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MINERAL SEQUESTRATION

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TAILORED SYNTHESIS OF PRECIPITATED MAGNESIUM CARBONATES AS CARBON-NEUTRAL FILLER MATERIALS DURING CARBON MINERAL SEQUESTRATION

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ABSTRACT

Predictions of global energy usage and demand trends suggest that fossil fuels will remain as the main energy source for the foreseeable future. Unfortunately, the increased amount of anthropogenic carbon emitted during the energy production leads to environmental issues, including climate change. Thus, reducing carbon dioxide emissions in order to stabilize atmospheric CO₂ levels is crucial, and this would not be achieved without significant changes in the energy conversion processes and the implementation of carbon capture and storage (CCS) technologies. Currently, the geological storage of carbon dioxide is considered to be the most economical method of carbon sequestration, while mineral carbonation is a relatively new and less explored method of sequestering CO₂. The advantage of carbon mineral sequestration is that it is the most permanent and safe method of carbon storage, since the gaseous carbon dioxide is fixed into a solid matrix of Mg-bearing minerals (e.g., serpentine) forming a thermodynamically stable solid product. The current drawback of carbon mineral sequestration is its relatively high cost. Therefore, this study focuses on tailored synthesis of high purity precipitated magnesium carbonate (PMC) to mimic commercially available CaCO₃-based filler materials, while sequestering CO₂. The effects of pH, reaction time and reaction temperature on the mean particle size, particle size distribution, and particle morphological structures, have been investigated for the synthesis of magnesium carbonates as carbon-neutral filler materials.

INTRODUCTION

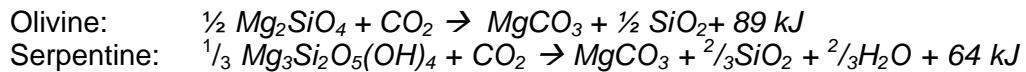
As shown during the recent and very rapid fluctuation in the cost of energy, the secure supply of energy resources and our ability to use them efficiently are extremely important for the world economy. One of the main issues related to the use of inexpensive energy sources (i.e., fossil fuels) is carbon management. Carbon dioxide is one of the greenhouse gases which are known to drive climate change (1; 2; 3). Even without climate change, a significant increase in the concentration of

atmospheric CO₂ would change surface ocean chemistry, which could then lead to other detrimental environmental impacts including the acidification of the ocean.

The current rate of global carbon emission is about 8 GtC per year (4), and it is predicted to increase to nearly 26 GtC per year by 2100 (5). Although this estimated value would vary significantly, based on each simulation scenario, with different parameters, such as the economic growth rate and the utilization of renewable energy, it is certain that carbon management is an important factor in the future of our energy outlook.

The containment of carbon dioxide generally involves several steps, including CO₂ separation, transportation, and sequestration, and new, integrated technologies are also under development to combine or eliminate some of these steps. Carbon storage in geological formations has been most widely investigated and demonstrated due to its low initial cost and the existence of the technology know-how based on the enhanced oil recovery (EOR) process. However, as the amount of CO₂ stored in geological formations increases, it becomes progressively more difficult to guarantee a physical barrier that prevents gaseous CO₂ from returning to the atmosphere. Thus, the cost of the long term monitoring of CO₂ deposits will further increase the overall cost of geological carbon sequestration, as well as raise the safety concerns. Therefore, the chemical conversion of carbon dioxide to a thermodynamically lower state (i.e., calcium and magnesium carbonates) would be desirable for the long term storage, and nature is already undertaking this chemical transition in the form of weathering of rocks.

Carbon mineral sequestration is achieved through mimicry of the natural inorganic chemical transformation of CO₂ (6). This sequestration process presents a safe and permanent method of CO₂ containment with the formation of geologically and thermodynamically stable mineral carbonates. The total accessible amounts of the minerals, including olivine (Mg₂SiO₄) and serpentine (Mg₃Si₂O₅(OH)₄), are estimated to significantly exceed the worldwide coal reserves, and they would react with CO₂ via the following chemical reactions (7; 8; 9).



