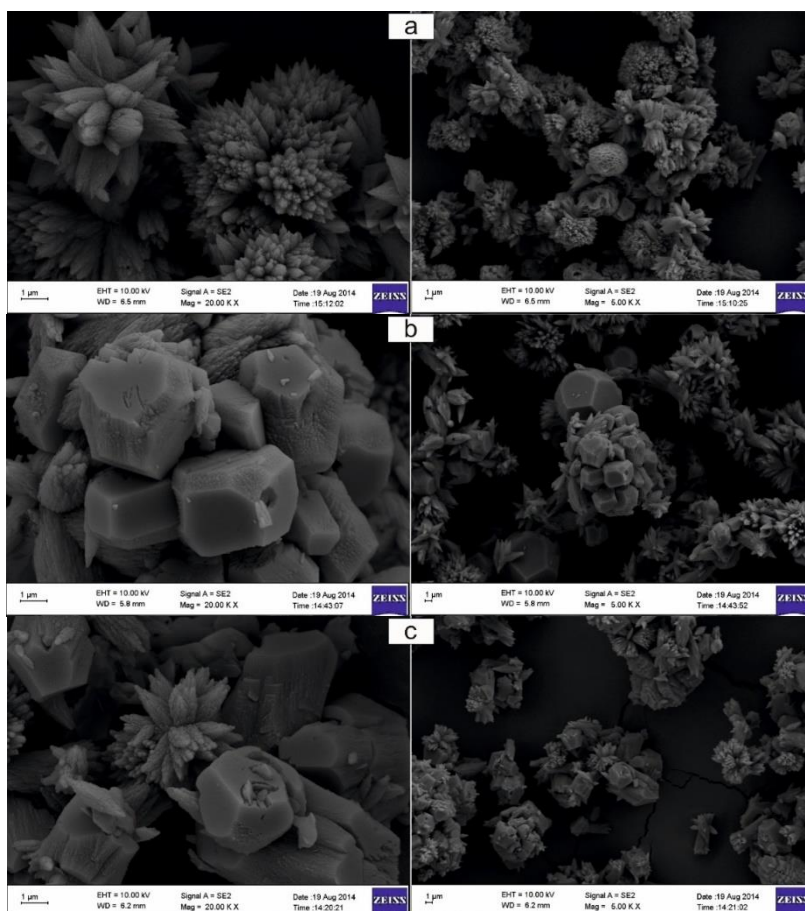

Fig. 3. SEM images of PCC produced in the presence of Mg^{2+} ions:
a) 3.00 dm^3/min, b) 6.00 dm^3/min, c) 9.00 dm^3/min
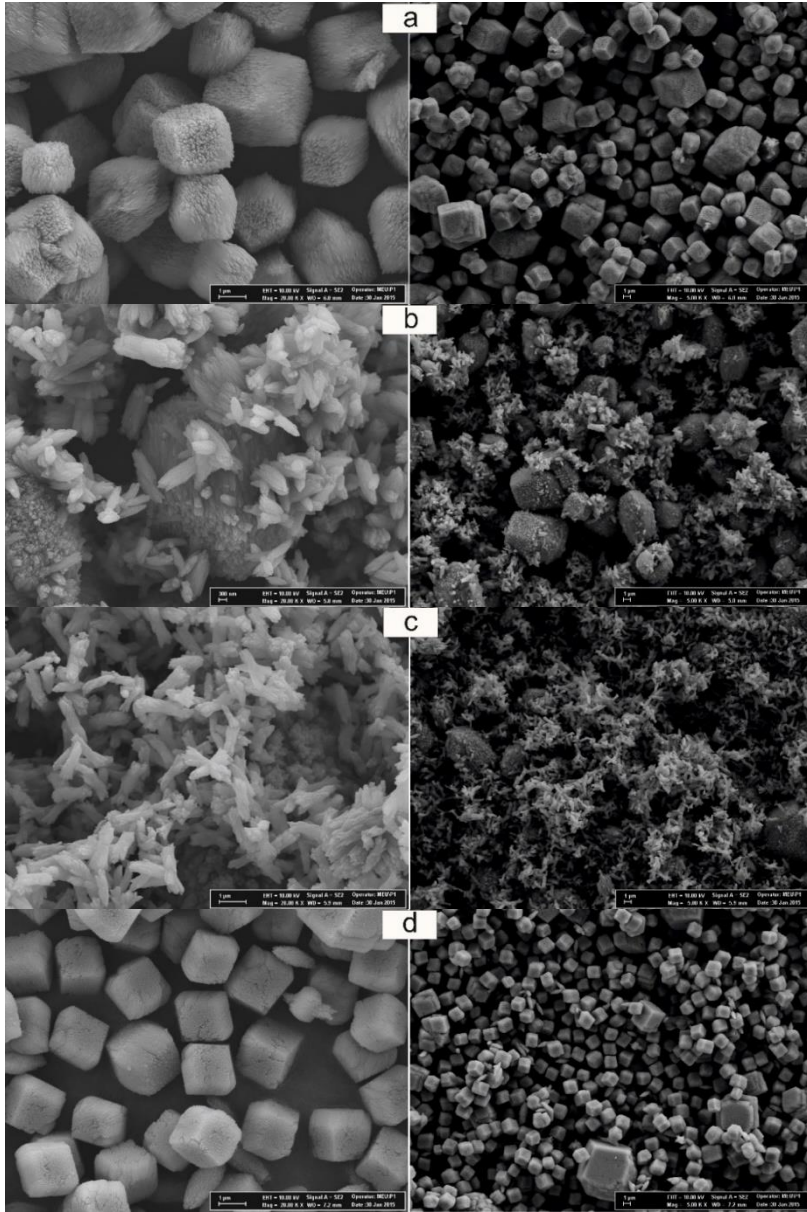
Fig. 4. SEM images of PCC produced in the presence of Na$^+$ ions: a) 3.00 dm^3/min,
b) 6.00 dm^3/min, c) 9.00 dm^3/min, d) 3.00 dm^3/min (reaction temperature 40°C)

