Improving precipitate calcium carbonate (PCC) particle size distribution for a continuous mineral carbonation system

M S Onn*, M G M Noh, M S M Shukor and M A Isa

Group Research and Technology, PETRONAS, Malaysia

*syazwan.onn@petronas.com.my

Abstract. Mineral carbonation is a process where carbon dioxide (CO2) is converted into solid carbonates. The product of mineral carbonation is obtained when CO2 is being contacted with alkaline earth metals, such as calcium and magnesium. In this research, the team focusing on producing precipitated calcium carbonate (PCC), as a solution to manage CO2 release which comes from high CO2 content natural gas field production. To make this process economically feasible, the team has researched obtaining valuable PCC quality which is marketable in various industries. The quality mainly measured in terms of particle size, where the particle size will determine the application of the PCC. This study investigates the effect of feed solution retention in reactor towards PCC particle size, using continuous mineral carbonation system. In this system, Milk of Lime, which is Calcium Hydroxide (Ca(OH)2) solution used as feed. To produce this solution, 7 g/L Calcium Oxide (CaO) is suspended in deionized water and stirred. This solution is injected in the range of 0.8 L/min to 1.2 L/min into pressurized CO2 in the range of 10 bar to 80 bar. The retention time is varied by using mechanically modified reactor inlet cap, where the feed inlet time is delayed by elongation of feed injector inside the reactor by 15 cm (NEWCAP). Particle size of the product was analyzed by using Malvern Mastersizer 3000. Experimental data show that by shortening the feed solution retention time inside the reactor, will produce smaller particle size. Using the unmodified reactor inlet, the obtained product particle size ranging (D50) from 15 micron to 25 micron. On the other hand, using NEWCAP reactor inlet the obtained particle size ranging (D50) from 8 micron to 20 micron.

1. Introduction

Solid carbonates are mainly formed during the mineral carbonation process which requires carbon dioxide (CO2) as the main reactant. Variety of alkaline earth metal carbonates are formed using this method, such as calcium carbonate and magnesium carbonate which comes from natural minerals, waste residues, or brines. The mineral carbonation reaction process which takes place in the reactor leads to the formation suspended solid in water, composed by mineral carbonate. The mineral carbonate formed varies in morphology and particle size distribution. These properties determine the commercial application of the formed calcium carbonates (e.g. filler in paper, aggregate in concrete)[1]. In this paper, the work is focusing on mineral carbonation based calcium, obtaining precipitated calcium carbonate (PCC) as the final product. This work highlights on findings of the effect of calcium feed solution retention in reactor towards PCC particle distribution, using a continuous flow carbonation system.
In investigating particle size distribution of PCC, laser diffraction analysis (LDA) is an effective technique in order to track the particle size changes between the set of experiments. Thus, this technology helps in elucidating the correlation of calcium solution feed retention time with changes in the particle size distribution of the product. Dry dispersion analysis (Malvern Mastersizer 3000) is selected due to prevent agglomeration of the PCC samples which will cause results inaccuracy. The results taken are Dv50, where represents the average diameter of a particle in a volume of sample. The detection range of the produced PCC in this experiment is between 8 microns to 25 microns.

2. Experimental

2.1 Reagents
Calcium oxide (Sigma Aldrich) used in this study is analytical grade, without further purification. The calcium oxide used to prepare calcium hydroxide solutions, by mixing with deionized water. Carbon dioxide for PCC reaction was purchased from Linde.

2.2 Reaction
Calcium carbonate was precipitated in a continuous flow tube reactor, where the dimension is 50 cm length and the diameter is about 10 cm. The reactor is pressurized with CO₂ and connected to a solution injection pump, where the injection flow rate is in the range of 0.5 liter per minute to 1.2 liter per minute, at reactor pressure range 5 to 80 bar. The calcium hydroxide concentration used was 7 gram per liter. The reaction product is ejected immediately after calcium hydroxide injected to the pressurized reactor, at a constant pressure. The product is collected in a vessel, and phenolphthalein applied in order to detect the basicity of the product. If the product is colorless after phenolphthalein applied indicates all calcium hydroxide has been consumed and become stable calcium carbonate. Vice versa, if the product turned into purplish color, there were calcium hydroxide which yet to be reacted.