The current research in this area concentrates on the pretreatment of minerals, or the optimization of the dissolution and carbonation processes for maximum carbon storage. However, due to the relatively high cost for the carbon mineral sequestration processes, a breakthrough in this technology will not be possible without considering the utilization of solid products. As a part of the author's prior research, a carbon mineral sequestration process based on pH swing has been developed (10; 11). By carefully controlling the pH, three solid products were generated from serpentine via the mineral carbonation process: high surface SiO₂-rich solids, iron oxide, and highly pure MgCO₃·3H₂O. Therefore, this study investigates the tailored synthesis of high purity precipitated magnesium carbonate (PMC) as filler materials with engineered morphological structures.

EXPERIMENTAL

Both a batch system and a 2 inch diameter fluidized bed system were used for this study. For the first set of experiments, 100 mL of 0.25 M K₂CO₃ solution (pH = 5.5)

and 50 mL of 0.5M $\text{Mg}(\text{NO}_3)_2$ solution (pH = 12.2) were prepared for each run, and they were mixed in a glass reactor placed in a water bath to achieve the precipitation of PMC. For all cases, the slurry mixtures were mixed at 800 rpm throughout the experiments. Slurry samples were periodically collected, and the mean particle size and the particle size distribution were determined using a Beckman-Coulter LS 13320 Particle Sizer. At the end of each run, the final pH of the slurry was measured and the slurry was filtered. The filter cake was thoroughly washed with the distilled water and the solid products were air dried at ambient temperature by placing them under the fume hood for 5 hours. Once dried, the solid samples were analyzed using a Scanning Electron Microscope (SEM) for their morphological structures.

The effect of the reaction time was determined by taking slurry samples at various time intervals up to 2 hours, while maintaining the temperature at 20 °C. Based on the findings from these experiments, the subsequent experiments were carried out with the reaction time of 1 hour. Next, the two sets of $\text{Mg}(\text{NO}_3)_2$ solutions were prepared by lowering the pH via the addition of HNO_3 . The pHs of the prepared $\text{Mg}(\text{NO}_3)_2$ solutions were 1.59 and 2.44, which were significantly lower than the pH of the original solution (pH 5.5). These two solutions were mixed with the original K_2CO_3 solution at 20 °C, and for each case, the solid products were analyzed using the particle sizer and the SEM. For the third run, the pH of the K_2CO_3 solution was brought to 13.26 by adding KOH, and this solution was reacted with the original $\text{Mg}(\text{NO}_3)_2$ solution at 20 °C to create a higher pH environment for PMC precipitation. For the next experiment, an equal molar amount of NH_4Cl was added to the original $\text{Mg}(\text{NO}_3)_2$ solution to simulate the condition in the mineral digestion system, which is a part of the pH-swing carbon mineral sequestration process. NH_4Cl is one of the chemical additives being investigated as a recyclable solvent for mineral dissolution (12). PMC was then synthesized by reacting the $\text{Mg}(\text{NO}_3)_2$ solution containing NH_4Cl with the original K_2CO_3 solution. Finally, the effect of the reaction temperature on PMC synthesis was investigated by reacting 100 mL of 0.25 M K_2CO_3 solution and 50 mL of 0.5M $\text{Mg}(\text{NO}_3)_2$ solution at 42 °C, 62 °C, and 97 °C. The stirring rate was again maintained at 800 rpm and the final products were collected after 1 hour. All the experiments were repeated using a fluidized bed reactor by bubbling CO_2 .

RESULTS AND DISCUSSION

Precipitated magnesium carbonate (PMC)'s application is broad including salt, cosmetics and toothpaste; however, its demand is rather limited (13). On the other hand, the demand for precipitated calcium carbonate (PCC) is enormous, in the paper, paints, and plastics/rubber industries (14; 15). Particularly, over the past few decades, the paper manufacturing industry has seen an increase in the use of PCC as paper filler as paper manufacturers moved away from the acid-based paper making process. This is especially true in North America, where 2.5 MM tons of PCC, approximately 70 % of the filler market, are consumed annually (16). Appropriate filler materials provide paper with desirable physical and optical characteristics, including improved dry strength, smoothness, and brightness (17). The ability to control to size, morphology, and uniformity, is paramount for filler materials, and thus, PCC has become the preferred filler of choice over alternatives such as ground calcium carbonate (17). Since the PMC produced during the above-mentioned pH-swing carbon mineral sequestration process is bright white powder with great thermal chemical and thermal stability, new applications of PMC are proposed to replace PCC in various applications. This will not only provide the

additional economic benefits to the carbon mineral sequestration process, but also lead to an avoidance of large quantities of CO₂ that is often emitted during the production of PCC. In order to achieve this goal, PMC was synthesized with tailored properties such as the mean particle size, particle size distribution and surface morphology, to emulate some commercially-made PCC particles (18) shown in Figure 1.

