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Improving the Yield of Sonochemical Precipitated-Aragonite Synthesis by Scaling-up Intensified Conditions

[Short Title: Sonochemical Aragonite Synthesis]

Rafael M. Santos[1], Jolien Thijs [2], Evangelos Georgakopoulos [1,3], Yi Wai Chiang [4], Ann Creemers [2], Tom Van Gerven [5]

[1] Sheridan Institute of Technology, School of Applied Chemical and Environmental Sciences, 7899 McLaughlin Road, Brampton, Ontario, Canada, L6Y 5H9.

[2] University Colleges Leuven-Limburg, Lab4U, Agoralaan Gebouw B, bus 3, 3590 Diepenbeek, Belgium.

[3] Cranfield University, Department of Offshore, Process and Systems Engineering, College Road, Cranfield MK43 0AL, United Kingdom.

[4] University of Guelph, School of Engineering, 50 Stone Road East, Guelph, Ontario, Canada,

N1G 2W1.

[5] KU Leuven, Department of Chemical Engineering, Celestijnenlaan 200F Bus 2424, 3001 Heverlee, Belgium.

Abstract

Precipitated aragonite can be synthesized at relatively low temperatures by combining the application of low-frequency sonication with the use of magnesium chloride additive, as demonstrated by our prior study. In the present study, new process conditions were found that promote aragonite formation while accelerating and increasing the reaction yield. It was found that Mg-to-Ca molar ratio of 3:1, together with higher slurry concentration (74 g/L $Ca(OH)_2$) and higher power-to-volume ratio (800 W/L gross, achieved by reducing slurry volume), promoted the aragonite formation while working at a higher CO_2 flow rate (2.0 NL/min), and consequently higher PCC production rate (1g/(L·min) $CaCO_3$). The yield was thus improved while conserving the desired product properties: high polymorph purity (95.7 wt%), small and narrow particle size distribution (D[3,2] = 0.74 µm), and unique shape (hubbard squash-like).

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1. Introduction

Calcium carbonate is a mineral with several applications, currently considered indispensable in the industries of paper, paint and plastic, where it is used as a filler or pigment (Stearn and Carroll, 1989). Due to the strict quality requirements for other industrial uses, however, it is preferable to synthesize calcium carbonate under controlled conditions as precipitated calcium carbonate (PCC). This product has the same chemical composition as any other naturally occurring calcium carbonate (chalk, limestone, marble, etc.), except it is produced artificially, under conditions to produce a high quality product of specific characteristics. Limestone of high purity in $CaCO_3$ (97–98 %) is typically used as the calcium source for the production of PCC (Tegethoff et al., 2001). A recent research trend, however, is the use of alternative sources of calcium for PCC synthesis. Mantilaka et al. (2013) have reported on the use of dolomite ($CaMg(CO_3)_2$) as the starting material, while De Beer et al. (2015) developed an indirect aqueous carbonation process for the production of high-grade PCC (>99 wt% $CaCO_3$) starting from waste gypsum ($CaSO_4 \cdot 2H_2O$).

This study focuses on the use of calcium carbonate as filler or pigment in paper industry. The polymorph that is mostly used in such applications is calcite, due to its stability and easier production route. However, aragonite has niche applicability due to its particular physical and mechanical qualities, offering to the produced paper improved brightness, opacity, strength and printability (Ota et al., 1995). There are several ways to synthesize PCC; for the purposes of this paper, only the carbonation method is analyzed. For the synthesis of aragonite through carbonation, a mixture of calcium hydroxide ($Ca(OH)_2$) and magnesium chloride ($MgCl_2$) has been successfully used in previous works (Katayama et al., 1992; Ota et al., 1995; Park et al., 2008). However, aragonite’s formation is favored at temperatures ranging between 60°C and 80°C (Arai, 1996; Hu and Deng, 2003; Zhou et al., 2004; Park et al., 2008), while at other temperatures calcite is most typically formed (Passe-Coutrin et al., 1995; Wang et al., 1999). Elevated temperatures lead to the formation of relatively large acicular crystals, not suitable for fine paper and coating applications. It is thus desirable to synthesize aragonite at low temperatures, ideally at room temperature.

Precipitated aragonite can be synthesized at relatively low temperatures by combining the application of low-frequency sonication with the use of magnesium chloride additive, as demonstrated by our prior study (Santos et al., 2012). Sonication intensifies the synthesis of calcium carbonate by enhancing multi-phase bulk mixing, activating precipitation sites via shockwaves that nucleate crystal growth, and minimizing diffusion barriers through micromixing as a result of microturbulence (Nalajala and Moholkar, 2011; Santos and Van Gerven, 2011). Sonication also creates regions of high temperature as a result of cavitation bubble collapse (Reddy et al., 2010); these regions can promote the formation of aragonite over calcite, as the former is the high-temperature polymorph of calcium carbonate.

