International Journal of Engineering & Technology, 7 (4.14) (2018) 172-174

International Journal of Engineering & Technology

Website: www.sciencepubco.com/index.php/IJET

Research paper



CO_2 Mineralization: Production of Precipitated Calcium Carbonate as a Method of CO_2 Utilization

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Abstract

CO_2 utilization into minerals is one of the most efficient methodologies although much research concerns the utilization of CO_2 to produce chemicals. The production of precipitated calcium carbonate (PCC) from three different starting materials has been reported. The gas-liquid reaction is carried out by bubbling carbon dioxide into a solution of lime products with fixed parameters of 99% CO_2 purity, 4.0 L/min of flow rate and 1500 rpm stirring rate at atmospheric pressure. The PCC was then characterized for X-Ray diffraction (XRD), field emission scanning electron microscopy (FESEM), X-Ray fluorescence (XRF) and particle size. Experimental results indicate that the PCC produced from quick lime showed the highest yield of 17.27 g, however there is no significant difference for both carbide lime and hydrated lime at 12.04 g and 11.57 g respectively. Morphology, phase structure and particle size of PCC produced reveals insignificant influence with different starting materials. Producing PCC from CO_2 and natural minerals can be a potential method of reducing CO_2 emissions by locking-up CO_2 in a stable mineral form, whilst at the same time turning low quality natural minerals into high valuable products.

Keywords: *CO_2 mineralization; CO_2 utilization; natural mineral; precipitated calcium carbonate; lime products*

1. Introduction

Extensive use of fossil fuels, is a major challenge which contributed to the global climate change. CO_2 concentration in the atmosphere has risen at an exceptional rate since the beginning of industrialization in the eighteen century. Different strategies and tools from various aspects have been proposed and implemented to mitigate rapid global warming and adapt to the climate change. There are lots of strategies for reducing CO_2 emissions which include the following: (1) improving overall energy efficiency, (2) implementing carbon capture and storage and (3) utilizing renewable energy and material recycling [1]. Another potentially important example of reducing CO_2 emission via CCU field is CO_2 mineralization, or mineral sequestration although it can be considered a CCS path. Mineral sequestration is the process of storing CO_2 in the form of a carbonate which involves an exothermic chemical reaction between CO_2 and basic minerals. This mineral sequestration normally happened in sub surface. However, for the surface, the concept is the same but the end product, precipitated calcium carbonate will be used as a filler/additive for many applications.

Precipitated calcium carbonate (PCC) is a synthetic calcium carbonate that has high purity of $CaCO_3$ content in its compound which is more than 98 wt%. Recent years, precipitated calcium carbonate (PCC) has received significant attention because of its wide application in the areas of papermaking, rubber, plastics, paints, pharmacy etc. Such a variety of applications, only the right PCC can boost the quality of the end products. PCC require to have different physical and chemical properties, among which particle size, specific surface area, morphology and chemical purity are the most important [2]. Many industries used carbonate rocks for the production of PCC. PCC can be synthesize either by carbonation (gas-liquid-solid) or solution (liquid-liquid-solid) process after calcination and hydration reaction of a carbonate rock [3]. However, carbonation is the most often used route in industrial because of its simple procedure, low cost, higher yield and higher purity [4]. Due to the low CO_2 solubility in water, the carbonation process is a slow process compared to solution process [5].

Industrially, carbonation is performed by bubbling CO_2 through a slaked lime slurry (i.e., $Ca(OH)_2$ aqueous suspension) resulted in PCC formation according to the process route as follows:

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

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

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

The overall chemical reaction is given as:

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

There are many materials that can be used as a starting material for PCC production. The quality of the starting material is one of the factor that affect the quality of PCC produced. Limestone, quick lime, hydrated lime, carbide lime, calcium silicate, dolomite, etc. are among the starting materials that can be used in producing PCC. Recently, focused by researchers is to improve the PCC production yield, control the polymorph and maintain the stability and size distribution to suite the final product [6]. Calcite, aragonite and vaterite are different crystal structures form by PCC,

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each represents different stability [7]. The most thermodynamically stable and the most important polymorph in the industry is calcite structure due to its possibility to form different morphologies [8]. This work investigates the effect of different starting material on the PCC yield, morphology, purity and particle size using gas-liquid-solid route at atmospheric pressure.

2. Experimental

2.1. Preparation of ionic solution

Refined sugar cane was used to prepare the sucrose solution. First, 100 g sugar was dissolved in 1000 ml filtered water in order to get 10° Brix of one litre ionic solution. The sucrose concentration was checked by using portable brix meter. The Brix was adjusted with addition of some sugar or water into the solution in order to achieve 10° Brix ionic solution.