It was understood from the SEM images given Figure 4 a–c that the morphology of PCC was controlled easily by the CO$_2$ flow rates in the presence of Na$^+$. Rhombohedral or scalenohedral calcite phases were produced, depending on CO$_2$ flow rates. As shown in Figure 4a, rhombohedral calcite phase was produced at 3.00

dm^3/min. Additionally, we performed the carbonation test at 40°C so as to determine the influence of reaction temperature on the morphology of PCC in the presence of Na^+ ions. Rhombohedral calcite crystals were produced at 40°C when the CO_2 flow rate was 3.00 dm^3/min (Fig. 4d). Therefore, it can be said that the increase of reaction temperature did not influence the morphology of PCC in this study.

PCC having similar phases were produced in the previous studies (Guo et al., 2006; Ibrahim et al., 2012) and can be used in paint industry in place of TiO_2 due to its dispersion property of light (Kontrec et al., 2008). The increase of CO_2 flow rates leds to the formation of scalenohedral calcite with rhombohedral calcite particles (Fig. 4.b). Figure 4 c indicates that the CO_2 flow rate should be 9.00 dm^3min^{-1} in order to produce pure scalenohedral calcite crystals.

Figure 5 shows the SEM images of PCC produced in the presence of NH_4^+. Although the morphology of PCC was similar to vaterite crystals prepared in previous study (Weiss et al., 2014), PCC was identified as calcite according to the XRD analysis (see Figure 2 g–i).
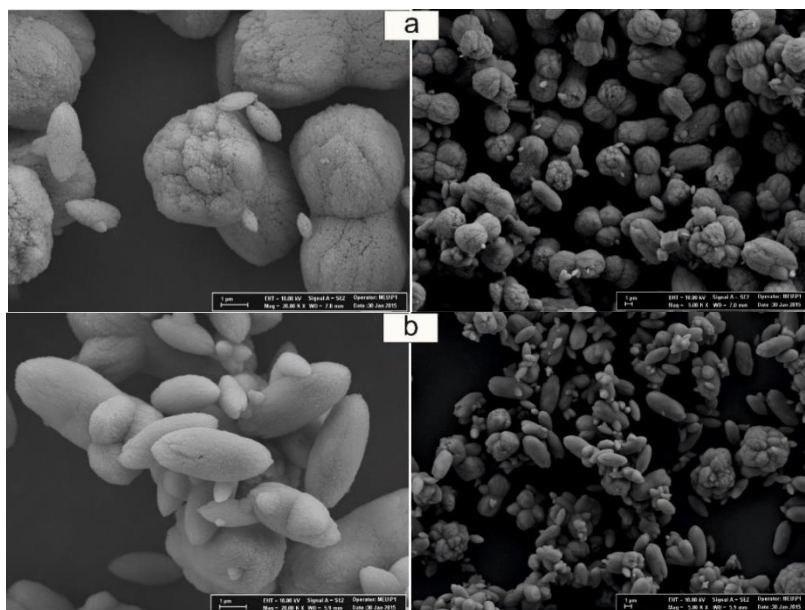