The optimized conditions of Santos et al. (2012) included: temperature = 30 °C; $Ca(OH)_2$ concentration = 3.7 g/L; magnesium-to-calcium ratio = 6 (61 g/L $MgCl_2{\cdot}6H_2O$); ultrasound amplitude = 60% (i.e. 75 µm); ultrasound cycle = 100% (i.e. continuous); CO_2 flow rate = 0.24 NL/min; pre-breakage time (i.e. sonication without carbonation) = 20 min. Reaction time under these conditions were in the order of 150 minutes, and product yield in the order of 5 g/L (resulting in a production rate of 0.033 g/(L·min) $CaCO_3$). Product properties included 99.0% aragonite purity, <5 µm particle size, and unique hubbard squash-like shaped particles. Under these formerly optimized conditions, however, the production rate is too low for industrialization.

In view of developing an industrially feasible process, the focus of the present work was on maintaining desired product properties (for the intended applications) while accelerating and increasing the volumetric yield of the reaction. To achieve this, several process parameters were modified to enable scale-up while preserving the intensified process conditions. The focus was on increasing the ultrasound power-to-slurry volume ratio, to improve the rate of crystal nucleation and crystal growth, thus allowing an increase in initial concentration of $Ca(OH)_2$ and in CO_2 flow rate to reach higher yields. An alternative source of calcium was also tested: calcium acetate

($Ca(CH_3COO)_2$), which can be recovered from iron- and steel-making slags (De Crom et al., 2015).

2. Materials and Methods

The basic experimental procedure for the production of high purity aragonite consists in carbonating a mixture of calcium hydroxide ($Ca(OH)_2$) and magnesium chloride hexahydrate (MCH, $MgCl_2·6H_2O$), with the assistance of sonication. For the purposes of this study, two different sets of reactants' concentrations were used. For the first set of experiments, the chosen amounts of the reacting phases were: $Ca(OH)_2$ = 3.7 g, and MCH = 30.5 g, this results in a molar ratio (MCR) of 3. During the second set of experiments, the amounts of the reactants were increased to: $Ca(OH)_2$ = 18.5 g/L, and MCH = 152 g/L, still maintaining an MCR of 3. The standard experimental process is described next.

One liter of ultra-pure water and the appropriate amount of commercial magnesium chloride (VWR Pro Labo) were placed in a 2 L glass beaker. The desired amount of calcium hydroxide (Acros Organics) with chemical purity of 98 % was added to the mixture. The solution was mixed with ultrasound (probe tip 3.5 cm from bottom) until the desired temperature was reached (this constituted the pre-breakage period and lasted 15 minutes, including het-up time). For sonication, a Hilscher UP 2000S was used, which operates at 24 kHz frequency. The probe used was an S14 sonotrode, which has a tip diameter of 14 mm, maximal amplitude of 125 µm and an acoustic power density of 105 W/cm^2. A PT100 temperature sensor (TI) is also connected to the device and was used to to monitor and record solution temperature. To make optimal use of the ultrasound, 60 % amplitude and 100 % cycle are used, as optimized in our previous study (Santos et al., 2012). During mixing, the solution was heated to 30 °C or 50 °C using solely sonication, which induces heat to cavitations, or to 70 °C by the combination of sonication and a hot plate (IKAMAG RCT). A water bath was also used for cooling purposes when using only sonication, as the heat would otherwise exceed the desired value. A schematic overview of the experimental set-up is shown in Figure S1 in the Supplemetary Materials.

Once the desired slurry temperature was reached, sonication continued and CO_2 was introduced to the solution from a compressed gas cylinder with flow controlled by a Brooks Sho-rate rotameter (FI, R-2-15-AAA) at 2 NL/min (normal liters per minute), and passing through an aeration stone that delivered finely dispersed gas bubbles. This particular flow rate is nearly twice as high the flow rate used in previous works (Santos et al., 2012). This was chosen, in order to achieve the production of higher quantities of aragonite in less time.

Each carbonation experiment lasted for 100 minutes. This value was selected as cap (i.e. under some conditions the reactions finished earlier and in some the reaction did not finish whithin this time). The aim was to cut by at least one third the duration required under optimal conditions of the previous study (Santos et al., 2012). After the end of each experiment, the slurry was vacuum filtered using a Whatman slow flow filter paper. The product was oven dried at 105 °C for 4 hours before being analyzed for morphological and mineralogical characteristics.

The particle size distribution of the produced materials was assessed by wet laser diffraction (Malvern Mastersizer). Their mineralogical composition was determined with X-Ray Diffraction (XRD, Philips PW 1830) with peak analysis done in EVA (Bruker) software and mineral quantification performed using the Rietveld refinement method in Topas Academic v4.1 (Coelho Software). The mineral phases analyzed for were: Portlandite ($Ca(OH)_2$), Calcite ($CaCO_3$), Aragonite ($CaCO_3$), Vaterite ($CaCO_3$), Tachyhydrite ($CaMg_2Cl_6\cdot 12H_2O$), Brucite ($Mg(OH)_2$), Magnesian-Calcite ($Mg_xCa_{1-x}CO_3$), Nesquehonite ($Mg(HCO_3)(OH)\cdot 2H_2O$), Hydromagnesite ($Mg_5(CO_3)_4(OH)_2\cdot 4H_2O$), and Bischofite ($MgCl_2\cdot 6H_2O$). Morphological assessment was accomplished by imaging with a scanning electron microscope (SEM, Philips, XL30 FEG).