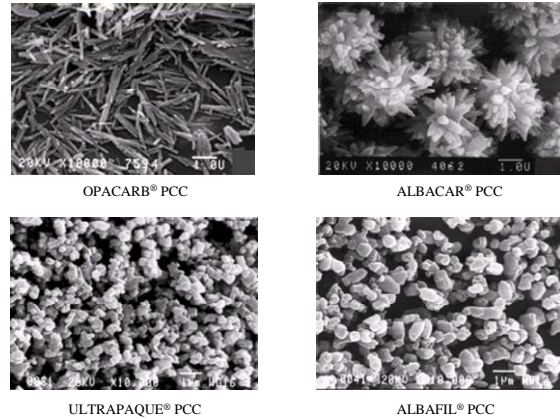


Figure 1. Examples of commercially available PCC morphologies (from (18))

The first set of experiments shown in Figures 2 revealed that the crystallization of PMC forms gel-like solid products during the first 30 min of the reaction process. The mean particle size was relatively smaller during the initial 30 min, and the particle size distribution was also narrower. When the dried samples were analyzed using the SEM (Figure 3), the gel-like solid samples collected at 5 min showed irregular broken pieces, whereas the samples collected at 120 min demonstrated clear needle shapes. Note that solid samples collected at 5 min were visibly much larger than the mean particle size measured by the particle sizer, due to the agglomeration occurred during the drying process. Particle agglomeration only took place for gel-like samples.

