Scaling Up of Continuous Mineral Carbonation Reactor for the Production of High Value PCC Products

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Abstract. The concept of supercritical CO2 mineral carbonation reaction was firstly proven and demonstrated in the laboratory scale using a 100cc high pressure PVT recombination chamber. Successful proof of concept led PETRONAS to scale up this reaction by developing a working prototype mineral carbonation reactor with the intention of demonstrating the continuous operation of the supercritical CO2 mineral carbonation process. The setup comprising of a feedstock tank, a high pressure liquid pump, a 0.8L high pressure tubular reactor, injector spray nozzle was thoroughly tested to understand the feasibility and robustness of the prototype reactor design and configuration. Another purpose was to study the effect of varying parameters such as reactor pressure, feedstock injection flow rate and compositional effect of methane in carbon dioxide gas reactant to the properties of the precipitated calcium carbonate produced from this process scheme. In summary, the setup was successful to demonstrate the concept of continuous supercritical mineral carbonation reaction up to 1.5 litre/min feedstock injection flow rate. The effect of reactor working pressure and feedstock injection flow rate was the main factors determining the properties and quality of precipitated calcium carbonate produced. Particle size distribution of the calcium carbonate precipitates produced from this setup averaged approximately 6 microns in size. Other parameters such as gas composition and recycling of carrier fluid sucrose have less effect on the properties of the product.

1. Introduction
Technologies to convert CO2 to valued products have been widely available for many decades now but unfortunately still at experimental or small pilot plants as researchers and technologist around the world are still investigating the most economic and sustainable pathway to convert CO2. Catalytic conversion of CO2 which relies heavily on cheap hydrogen are not feasible unless cost of producing renewable hydrogen is further reduced at par with hydrogen produced from methane reforming[1]. Technology to convert CO2 via the electrochemical route is still at its infancy in terms of the technology maturity due to the excessive amount of electricity required to perform such reaction. Another promising CO2 conversion route is CO2 to Precipitated Calcium Carbonate PCC. It is estimated that the global high value PCC market is approximately 98MTPA[2].
2. Current Progress on CO\textsubscript{2} Mineral Carbonation Process

The CO\textsubscript{2} mineral carbonation process is reacted in a continuously stirred batch reactor where CO\textsubscript{2} gas is pressurized to a specific pressure to promote the desired dissolution rate of CO\textsubscript{2} into the charged solution [3]. The charged solutions which are earlier introduced into the batch reactor are usually aqueous solution of alkali metal ions dissolved in water. The governing equation [4] of the reaction steps for the CO\textsubscript{2} carbonation process is as mentioned below:-

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\begin{align*}
\text{Ca(OH)\textsubscript{2}} + \text{CO}_2 & \rightarrow \text{CaCO}_3 + \text{H}_2\text{O} \quad (1) \\
\text{CO}_2(g) & \rightarrow \text{CO}_2(aq) \quad (2) \\
\text{Hydration of dissolved CO2} \quad & \\
\text{CO}_2(aq) + \text{H}_2\text{O} & \leftrightarrow \text{H}_2\text{CO}_3(aq) \quad (3) \\
\text{Reaction of hydroxyl ions with dissolved CO2 in the case of high pH of the solution} \quad & \\
\text{CO}_2(aq) + \text{OH}^-(aq) & \leftrightarrow \text{HCO}_3^-(aq) \quad (4) \\
\text{HCO}_3^-(aq) + \text{OH}^-(aq) & \rightarrow \text{CO}_3^{2-}(aq) + \text{H}_2\text{O} \quad (5) \\
\text{Dissociation of calcium hydroxide} \quad & \\
\text{Ca(OH)}\textsubscript{2}(aq) & \rightarrow \text{Ca}^{2+} + 2\text{OH}^- \quad (6) \\
\text{Precipitation} \quad & \\
\text{Ca}^{2+}(aq) + \text{CO}_3^{2-}(aq) & \rightarrow \text{CaCO}_3(s) \quad (7)
\end{align*}
\]

Such process schemes require CO\textsubscript{2} to dissolve in the aqueous phase solution becoming CO\textsubscript{3}\textsuperscript{2-} anion before any carbonation reaction can take place. Hence the overall rate of reaction is determined by the dissolution rate of CO\textsubscript{2} [5, 6]. Many researches have been conducted to study various methods or conditions to increase the rate of dissolution of CO\textsubscript{2}. Lopez-Periago et al. [7] had investigated the usage of supercritical CO\textsubscript{2} on the efficiency of carbonation kinetics by allowing supercritical CO\textsubscript{2} to diffuse into a layer of activated solution in a continuously stirred tank reactor.