In order to achieve the production of the highest possible purity under the desired conditions (T = 30 °C, reaction time = 100 minutes, CO_2 flow rate = 2.0 NL/min), two parameters were principally varied during both sets of experiments; these were MCR and solution volume. In addition, temperature and reaction time were varied in select experiments to obtain additional clarity. The reutilization of MCH containing filtrate after product separation was also investigated in view of reducing production costs. The results exerted from them are discussed in detail in the following section.

In a follow-up series of tests conducted at the University of Guelph, calcium acetate was utilized as the calcium source for the reaction, in place of calcium hydroxide. An additional change required in this process is the addition of a strong base (e.g. NaOH) to neutralize the acetate anion that is released during carbonation. The process conditions utilized were similar to the ones aforementioned for the $Ca(OH)_2$ part of the study: temperature = 36- 49°C, MCR = 3-6, CO_2 flow rate = 0.24-0.40 NL/min, time = 80-112 min, reaction volume = 200 ml, calcium acetate ($Ca(CH_3COO)_2$) = 0.056 mol, NaOH = 0.102 mol. Ultrasound was provided by a high intensity ultrasonic processor (Sonics VC-750) of 750 W maximum power, operated at 50% amplitude and using a 13 mm diameter probe. The beaker size was 400 ml.

3. Results and Discussion

3.1 First set of experiments (3.7 g Ca(OH)2)

3.1.1 Influence of temperature

The first set of experiments aimed at observing the aragonite purity achievable using a relatively high CO_2 flow rate (compared to optimal conditions of Santos et al. (2012)) of 2.0 NL/min. Experiments were performed under three different reaction temperatures (30 °C, 50 °C, 70 °C), which cover high temperatures most suitable for aragonite formation and lower temperatures not traditionally suitable. Mineralogical analysis regarding the three dominant phases of the produced material is reported in Table 1. The results confirm that the formation of aragonite is favored at higher temperatures, however, under the particular conditions used (3.7 g/L $Ca(OH)_2$, MCR = 3, volume = 1 liter), pure aragonite was not formed at any tested temperature. According to the results, the temperature decrease favors the formation of calcite over that of aragonite. This is evident from the XRD diffractograms of the synthesized PCC at the different temperatures (Figure S2 in the Supplementary Materials); the calcite peaks increase as the temperature is lowered, whereas aragonite is the dominant phase at 70 °C. Moreover, the variation of reaction temperature also has an impact on the particle size of the produced precipitates. It is clear from the SEM images (Figure S3 in the Supplementary Materials), that the reduction of reaction temperature is accompanied by a particle size reduction. Lower crystal growth rates at lower temperatures, in the presence of a high rate of nucleation due to the sonication (Nalajala and Moholkar, 2011), leads to smaller particles.

This set of results differs from those obtained in our previous study (Santos et al., 2012), which used identical conditions except for the flow rate. In the previous work, at 30 °C, 92.7 wt% of aragonite was synthesized, whereas at the same temperature, only 24.3 wt% of aragonite is produced in the present study (upon performing three replicates, an average value of 16.7±7.5 wt% aragonite was obtained at this condition). This difference can be attributed to the higher CO_2 flow rate that was chosen for the experiments in the present work (2.0 NL/min versus 0.72 NL/min). A higher supply rate of CO_2 improves the mass transfer rate from the gas bubbles to the aqueous solution, as a result of greater gas-liquid surface area. A higher rate of CO_2 dissolution speeds the carbonation reaction. Since aragonite formation requires high temperature regions created by cavitation, if the rate of carbonation increases while the rate of cavitation is constant, it will be more likely that calcite can crystallize in localized lower temperature regions of the reaction solution in parallel to the formation of aragonite at the high temperature regions. These differing zones are characteristic of sonicated solutions as cavitational activity in sonochemical reactors is non-uniform in nature; there is maximum cavitational activity very near to the ultrasound irradiating surface and wide variation in the energy dissipation rates in the remaining bulk of the liquid (Sutkar and Gogate, 2009).

In order to accomplish the production of a considerably higher aragonite purity at the desired temperature (30 °C), flow rate (2.0 NL/min) and reaction time (100 min), several other parameters were subjected to changes and tested for their influence on the mineralogical and morphological properties of the produced material.