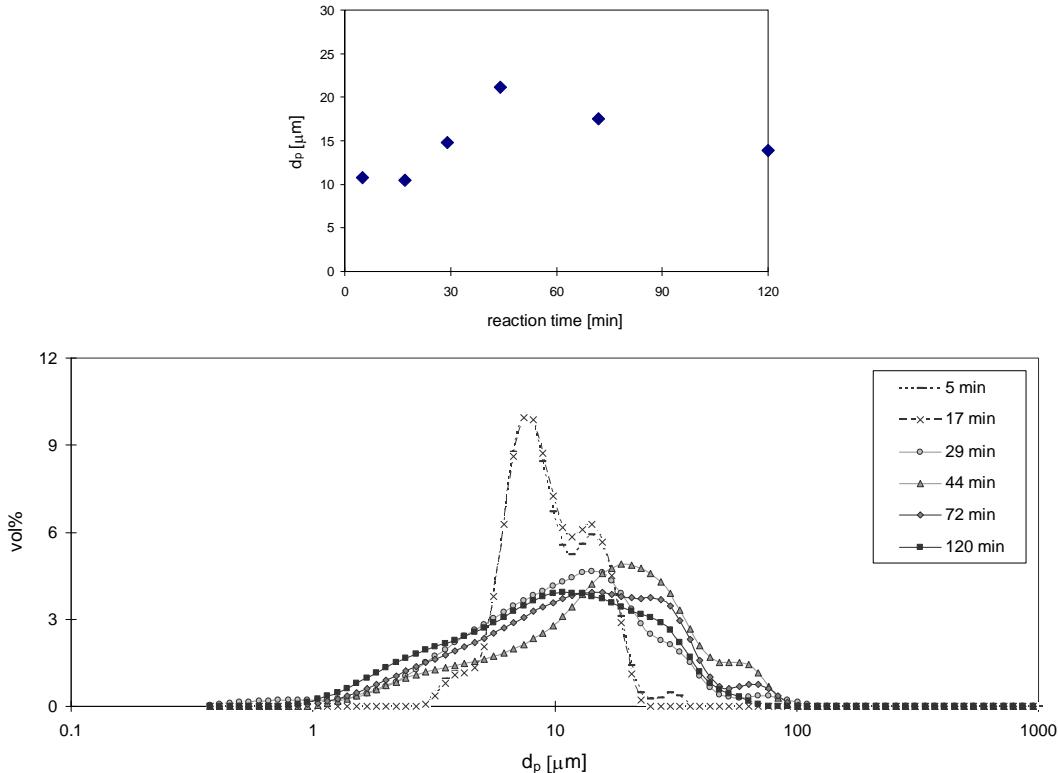


Figure 2. Effect of reaction time on mean particle size and particle size distribution (0.25M K₂CO₃ 100mL + 0.5M Mg(NO₃)₂ 50 mL, T = 20 °C, stirring rate = 800 rpm)

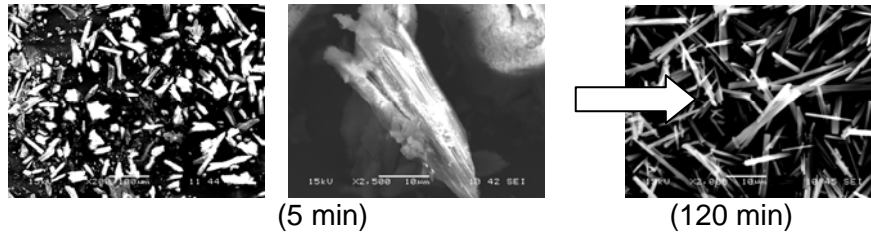


Figure 3. Effect of reaction time on the particle morphological structure (0.25M K_2CO_3 100mL + 0.5M $Mg(NO_3)_2$ 50 mL, T = 20 °C, stirring rate = 800 rpm)

It has been reported that magnesium carbonates can be synthesized with needle, rosette, spherical, sheet, and cake-like shapes by controlling the reaction temperature or pH (19). The next set of experiments show the effect of pH on the synthesis of PMC. As shown in Figure 4, the mean particle size of PMC did not change with pH of the reacting solutions. However, the particle size distribution became significantly narrower when PMC precipitation was carried out at higher pH. SEM analysis also revealed that at 20 °C, all the PMC particles were found to be needle-shaped (see Figure 5), while the aspect ratio of the PMC particles was smaller at a higher pH, resulting in shorter particles. As shown in Figures 4 and 5, the addition of NH_4Cl did not change the synthesis of PMC, although the final pH of the slurry was measured to be lower. PMC particles were still needle-like with a mean particle diameter of 19 μm .