Literature review on the developmental work towards establishing a continuous mineral carbonation reaction is briefly included here. Park et al. [8] used amine molecules to increase dissolution of CO\textsubscript{2} into aqueous phase to control the formation of MgCO\textsubscript{2} under low pressure and temperature. Onimisi et. al [9] reported on the usage of a tubular reactor with CO\textsubscript{2} bubbling in aqueous milk lime suspension treated with naturally occurring morphological modifier with the purpose of promoting better mixing and continuous mineral carbonation process. Onimisi et al. also developed method for spontaneity of PCC crystallization using a tubular reactor with the bubbling of CO\textsubscript{2} reactant. A tall and narrow tubular column reactor was developed for continuous PCC production in a Ca(OH)\textsubscript{2} (aq)–CO\textsubscript{2} (g) reacting system with the assumption that the ideal mixing of the steady upward flow of the aqueous slurry with bubbling CO\textsubscript{2} in the column can initiate a spontaneous reaction and ultimately result in continuous and steady PCC crystallization. Rafael M. Santos et al. [10] on the other hand studied the effect of ultrasound in reducing the particle size of several powders such as Ca(OH)\textsubscript{2}, CaCO\textsubscript{3} and stainless steel slags while enhancing the carbonation kinetics and conversion of calcium oxide feedstock. Du-Re Han et al. [11] worked on the concept of CO\textsubscript{2} sequestration by aqueous mineral carbonation of limestone in a conventional bubbling CO\textsubscript{2} supercritical reactor. Ana M. Lopez-Periago [12] claimed of a breakthrough technique for the preparation of high-yield precipitated calcium carbonate based on the combination of supercritical carbon dioxide (scCO\textsubscript{2}) and ultrasonic agitation. Concepcion Domingo[13] reports of a new method to produce calcite crystals with scalenohedral and rhombohedral morphologies in the Ca(OH)\textsubscript{2}–H\textsubscript{2}O–CO\textsubscript{2} system without the use of any tailor-made additive with the usage of compressed supercritical CO\textsubscript{2} to precipitate.
CaCO₃. However, except for Ominisi et al. [11] all of the authors reported the usage of a batch reactor to perform the various type of improvements on the carbonation reaction.

Hence, the abovementioned literature review strongly suggests that current technology in converting CO₂ into mineral carbonates are performed while CO₂ is in gaseous phase. Most technology to separate and capture CO₂ which are either amine or membrane type separates, and subsequently permeates CO₂ in low pressure gaseous form. The mineral carbonation process which feeds in CO₂ in gaseous form are mainly batch type processes which require large reactor footprints. These types of processes are not suitable for offshore deployment as space and tonnage available to accommodate the deployment of such facilities related to gaseous phase mineral carbonation are under huge constraint due to the limited availability of offshore platform area. Hence, there is a need to drastically reduce the footprint and tonnage of such processes if it is under consideration for offshore deployment.

The CO₂ capture technology suitable for ultra high CO₂ field development is phase separation type which separates and subsequently converts CO₂ to liquid or supercritical phase as bottom product offtake. Direct conversion of these liquid phase or supercritical CO₂ to high value compounds is highly desirable as it provide major reduction of reactor size.

3. Summary on the Proof of Concept using PVT Recombination Chamber

The laboratory proof of concept was performed using the 100ml high pressure sapphire crystal PVT recombination chamber. The experiment work was conducted at nine different pressure and temperature operating conditions within the supercritical CO₂ phase diagram as provided in Figure 1(a) and (b) below.