3.1.2 Influence of Mg-to-Ca molar ratio (MCR)

In pour previous study was shown that the combined use of ultrasound carbonation and magnesium ions improves the production of aragonite at low temperatures (Santos et al., 2012). To reaffirm the influence of Mg-to-Ca molar ratio (MCR) in the production of aragonite at a higher CO_2 flow rate, three different MCH concentrations were tested: a) MCH = 0 g/L, b) MCH = 30.5 g/L, and c) MCH = 61 g/L. These correlate to Mg-to-Ca molar ratios of: a) MCR = 0, b) MCR = 3 and, c) MCR = 6. The obtained results (table 2) demonstrate that although the production of aragonite is rather low (due to the high CO_2 flow rate), there is a strong influence of Mg^{2+} ions on its formation. Without the use of magnesium additive, nearly pure calcite is formed, while by adding a moderate proportion of MCH (MCR = 3), some Ca^{2+} ions are partially replaced by Mg^{2+} ions in the calcite crystal matrix, and a significant amount of magnesian-calcite ($Mg_{1-x}Ca_xCO_3$) is synthesized. Finally, by further increasing the MCR, calcite formation is suppressed (Mg is thought to poison the crystal growth of calcite) and the formation of aragonite is magnified. Still, under these conditions tested (3.7 g $Ca(OH)_2$, temperature = 30 °C, volume = 1 liter, MCR = 6), the maximum aragonite fraction obtained, 49.5 wt%, is still well short of the desired purity (≥95wt%, as targetted for papermaking applications 95% (Yaniv, 2004)). This sample also contained a significant amount of residual brucite, indicating incomplete reaction. These findings are also supported by the SEM images (Figure S4 in the Supplementary Materials), which clearly show that aragonite crystals are predominantly formed when using the highest Mg-to Ca molar ratio.

3.1.3 Influence of reaction volume

The liquid volume in the reaction vessel is a process parameter that has not been studied before. By varying the liquid volume, two parameters directly change: the concentration of the reactants in solution (e.g. if the volume is reduced, the concentration increases for a constant initial loading), and the ultrasound intensity (e.g. if the volume is reduced, theultrasound intensity increases for a constant ultrasound power). In this study the influence of the reaction volume on the formation of aragonite was tested; three volumes were tested: a) 0.25 L, b) 1.0 L, and c) 2.0 L. In order to keep the fluid level suitable for sonication (i.e. to maintain an approximately constant immersion depth of the probe and distance of probe tip from the vessel bottom), the beaker volume was also changed: a) 600 mL beaker for 250 mL of fluid, b) 2 L beaker for 1.0 L of fluid, and c) 3 L beaker for 2.0 L of fluid.

According to Ahn et al. (2004), for the synthesis of aragonite, both the concentrations of magnesium and calcium ions have to lie within a specific range. The concentration of calcium ions must be below the range of 0.16 to 0.25 M and the concentration of magnesium ions must be located within the range of 0.10 to 0.26 M. As seen from Table 3, by maintaining the amounts of reactants steady and varying the amount of water, the concentration of the reactants in some cases departed from the aforementioned ranges, resulting in considerable variations regarding the formation of aragonite, calcite and magnesian-calcite. At high reactant concentrations, magnesian-calcite was the dominant phase. This confirms the observation of Ahn et al. (2004) that excess magnesium is detrimental to aragonite formation, since the magnesium acts no longer as a poison to calcite crystal growth but as a building block to magnesian-calcite crystal growth.

The production of aragonite was favored once the calcium concentration dropped, as a result of the higher amount of fluid volume used, below the aforementioned 0.16–0.25M range, as recommended. Reduction of calcium concentration will lower the rate of “low temperature” nucleation (i.e. nucleation not caused by cavitation), which should aid in the formation of the less favored polymorph, aragonite, which nucleates in the “high temperature” cavitation zones. In this case, however, the ultrasound intensity also dropped considerably, and the magnesium concentration dropped below the recommended range. This would explain why aragonite formation was promoted but the purity levels remained well below the desired value of ≥95 wt%. Therefore, further tests aimed at increasing the concentrations of reactants in solution to remain within, or depart less from the recommended ranges were conducted. These results are presented in Section 3.2. The brucite phase ($Mg(OH)_2$) is added in Table 3 in order to show the level of the reaction completeness, since the particular phase should not be present in the solution after a complete reaction, having been re-converted to $MgCl_2$ during the formation of $CaCO_3$. The higher levels of brucite at higher volumes imply that reduced sonication energy density (intensity) and higher dispersion of the reactants in the solution slightly hinder full conversion (in the allotted reaction duration of 100 minutes).

3.2 Second set of experiments (18.5 g $Ca(OH)_2$)

Despite the optimizations that were carried out in the first set of experiments, the aragonite remained satisfactory. In an effort to substantially improve it, both the concentrations of $MgCl_2$ and $Ca(OH)_2$ were increased by a factor of five, to 18.5 g. This change in experimental conditions is also in line with the objective to increase productivity of the reaction (grams of $CaCO_3$ per liter per minute).

3.2.1 Influence of reaction volume

Tests were again performed using the three different volumes (0.25 L, 1.0 L, and 2.0 L), maintaining the amounts of reactants constant (but at a higher level compared to the previous set of experiments), to determine the optimal reaction volume. The results are presented in Table 4. The synthesis of aragonite was considerably improved when using a higher initial loading of $Ca(OH)_2$. Also, the selectivity for aragonite over magnesian-calcite improved significantly, meaning that magnesium no longer participated significantly as a building block to crystal growth.