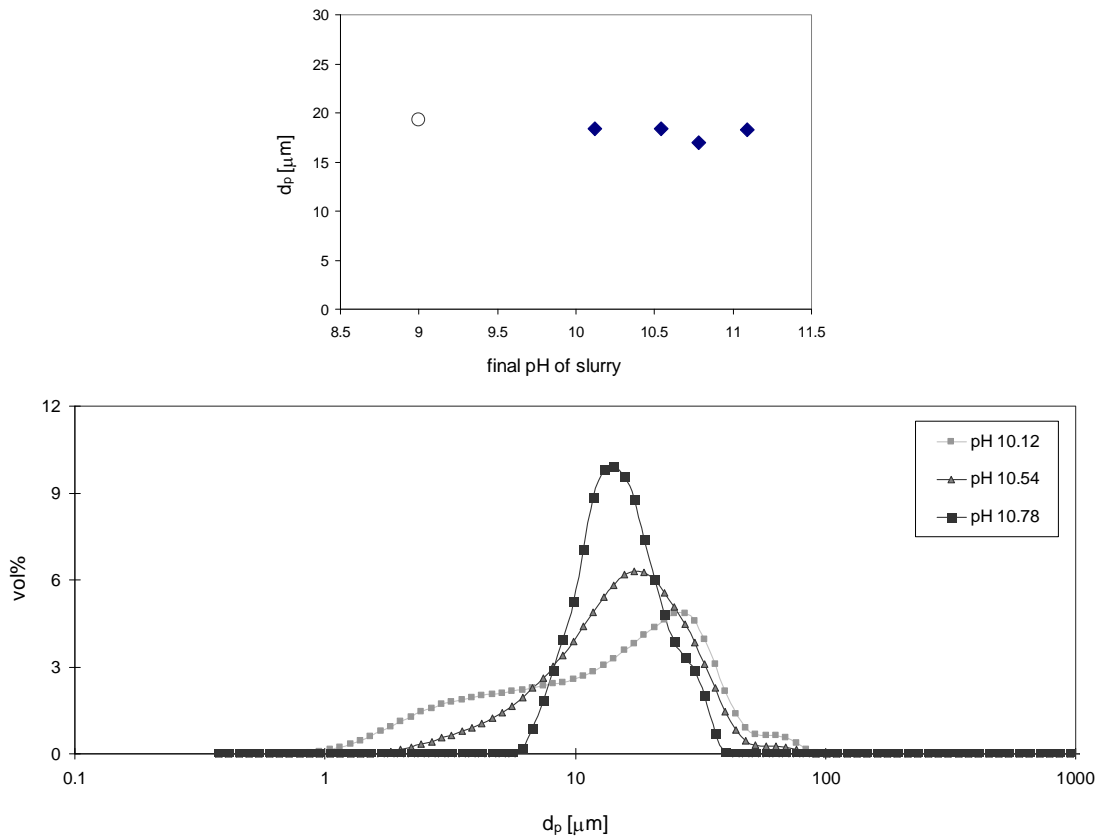
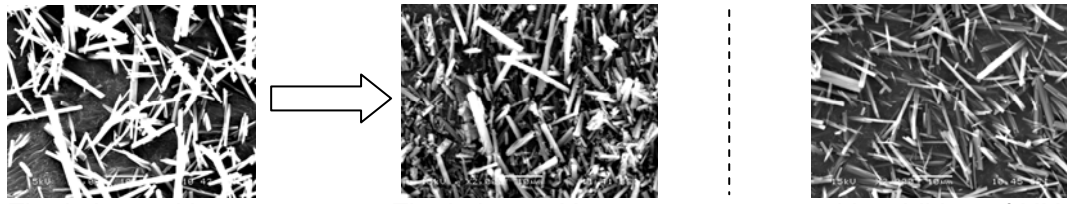


Figure 5. Effect of pH on mean particle size and particle size distribution (0.25M K_2CO_3 100mL+0.5M $Mg(NO_3)_2$ 50 mL, T = 20 °C, stirring rate = 800 rpm, reaction time = 1 hour)



Final slurry pH = 10.12 Final slurry pH = 10.78 with addition of NH_4Cl
 Figure 5. Effect of reaction time on the particle morphological structure (0.25M K_2CO_3 100mL + 0.5M $\text{Mg}(\text{NO}_3)_2$ 50 mL, T = 20 °C, stirring rate = 800 rpm, reaction time = 1 hour)

On the other hand, the effects of the reaction temperature on the particle size and the morphological structure were found to be quite strong. As the reaction temperature increased from 42 °C to 92 °C, the particle shape changed from needle-like to spherical-like crystallites, and the mean particle size was reduced from 24.8 μm to 3.5 μm . The particle size distribution also became considerably narrower at higher reaction temperatures. These changes in size and morphology are attributed to a combination of factors. This may be due to the increased nucleation rate at higher temperatures resulting in the growth of nuclei into smaller particles (19; 20). The solid sample prepared at 67 °C resembled the sample collected at 92 °C, but it showed a wider particle size distribution as illustrated in Figures 6 and 7.