Fig. 5. SEM images of PCC produced in the presence of NH_4^+ ions:
a) 3.00 dm^3/min, b) 9.00 dm^3/min

Particle Size Distribution Examination

Figure 6 shows the particle size distribution of PCC produced in the presence of various OH^- additives. It was determined that the CO_2 flow rate influenced not only morphology but also particle size distribution of PCC. The d_{97} values of PCC determined by means of Figure 6 are given in Table 2. In the presence of Mg^{2+} ions,

PCC having large particles in the range of 22.17 to 72.84 µm was prepared. The d_{97} value of PCC increased with the CO_2 flow rates. It was thought that the particles were aglomerated due to high speed injection of CO_2. Therefore, the particle size distribution of PCC increased. On the contrary, PCC having smaller particles were produced in the presence of Na^+ or NH_4^+ ions in comparison with PCC produced in the presence of Mg^{2+} ions. When NaOH was used as OH^- sources, the d_{97} values of PCC were determined in the range of 15.46 and 20.12 µm, depending on the CO_2 flow rates. Likewise, the d_{97} value of PCC produced in the presence of NH_4^+ ions was determined 12.74 µm at 3.00 dm^3min^{-1}, 20.35 µm at 9.00 dm^3min^{-1}. However, the particle size distrubition of PCC decreased with the increase of reaction temperature in the presence of Na^+. The d_{97} value of PCC produced at 40°C was 11.45 µm that was lower than that of the d_{97} value of PCC produced at ambient temperature.
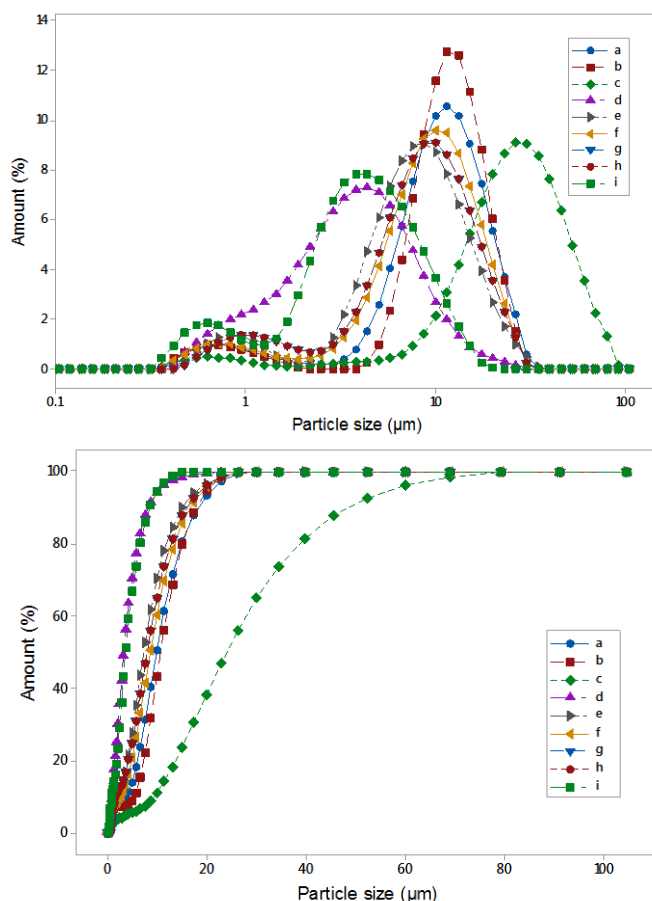

Fig. 6. Particle size distribution of PCC produced in the presence of various OH^- sources:
a) $Mg(OH)_2$ – 3.00 dm^3/min, b) $Mg(OH)_2$ – 6.00 dm^3/min, c) $Mg(OH)_2$ – 9.00 dm^3/min,
d) NaOH – 3.00 dm^3/min, e) NaOH – 6.00 dm^3/min, f) NaOH – 9.00 dm^3/min,

g) NH_4OH – 3.00 dm^3/min, h) NH_4OH – 9.00 dm^3/min, i) NaOH – 3.00 dm^3/min,
reaction temperature: 40°C

The uniformity coefficient values of the PCC indicate that the PCC produced at each CO_2 flow rates had a homogeneous particle size distribution in the presence of Mg^{2+} or Na^+ ions, even if the d_{97} value of PCC increased with the increase of CO_2 flow rates.