Figure 1 depicts a direct comparison between the aragonite content achieved in both sets of experiments with lower and higher reactant loadings. It is evident that by increasing the concentration of the reactants within the reaction medium, the formation of aragonite is significantly favored. This improvement becomes magnified in the case of smaller reaction volumes, with an upper value of 91.2 wt% aragonite reached. In the larger reaction volumes the reaction was incomplete, as indicated by high brucite contents, and thus the aragonite amount were lower, although in all cases calcite formation was relatively well suppressed. In a larger reaction volume the CO_2 concentration takes longer to build up in the batch reactor, so the $CO_{2(aq)}$ concentration will be lower with a constant CO_2 bubbling rate, and the greater $Ca(OH)_2$ amount will take longer to fully react. In the smaller reactor, the solution achieves saturation faster and the bubbling rate of CO_2 can more readily maintain it, hence the absence of brucite after 100 minutes.

The presence of magnesian-calcite in the samples not fully reacted suggests that this compound may be an intermediate reagent. It forms, preventing pure calcite crystallization, but eventually re-dissolves and the release calcium is converted into aragonite. This mechanism has basis in the solubility of magnesian-calcite, which is higher relative to pure calcium carbonates when the $MgCO_3$ content exceeds 12 mol% (Railsback, 2006), as the Mg substitution in the $CaCO_3$ matrix creates strains on the crystalline structure that cause lattice instability.

It is also worth noting that the Mg-to-$CO_{2(aq)}$ ratio changes with reaction volume. At lower reaction volumes the Mg-to-$CO_{2(aq)}$ ratio is greater due to limited solubility of CO_2 per unit volume. Under these conditions not only was the greatest aragonite fraction achieved, as a result of complete reaction, but also the lowest amount of calcite was formed. Here the excess of Mg may be less detrimental since there is less carbonate ions available for crystallization, hence the magnesium's role is limited to being a calcite poison rather than a magnesian-calcite building block. The level of supersaturation may also play a role here, as it has been shown that supersaturation control can influence the $CaCO_3$ polymorph formation (Ahn et al., 2015).

Although the improvement in aragonite purity is rather pronounced with higher reactants loading, and the PCC yield is much greater (approx. 25 grams of PCC in the second set versus 4 grams in the first), high purity aragonite was still not formed. In an effort to achieve the production of aragonite with purity greater than 95wt%, the experimental parameters are varied again, fixing the increased amounts of $Ca(OH)_2$ (18.5 g) and the reaction volume (0.25 L).

3.2.2 Influence of temperature

To study the effect of the reaction temperature on the sonochemical synthesis of aragonite at elevated reactants concentrations coupled with reduced reaction volume, three different temperatures were tested (30 °C, 50 °C, and 70 °C). The results demonstrate the greatest promotion of aragonite purity at 50 °C, whereas at 70 °C that purity moderately drops (Table 5). This is not in accordance with the results obtained previously, when lower amount of reactants were used and the formation of aragonite was promoted with increasing temperature up to 70 °C. This appears to be related to the incomplete reaction at 70 °C, as affirmed by the increased presence of brucite in this case.

Furthermore, as aforementioned, the particle size and particle size distribution are important characteristics of the synthesized powder materials for their use as a filler or pigment in the paper industry. The particle size distributions for the carbonation precipitates produced at the three different temperatures are presented in Figure 2, average particle sizes are given in Table 6, and SEM images of the precipitates as illustrated on Figure S5 in the Supplementary Materials.

Particle size distributions and average particle size values of the three synthesized samples did not appreciably change as a function of temperature. However, with the help of the respective SEM images, it becomes more evident that the particle size of aragonite progressively increase with increasing temperature. This is also evidenced from the increasing D[3,2] values, which is more sensitive to slight particle growth than the D[4,3] value, and the shift of the D50 values from under 1 µm to over 1 µm (nearly 50% greater). This reaffirms the reduction of the particle size by lowering the temperature as already indicated in the previous experiments. This is due to a reduction of crystal growth rate with temperature, coupled to the presence of a high rate of nucleation due to the sonication (Nalajala and Moholkar, 2011). Unlike the previous experiments, however, where the aragonite particles had uniform shape, this time in addition to the hubbard squash-like aragonite particles, there are also smaller aragonite particles visible. These smaller particles are due to the bigger influence of sonication in the smaller reaction volume, whereby the particle size of the already reacted aragonite particles is reduced by attrition between particles, and the impact of shockwaves on particle surfaces.

Although the temperature of 50 °C was proven to be most favorable for the sonochemical production of aragonite with the highest purity, it is important for this study to manage to increase the aragonite yield while maintaining low temperatures that ensure the smaller particle size. To this end, further optimization was performed at 30 °C.

3.2.3 Influence of the reaction time

By adjusting the concentration of the reactants and the volume, significantly high aragonite yields were formed at the standard reaction conditions (T = 30 °C, flow rate = 2 NL/min, t = 100 min). In order to find out the impact of the reaction time on the sonochemical aragonite yield, and to see if high purity can still be accomplished at even shorter durations than so far tested, four different reaction times (25 min, 50 min, 75 min, and 100 min) were tested. Table 7 summarizes the results.