![Figure 1(a)](image1.png)

![Figure 1(b)](image2.png)

**Figure 1(a).** Experimental test points for Proof of Concept for Supercritical CO₂ Mineral Carbonation reaction. **(b).** Visual observation of the instantaneous mineral carbonation reaction in the PVT chamber.

The experimental results for all the nine different pressure and temperature operating conditions observed instantaneous conversion of the initially transparent or clear aqueous calcium hydroxide feed turning into whitish slurry droplets as liquid feedstock is injected into the high pressure supercritical CO₂ environment. The visual of the above phenomenon is provided in figure 1(b) above. The precipitate formed at the bottom of the PVT chamber was extracted out and characterised using x-ray diffractography XRD to identify the chemical composition. XRD diffracto-gram results in figure 2 confirm that calcium hydroxide solution was fully converted into solid calcium carbonate compound for all nine testing conditions.
3.1 Design and Fabrication of Continuous Mineral Carbonation Prototype Reactor. The apparatus main component includes the following component in its assembly:

- Plunger type pump, motor driver and speed controller
- Inlet to reactor liquid flow meter and pressure gauge
- Feedstock tank
- 800ml high pressure tubular reactor with inlet flow valve, outflow backpressure regulator with pressure indicator

The schematics of the laboratory proof of concept reactor are also shown in figure 3 below.

3.2 Experimental Design. The experimental design matrix is designed to investigate the effects of variations in reactor working pressure, effects of variable CO$_2$ gas and CH$_4$ gas compositions and the effect of sucrose concentration and recycling. The experimental design matrix is shown in Table 1 below.
4. Results and Discussion

4.1 Baseline Reactor Characterization. The reactor was subjected to a 2 run batch with each batch consisting of three back to back runs. A total of 6 runs were completed within two days of operation. Analysis of the PCC particle produced was conducted using x-ray diffraction XRD and particle size distribution PSD to confirm the conversion of calcium hydroxide to precipitated calcium carbonate compounds and the distribution of the PCC particle size produced. The results are enclosed in figure 4(a) and (b) below.

![Figure 4(a)](image)

**Figure 4(a).** X-Ray Diffractogram and particle size distribution for reactor condition operating at 80bar CO₂ gas pressure and 0.1 litre/min flow rate. (b). Effect of liquid feedstock flow rate on the calcium carbonate precipitation.

Generally, the aqueous calcium oxide feedstock was consistently converted to calcium carbonate with calcite morphology. No traces of calcium oxide was detected in the x-ray diffractogram suggesting a complete conversion was consistently achieved with the condition of 80bar CO₂ gas pressure and a liquid feedstock injection flow rate of 0.1 litre/min. The average particle size P50 was consistent at 6micron in size except for Run#2 where P50 was at 8 micron. P90 cut was consistently below 300micron for all test runs as indicated in figure 4(a).
4.2 Effect of Feedstock Injection Flow rate. Feedstock injected into the reactor was performed using a manually operated mechanical hand pump providing an injection flow rate of 0.1 litre/min and increased to 1 litre/min by incorporating a motorised plunger type mechanical pump. The results of the precipitates obtained from the manual hand pump at 0.1 litre/min and motorised pump at 1 litre/min is tabulated above in figure 4(b). The results for x-ray diffractogram confirm that the feedstock is fully converted to calcium carbonate precipitate for both 0.1 litre/min and 1 litre/min flow rates. However a reduction was observed in terms of average particle size distribution P50 for the precipitate corresponding to 1lpm injection flow rate. This observation can be explained from the fact that at higher injection flow rate, the liquid reactant spray will be exposed to the high pressure CO$_2$ surrounding with a smaller retention time in the reactor. This smaller retention time will limit the crystallization process resulting in smaller particle size.