Table 2. Particle size distribution values of PCC produced in the presence of various OH^- sources

OH⁻ source: $Mg(OH)_2$				
Flow rate (dm^3/min)	d_{10}	d_{60}	d_{97}	UC*
3.00	4.02	11.50	22.17	2.88
6.00	5.50	12.03	62.58	2.18
9.00	9.33	28.02	72.84	3.00
OH⁻source: NaOH				
Flow rate (dm^3/min)	d_{10}	d_{60}	d_{97}	UC*
3.00	1.02	4.15	15.46	4.00
6.00	2.18	8.03	21.05	3.67
9.00	2.50	10.02	20.12	4.00
3.00 (40°C)	0.85	3.05	11.45	3.58
OH⁻ source: NH_4OH				
Flow rate (dm^3/min)	d_{10}	d_{60}	d_{97}	UC*
3.00	1.60	10.02	12.74	6.25
9.00	1.70	11.65	20.35	6.85

* UC represents the uniformity coefficient determined by the equation(d_{60}/d_{10})

Brightness Property and FT-IR Examination

The average brightness value of PCC produced in the presence of various OH^- sources was determined as 95.99, 95.65 and 94.65 in the presence of Mg^{2+}, Na^+ and NH_4^+, respectively.

Table 3. Brightness value of PCC produced in the presence of various OH^- sources

OH⁻ source: $Mg(OH)_2$	OH⁻source: NaOH	OH⁻ source: NH_4OH
95.99	95.65	94.65

FT-IR spectrum illustrated in Figure 7 a confirms that PCC was composed of pure aragonite crystals at the fixed flow rate of 3.00 dm^3/min as the sharp peaks (1082, 857 and 698 cm^{-1}) were the characteristic peaks for the aragonite crystals (Seo et al., 2005; Shen et al.2010; Guo et al., 2011). On the contrary, the characteristic peaks (1082, 857 and 713 cm^{-1}) for the calcite crystals were determined, and PCC was composed of pure calcite crystals in the presence of Na^+ or NH_4^+ (Schmidt et al., 2010).
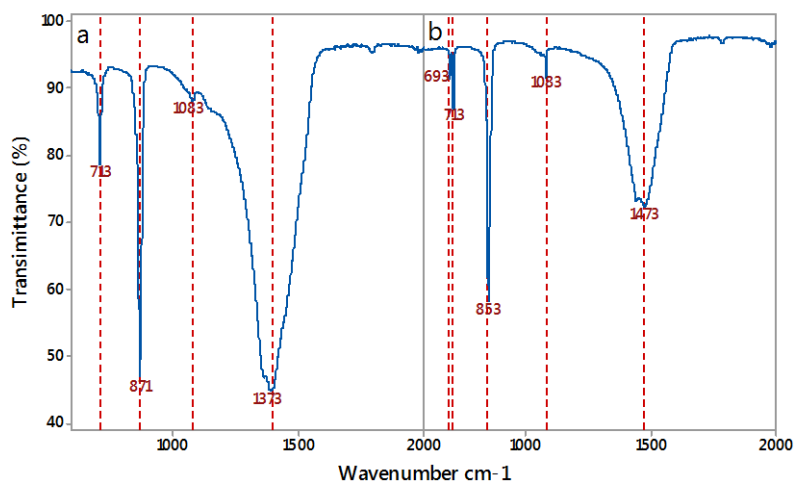
Fig. 6. Representative IR spectrum graphics of PCC : a) calcite, b) aragonite

Conclusions

In this paper, we produced PCC with various morphologies from dolomite ore via leaching and carbonation process in the presence of various OH^- sources. It was understood from the experimental findings that OH^- additives influenced the morphology and particle size properties of PCC produced. The CO_2 flow rate was an important parameter to produce pure aragonite crystals. The increase of CO_2 leads to the formation of calcite crystals together with aragonite. More specific experimental conditions were required to produce aragonite in comparison with the calcite production. Moreover, rhombohedral or scalenohedral calcite crystals were produced easily in the presence of Na^+ or NH_4^+ ions depending on the CO_2 flow rates. The solution obtained after the aragonite production can be used to produce MgO or $MgCl_2$ crystals whereas that of after the aragonite production was not suitable due to consisting of Na^+ or NH_4^+ ions.

Acknowledgment

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