It is evident from the brucite mass fraction that the reaction is far from complete after only 50 or 25 minutes, whereas after 75 minutes the completeness of the reaction is the same as after 100 minutes, synthesizing a significantly high yield of the aragonite phase, comparable to that synthesized after 100 minutes of reaction. Consequently, the reaction time could be reduced to, at least, 75 minutes and while still producing high purity of aragonite at high yield.

3.2.4 Influence of the Mg-to-Ca ratio (MCR)

For the promotion of aragonite formation, an MCR of 3 was used as the standard condition. In this section, five different Ca-to-Mg molar ratios (0, 1, 1.5, 2, 2.5, 3) were used to test their effect on the sonochemical synthesis of aragonite. For the production of these different MCRs, the amount of $Ca(OH)_2$ was maintained stable (18.5 g), while the amount of $MgCl_2{\cdot}6H_2O$ was changed accordingly. The obtained results are shown in Figure 3.

At the higher $Ca(OH)_2$ used, the amount of MCH can be reduced to an MCR of 2 while still producing aragonite of a sufficiently high purity. This is in accordance with Park et al. (2008), who stated that the production of pure aragonite is possible at MCR higher than 2. For MCH amounts corresponding to MCR lower than 2, the synthesis of aragonite was reduced, whereas the generation of calcite was increased, as had been demonstrated in the earlier lower concentration experiments. Note that for the experiment done without MCH, unreacted portlandite ($Ca(OH)_2$) also remained.

Since it has been shown that the reaction time can be reduced down to 75 minutes and the Mg-to-Ca ratio down to 2.0, and still a sufficiently high aragonite purity can be achieved, an experiment combining these two parameters was performed. However, the outcome of that experiment was rather disappointing regarding the aragonite purity (82.5 wt%), and overall carbonation extent (12.0 wt% brucite remaining). This means that although these two parameters gave encouraging results when tested separately, they cannot be combined to still produce high aragonite purity. In this case, the surplus of severity of the reaction, defined in Santos (2013), is insufficient. The main reason appears to be the short reaction time, since the calcite and magnesian-calcite fractions were still relatively low (2.5 wt% and 0.7 wt%, respectively).

3.2.5 Reuse of $MgCl_2$-containing filtrate

The high significance of magnesium ions in the production of aragonite has already been highlighted. However, an alternative to its high consumption should be found. In an effort to reduce the amount of MCH that is required for each test, two potential alternatives were investigated: a) the reuse of the magnesium chloride-containing filtrate after each test, and b) the use of alternative additives.

It is known that $MgCl_{2(aq)}$ is released back into solution during the formation of $CaCO_3$ (and consequent dissolution of brucite). As such, the reacted solution may be reusable after its filtration. To check this probability, aragonite was sonochemically produced under the conditions used in the second set of experiments. After the filtration, the $Ca(OH)_2$ is added directly to the filtrate. This is repeated three times to examine the impact of solution recycling on the aragonite purity. That impact is depicted in Table 8. After a single re-use, the aragonite purity was slightly increased. This may have happened due to remaining aragonite that is still present in the solution acting as nuclei for the aragonite formation. However, a second or third re-use of the produced solution proved to be ineffective regarding the formation of high purity aragonite. At the same time as the aragonite fraction decreased, the brucite fraction increased, indicating the incompleteness of the reaction during the last two re-uses (calcium remaining dissolved in solution, as seen in Table 9). This is likely due to the appreciable thickening of the recycled solution, which hindered CO_2 gas dispersion and sonication-induced mixing. Furthermore, calcite fraction increased after the last two re-uses, mainly due to the significantly decreased presence of Mg^{2+} ions (Table 9) that were lost in the filtration as solid-phase brucite. It is evident that more advanced separation of the PCC and purification of the filtrate is required before reuse to enable continued production of high purity aragonitic PCC.

3.3 Optimal Conditions

Based on the findings of the present study, new process conditions were found to promote the production of hubbard squash-shaped aragonite while maintaining low reaction temperature (30 °C). The results confirm that shortening the reaction time and lowering the Mg-to-Ca ratio are not ideal to improve the formation of the aragonite, but can be reduced to a certain extent to improve overall PCC productivity and reduce reagent requirements. On the other hand, it was found that an elevated MCH value together with a higher concentration of $Ca(OH)_2$ feed, in a smaller reaction volume, is preferred while working at a higher CO_2 flow rate (2.0 NL/min). The optimal conditions regarding the promotion of aragonite synthesis are summarized in Table 10.

Under these conditions, the aragonite purity achieved was 95.7 wt% (the balance consisting of 1.4 wt% calcite, 1.2wt% magnesian calcite, 1.1 wt% nesquehonite, bischofite 0.3 wt%, and all remaining possible phases below 0.1 wt%). The average particle size of this synthesized PCC is shown in Table 10. Due to some agglomeration, the D[4,3] value is higher in this table comparing to the D[4,3] value at the same conditions (30 °C) in Table 6. The particle morphology at the optimal process conditions is shown in Figure 4. The XRD diffractogram in Figure 5a shows the high aragonite formation at these optimal process conditions.