Then, 120 g carbide lime was mixed into the sucrose solution and stirred to make sure carbide lime was fully dissolved. The mixtures were then filtered to remove unreacted carbide lime. The clear solution obtain was called ionic solution that contained calcium ions and used in the experiments. Same procedure was repeated for hydrated lime and quick lime as starting materials.

2.2. Carbonation at atmospheric condition

1 litre of ionic solution was stirred using mechanical stirrer at 1500 rpm. Then, carbonation process was carried out, whereby CO_2 gas was introduced at 4.0 L/min into the pregnant solution until the pH reached at 8. The synthesized PCC was filtered and rinsed with warm water to remove sugar and unreacted lime products. The collected PCC was dried at 60 °C and weighed to determine the weight of PCC produced. The dried PCC was further characterized.

3. Results and Discussion

XRF analysis was done to characterize the amount of calcium oxide (CaO) content in different starting material. Table 1 indicates the percentage amount of components in different starting material. Quick lime shows the highest CaO content followed by carbide lime and hydrated lime.

Table 1: XRF analysis on raw materials

Composition (%)	Raw materials		
	Carbide lime	Quick lime	Hydrated lime
CaO	67.20	69.68	59.31
Fe_2O_3	0.05	0.13	0.12
MnO	-	0.02	0.03
TiO_2	-	0.02	0.02
SiO_2	2.13	0.04	0.04
Al_2O_3	-	0.12	0.05
P_2O_5	0.03	0.31	0.12
MgO	0.43	0.81	0.85
Na_2O	-	0.05	0.04
K_2O	-	0.05	0.02
LOI	30.00	28.75	39.38

PCC production yield from different starting material was shown in Fig. 1. Quick lime shows the highest yield of 17.27 g. There is no significant difference in PCC yield produced by both carbide lime and hydrated lime. This results indicate that there is significant correlation between calcium oxide content reported in Table 1 & PCC yield produced.

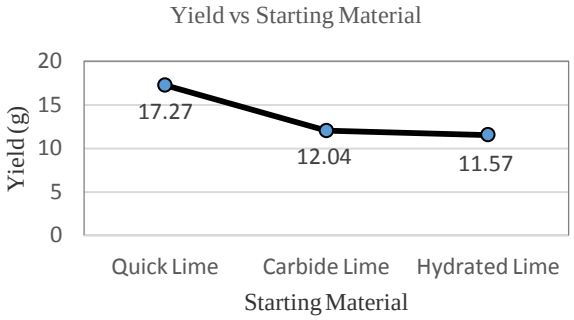

Fig. 1: Effect of starting material on PCC yield

The PCC morphology was examined using FESEM analysis. Fig. 2 shows FESEM images of PCC produced from quick lime (Fig. 2(a)), carbide lime (Fig. 2(b)) and hydrated lime (Fig. 2(c)) at different magnification. At fixed parameter of 99% CO_2 purity, 4.0L/min flow rate and 1500 rpm stirring rate, cubic shape PCC was formed regardless of using quick lime, carbide lime or hydrated lime. The surface of the PCC particles produced by using quick lime is smoother as compared to hydrated lime and carbide lime. The morphology of carbide lime portrays the perforated surfaces. This result similar to that reported by Othman et al. [9].