Figure 1. PCC Reactor Setup.
Table 1. Experiment condition.

| Length of Feed Entry Point from Reactor Bottom (cm) | Injection Speed (liter per minute) | Pressure range (bar) |
|---------------------------------------------------|-----------------------------------|---------------------|
| 42                                                | 0.5                               | 5 – 80              |
|                                                   | 1.0                               |                     |
| 15 (NEWCAP)                                       | 0.8                               | 5 – 80              |
|                                                   | 1.2                               |                     |

The figure shows the experimental setup of the continuous PCC reactor. In this experiment, the residence time of the feed is varied by using different injection point from the top of the reactor. The injection point is varied by modifying the length of the feed entry point from the reactor bottom, which means for the NEWCAP, the feed inlet is near to the reactor bottom compared to the unmodified reactor cap. The product comes out in the form of a slurry, where the product is filtered by using Whatman Grade 42 filter paper and being dried in an oven (Mermet) at temperature 80°C.

2.3 Characterization of PCC particles

The size of calcium carbonate particles determined by the laser diffraction method (Malvern Mastersizer 3000), where the average volume size Dv50 is taken. The analysis was done by using Aero method, which is the dry analysis. This is because the PCC samples tend to agglomerate in wet analysis resulting in inaccurate particle size reading. Each analysis was done at least 3 times in order to ensure consistency of the results. Meanwhile, the morphology of PCC particles is quantitatively analyzed using FESEM (Hitachi FESEM SU8020). As for determining the crystalline structure and polymorph composition, XRD analysis (Shimadzu XRD-6100) is used. Here, the XRD spectra were collected at a scan rate 0.2⁰ and theta range 20-60⁰ at room temperature. This method also is used to confirm the existence of calcium hydroxide existence, to ensure whether the calcium hydroxide is fully converted or not.

3. Results

3.1 Particle size analysis

The mean size of produced particles is as shown in Figure 2. It is found that the particle size reduces when injection rate increases from 0.5 liter per minute to 1.2 liter per minute. This result indicates when the residence time is reduced, the time for the PCC particles to agglomerate with each other becomes reduced as well. Furthermore, when the injection rate is higher, the erosion rate of the formed product also higher due to the velocity of the product movement from top to bottom of the reactor. This phenomenon also helps in reducing the particle size. The particle size is further reduced when the residence time of the reactant is shortened. As shown in Table 1, the length between the feed entry point to the reactor bottom being reduced from 42 cm to 15 cm. This means, the contact time between the reactant and pressurized CO₂ becomes shorter. Thus, there is limited time for the PCC particles to agglomerate and grow, leading to a smaller product particle size. It is also observed that, at higher pressure, the particle size reduced. This indicates that the growth of the particles being suppressed by the high pressure environment. However, the economics of higher operating pressure needs to be evaluated before upscaling, due to high energy consumption on gas compressing.

3.2 Morphology of calcium carbonate particles

The morphology of the produced PCC samples examined by FESEM. It is observed that the crystal habits of the produced PCC are rhombohedron calcite, which is the most stable form of calcium carbonate. Change of experimental condition not having influences in terms of crystal structure, since no additional chemicals involve to retard the arrangement of produced calcium carbonate crystals.
Another important thing to be highlighted is that, as shown in Figure 5, the sample contains no calcium hydroxide residue. This result suggested, at concentration 7 gram per liter, all of the reactants consumed to form calcium carbonate.

Figure 2. Particle Size Distribution versus Reaction Pressure for Various CaOH Feed Rate.

Figure 3. FESEM images of produced PCC samples.