3.4 Alternative Calcium Source for Improved Sustainability

Finally, to increase the sustainability of the sonochemical synthesis process, an alternative source of calcium would be desirable. Instead of using pure $Ca(OH)_2$, an option would be to extract calcium from waste materials, such as metallurgical slags, combustion ashes or mineral tailings. The results of four experiments (conditions listed in Table 11) are depictedin Figure 5b.

It is seen that all PCC samples had nearly identical diffractograms compatible with high aragonite purity (refer to Figure 5a). The next step in the development of this synthesis route will be to utilize calcium extracted from actual ironmaking slag. Under standard carbonation conditions (i.e. without ultrasound and MCH), we have proven, in De Crom et al. (2015), that such calcium source is very suitable for production of high quality calcite PCC once the extraction solution is sufficiently purified by physicochemical methods and carbonation conditions are optimized.

4. Conclusions

The objective of this project was to synthesize the highest possible precipitated-aragonite yield in a short reaction time while maintaining the desired product properties. Due to the shortening of the reaction time (100 minutes or lower) it was chosen to work at a higher CO_2 flow rate (2.0 NL/min) during the synthesis, compared to that in our previous study (Santos et al., 2012). Under these conditions, it was found that a higher initial loading of $Ca(OH)_2$ (five times greater than the original process) in a smaller reaction volume (a quarter of the original process) allowed scaled-up production of PCC (1g/(L·min) $CaCO_3$) with a high aragonite content and desired properties. Two key benefits of this condition aided in the aragonite formation: higher ultrasound intensity (800 W/L gross power-to-volume ratio), which is beneficial for nucleation of aragonite crystal growth, and higher magnesium concentration in solution, which as a consequence increased the Mg-to-$CO_{2(aq)}$ ratio. By working at the selected higher CO_2 flow rate and at optimal operating conditions, it is thus possible to produce more PCC per unit time and in a smaller reactor footprint, thereby increasing the overall efficiency of the sonochemical process.

The highest purity synthesized in this study corresponds to 95.7 wt% aragonite, which meets the purity target set by Yasiv (2004) of 95wt%, but is short of the 99.0wt% achieved in our previous study (Santos et al., 2012). This is because approximately 4 % of the reactants were converted to other mineral phases, mainly calcite and magnesian-calcite.

Since pre-breakage (sonication without carbonation) promotes the aragonite formation by improving the reaction between $Ca(OH)_2$ and $MgCl_2$ (Santos et al., 2012), an extended pre-breakage (>15 min) may prevent the calcite formation.

Seeding the solution with aragonite crystals could be a strategy for further reducing MCR, reaction duration and process temperature, as it was evidenced in this study that unintended seeding helped boost aragonite synthesis in the filtrate re-use tests.

The presence of impurities may also be the result of the rather simple set-up used for the synthesis of PCC. Both the control of the CO_2 flow rate and the temperature were checked and manually adjusted every few minutes, resulting in some fluctuation of these parameters during each experimental run. As a result, these fluctuations may have had an important influence on the aragonite formation. Working with an improved automated set-up, and potentially a closed vessel to maintain a constant CO_2 pressure, can possibly further increase the aragonite purity. Non-uniform distribution of cavitational activity in the reactor can also be a culprit for the formation of other mineral phases, and could be improved by optimizing the location and power output (W/m^3) of ultrasound transducers, the frequency of ultrasound, and the dimensions and shape of the reactor and the irradiating horn (Gogate et al., 2011).

5. Acknowledgements

Rafael Santos is thankful for the postdoctoral financial support (PDM) from the KU Leuven Special Research Fund (BOF). Yi Wai Chiang is grateful to Tatiane Tomazi for conducting the calcium acetate experiments and to the Brazilian National Council for Scientific and Technological Development (CNPq) for funding her Science Without Borders (SwB) scholarship. The KU Leuven Department of Earth and Environmental Sciences is acknowledged for the use of XRD and LDA equipment.