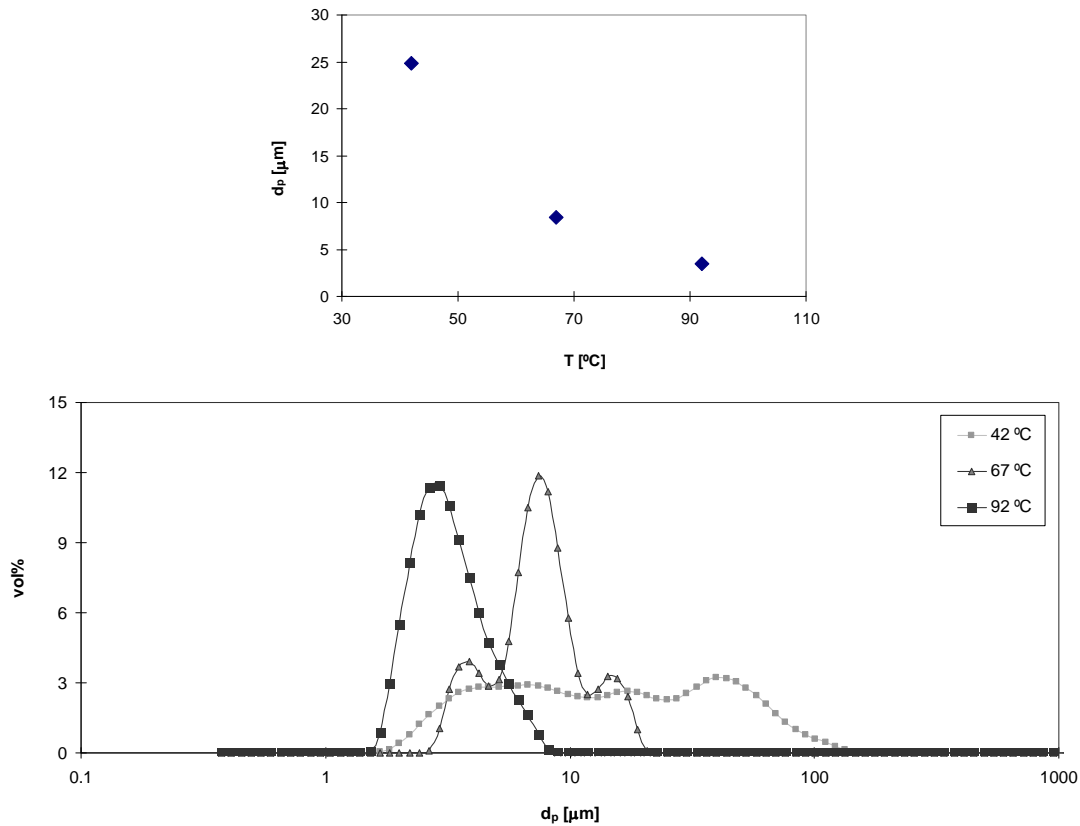


Figure 6. Effect of reaction temperature on the mean particle size and the particle size distribution (0.25M K_2CO_3 100mL + 0.5M $\text{Mg}(\text{NO}_3)_2$ 50 mL, stirring rate = 800 rpm, reaction time = 1 hour)

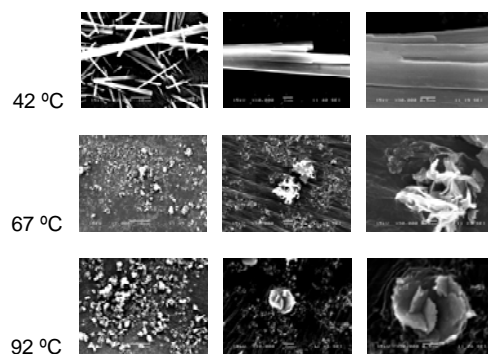


Figure 7. Effect of reaction time on the particle morphological structure (0.25M K_2CO_3 100mL + 0.5M $Mg(NO_3)_2$ 50 mL, stirring rate = 800 rpm, reaction time = 1 hour)

Both needle-like and spherical-like PMC particles are quite similar to PCC commercial samples shown in Figure 1. In particular, based on the trends in the particle size and morphological structure of PMC particles synthesized at 67 – 92 °C, it seem very suitable to use PMC as paper filler materials which require spherical shape with 2-4 μm in diameter (16).

CONCLUDING REMARKS

In this study, precipitated magnesium carbonates (PMC) were synthesized as a part of the pH swing carbon mineral sequestration process, for the goal of replacing the filler market for precipitated calcium carbonates. By controlling pH and temperature of the crystallization system, the PMC was synthesized with the morphological structures that are suitable for the filler materials. The results from a batch reactor and a fluidized bed reactor were very similar. The synthesized PMC qualifies as carbon-neutral filler materials, and the use of solid products such as PMC, will provide much needed economic benefits for carbon mineral sequestration technology, as well as minimize the amount of carbonate minerals to be disposed.

ACKNOWLEDGEMENT

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