Figure 4. XRD result of produced PCC sample
### 4. Discussion

The reactions to produce precipitated calcium carbonate can be written as:

\begin{align*}
CaO(s) + H_2O(l) &\leftrightarrow Ca^{2+}(aq) + 2OH^-(aq) \quad (1) \\
CO_2(g) + OH^-(aq) &\leftrightarrow HCO_3^-(aq) \quad (2) \\
HCO_3^-(aq) + OH^-(aq) &\leftrightarrow CO_3^{2-}(aq) + H_2O(l) \quad (3) \\
Ca^{2+}(aq) + CO_3^{2-}(aq) &\leftrightarrow CaCO_3(s) \quad (4)
\end{align*}

Feed prepared by mixing calcium oxide and deionized water to produce calcium hydroxide, which part of the calcium hydroxide is dissolved to form calcium and hydroxide ions. However, the calcium hydroxide is slightly dissolved in water. Feed prepared at room temperature and pressure. In this condition, calcium oxide solubility is 0.12 gram per liter. In this case, 7 gram calcium oxide is mixed with 1 liter of deionized water. This means the balance of calcium oxide remains in the form of a slurry. The feed, in the slurry form is fed straight away to the CO\textsubscript{2} pressurized reactor. In the reactor, the feed is fed in the form of water spray, in the form of tiny droplets. The CO\textsubscript{2}, which in contact with the tiny calcium solution droplets dissolved to form carbonate ion. This carbonate ion instantaneously reacts with calcium ion and forming precipitated calcium carbonate. At the same time, the calcium ion consumed by carbonate ion being replaced by undissolved calcium oxide, which maximizes the amount of precipitated calcium carbonate production.

![Illustration of PCC Reaction Mechanism](image)

**Figure 5.** Illustration of PCC Reaction Mechanism.

In general, the calcium carbonate formation goes through two stages of crystallization, namely nucleation and growth stages. In a detailed study on calcium carbonate crystallization, the crystal growth found to be more complex. Initially, calcium carbonate crystal growth is the formation of amorphous calcium carbonate. After this stage completed, the amorphous calcium carbonate transformed to be more stable polymorphs, which are the metastable forms (vaterite, aragonite) or thermodynamically stable calcite. In these experiments, the precipitated calcium carbonate found to rhombohedron, which is fourth in the ranking of the most frequently occurring form of natural calcites. According to Aquilano et al. [2][3] this morphology is usually produced in a pure aqueous solution at low temperature and supersaturation.

This study intends to control the particle size of the produced PCC by manipulating the calcium solution injection rate and reactant residence time. It is observed in the results, the higher the injection rate, the produced PCC particle size is smaller. This is due to the relationship between liquid flowrate and erosion. According to Liu et al [4], erosion rate will be increased when the fluid velocity increased. In this case, the PCC particle forms instantaneously after the solution contacted with pressurized CO\textsubscript{2} in the reactor, forming PCC particles. The particles will keep flowing past through the reactor until the bottom part and erosion occurs as the particles move toward the reactor outlet. This phenomenon causes PCC particles to tear apart and become smaller than the initial size.

Apart from controlling the injection rate, the residence time of the reactant can also influence the particle size. According to Li et al [5], based on their experiments on controlling the growth of
covalent organic framework nanoparticles, the particle size of a crystal is directly proportional to time of reaction. Time is very important in crystal growth, where the nucleates of the crystal take time to agglomerate and rearrange to become bigger crystal in the growth phase. Therefore, in order to achieve smaller particle size, the growth of the crystal needs to cut by shortening the contact between reactants and preventing from the formation of new nucleates. This will limit the agglomeration of nucleates thus achieving smaller particle sizes.

5. Conclusions
The particle size of produced PCC in a continuous reactor system can be controlled by manipulating the feed solution injection rate and feed residence time. In this study, milk of lime is used as a feed solution, where 7 g/L calcium oxide being mixed in water. Using unmodified reactor cap, which the feed injection point is 42 cm from reactor bottom, the feed injected in the range of 0.5 L per minute to 1.0 L per minute, the obtained particle size ranging from 15 micron to 25 micron. Meanwhile, using the modified reactor inlet cap, where the feed solution inlet is 15 cm from the reactor bottom (NEWCAP), the obtained particle size ranging from 8 micron to 20 micron. The NEWCAP manipulates the feed solution residence time which means the contact time between the feed solution droplets and CO₂ inside reactor being limited. Thus, the obtained PCC particle size range is smaller compare to the unmodified reactor inlet.

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