4.3 Effect of reactor working pressure. The continuous mineral carbonation reactor is compressed with CO2 gas prior to every test by a high pressure CO$_2$ compressor until the desired pressure is achieved at 80 bar. The liquid feedstock is injected at 1lpm with the gas composition at 100% CO$_2$. Approximately 1L of the liquid product off take is sampled at the bottom of the reactor section by controlling the valve V3. Allow the liquid injection to continue while the reactor pressure simultaneously decreases. Collect additional 1L samples at four other measurement points. The results are provided in figure 5(a) and 5(b) below.

| Reactor Pressure | Average Particle Size Distribution P50 |
|------------------|---------------------------------------|
| 80bar            | P50 Distribution = 6 micron           |
| 50bar            | P50 Distribution = 6.5 micron         |
| 30bar            | P50 Distribution = 5.6 micron         |
| 20bar            | P50 Distribution = 6 micron           |
| 10bar            | P50 Distribution = 6micron            |

The general trending of the average particle size distribution P50 from higher reactor working pressure 80bar to lower working pressure 11 bar can be observed in figure 5(a) above as steadily increasing from 5micron to 6.8 micron. At higher CO$_2$ gas working pressure, the dissolution of CO$_2$(g) to its aqueous form CO$_2$(aq) or carbonic ion CO$_3^{2-}$(aq) will be accelerated by the high pressure as a driving force for the CO$_2$ dissolution. As a result at higher CO2 pressure, the seeding process of the calcium carbonate precipitation is happening at a higher rate initially in multiple locations. At lower pressure, the seeding process occurs
at a lesser rate or number of seeds resulting in subsequent crystal growth focusing at a particular site yielding a larger calcium carbonate particle.

4.4 Effect of feedstock solution recycling. In a fully up-scaled plant operation, the 10° Brix feedstock will be continuously operate in a recycled mode after undergoing a solid calcium carbonate precipitate filtering process. The recycled solution with traces of very fine calcium carbonate particles slip past the filtering medium will undergo another cycle of calcium enrichment process. In the laboratory simulation, the mineral carbonation reaction is repetitively carried out using the same enriched feedstock solution for several times to investigate the effect of sucrose solution recycling. The sucrose feedstock solution recycling is observed to have an effect to the average particle size distribution P50 as shown in figure 5(b) above. The recycling to the sucrose feedstock solution carrier has affected the average particle size distribution P50 in a manner steadily reducing the particle size from 5.0micron to 4micron and subsequently to 3.5micron after each recycle pass. After the third recycle pass, the average particle size distribution was observed to stabilize at 3.5micron. The steady reduction in particle size distribution can be explained in terms of the particle seeding initiated from the ultra-fine calcium carbonate particle from earlier reaction cycles that may have slip through the filtration process. As results, the crystallization growth happens at multiple sites as compared to the initially introduced feedstock solution yielding smaller size particles.

4.5 Effect of methane in feed gas. The process of converting carbon dioxide gases to calcium carbonate precipitates may involve the usage of feed gas with high level of methane slippage in the case of separation process upsets. The effect of having up to 60% of methane in the reacting gas phase was investigated at various pressures. The results are tabulated in Figure 6 below.

![Figure 6. Effect of methane in feed gas.](image)

The effect of methane in the feed gas is minimal or non-effect. As observed from table 6 above, the average particle size P50 still maintain at 5micron and the normal trend of having higher particle size distribution at decreased reactor working pressure is similar to the trending observed with pure CO₂ feed gas composition.

5. Conclusion
The scaling up of the continuous supercritical mineral carbonation process was successfully carried out from the design and fabrication of the prototype reactor above. The prototype reactor system assembled was subjected to various testing to understand the characteristics of the calcium carbonates precipitate produced under various working conditions. The continuous production of calcium carbonate particles was proven to have a 100% conversion rate between 0.1 to 1 litre/min feedstock injections rates with stable calcite crystal morphology formed. The effect of increasing the liquid feedstock injection flow rate
was dominant in which when flow rate was increased from 0.1 to 1 litre/min, the average particle size was reduced from 6micron to 5micron. The effect of reactor working pressure was also major whereas lowering reactor working pressure yields higher calcium carbonate average particle size of up to 6.8micron at 11bar reactor working pressure. Another major effect established was the continuous recycling of the sucrose carrier solution affecting the average calcium carbonate particle size. The results of this scaling up of the supercritical mineral carbonation process from a laboratory equipment proof of concept to a fully functional working prototype have established critical physical relationship in the future design of a successful industrial pilot plant of larger scale.

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