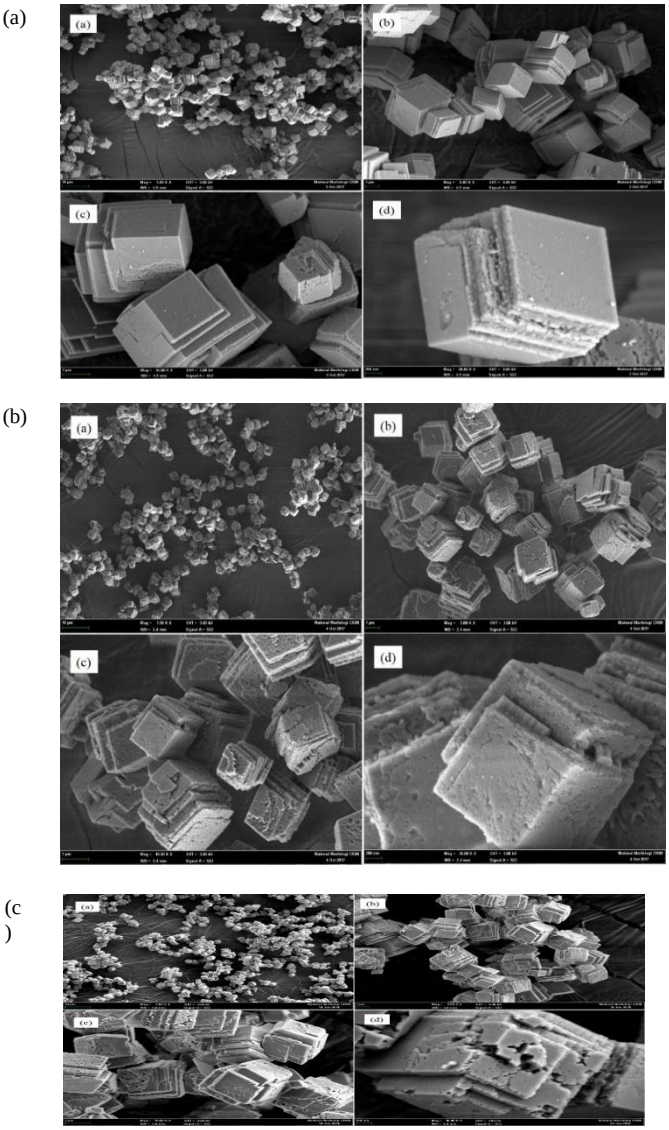

Fig. 2: FESEM micrographs of PCC produced from different starting material (a) quick lime (b) hydrated lime and (c) carbide lime at different magnification (a) 1kx, (b) 5kx, (c) 1 0kx and (d) 30kx.

XRD analysis in Fig. 3 identified calcite as the $CaCO_3$ polymorph precipitated for all different starting material. This observation indicates that when solid $Ca(OH)_2$ is suspended in an aqueous medium, where heterogeneous nucleation induced by foreign particles is favoured, the precipitation of the stable calcite polymorph as the main phase is the common result for carbonation processes [10].

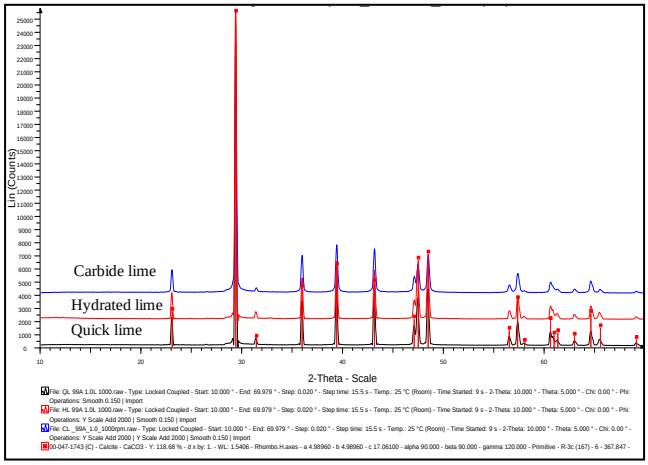

Fig. 3: XRD analysis on PCC produced from different starting materials

Table 2 shows the results of particle size for PCC produced using different starting material. At same parameter (99% CO_2 purity, 4.0 l/min, 1500 rpm), the particle size of PCC produced from different type of starting materials were almost the same which is below 20 µm. The results explain that different type of starting materials did not influence on the PCC particle size.

Table 2: Particle size analysis of PCC produced from different starting materials

Starting Materials	Parameters			d10 (µm)	d50 (µm)	d90 (µm)	Size range (µm)
	Gas (CO_2 %)	Flow rate (l/min)	Stirring rate (rpm)				
Quick Lime	99	4	1500	1.526	6.028	12.233	<20
Hydrated Lime				1.325	6.423	11.873	<20
Carbide Lime				1.212	4.821	8.117	<20

4. Conclusion

The experimental study of calcium carbonate precipitation using different starting materials had insignificant influence on the morphology, phase structure and particle size with fixed operating experimental conditions of 99% CO_2 purity, 4L/min flow rate and 1500 rpm stirring rate. However, different starting materials used only showed that the PCC yield produced were different because of the CaO composition in each of lime product. Quick lime indicates the highest PCC yield of 17.27 g while no significant difference in PCC yield produced by both carbide lime and hydrated lime at 12.04 g and 11.57 g respectively.

Acknowledgement

Authors express their gratitude to Petronas Research Sdn.Bhd. and Mineral Research Centre for the support provided throughout the project.

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