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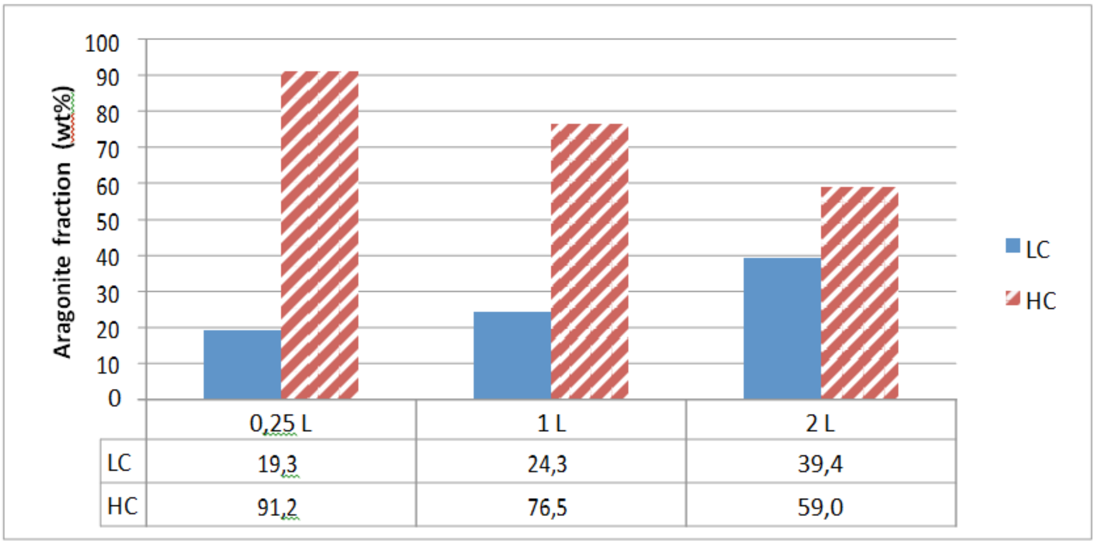
Figure 1: Influence of the reactant concentration and reaction volume on the aragonite mass fraction of carbonation precipitates (T = 30°C, MCR = 3, LC = Low Concentration (3.7g $Ca(OH)_2$), HC = High Concentration (18.5 g $Ca(OH)_2$)).

Figure 2: Particle size distributions of carbonation precipitates as a function of temperature (18.5 g $Ca(OH)_2$, MCR = 3, reaction volume = 250 ml): a) T = 30 °C, b) T = 50 °C, and c) T = 70°C.

Figure 3: Mineral mass fractions as function of MCR (temperature = 30 °C, 18.5 g $Ca(OH)_2$, time = 100 min, reaction volume = 250 ml).

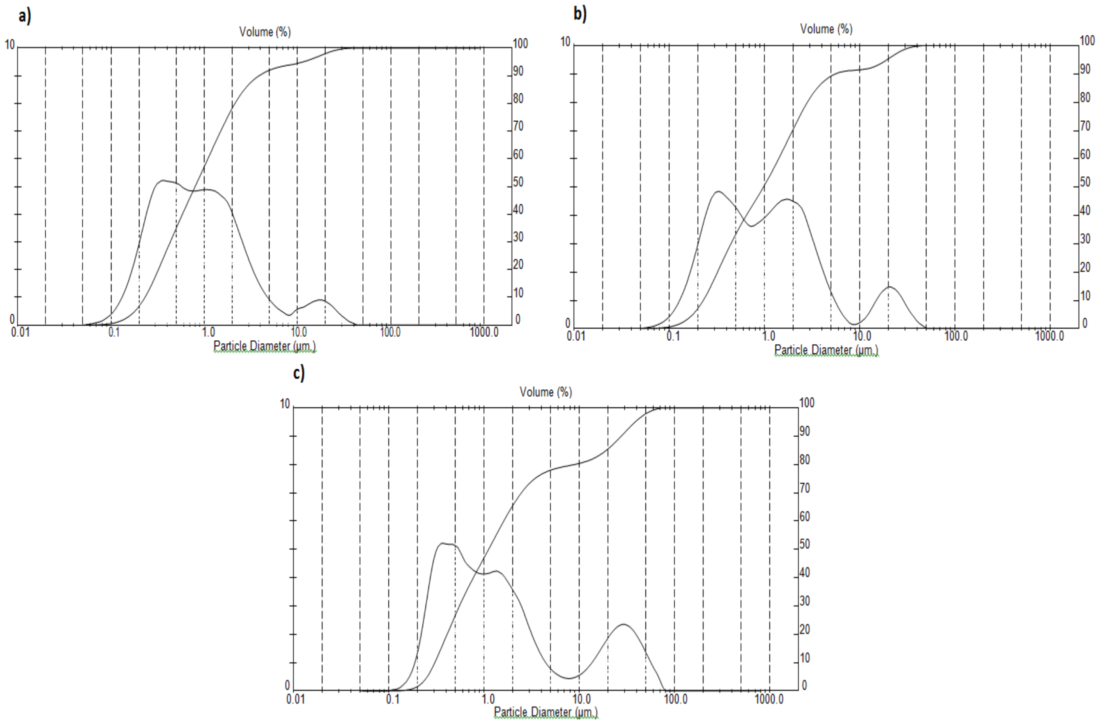
Figure 4: Particle morphology at optimal process conditions and different magnifications.

Figure 5: (a) Mineral analysis by XRD at optimal process conditions; (b) Mineral analysis by XRD of precipitated-aragonite sonochemically synthesized from calcium acetate solution. A = aragonite phase.



	0,25 L	1 L	2 L
LC	19,3	24,3	39,4
HC	91,2	76,5	59,0

Figure 1: Influence of the reactant concentration and reaction volume on the aragonite mass fraction of carbonation precipitates (T = 30°C, MCR = 3, LC = Low Concentration (3.7g $Ca(OH)_2$), HC = High Concentration (18.5 g $Ca(OH)_2$)).



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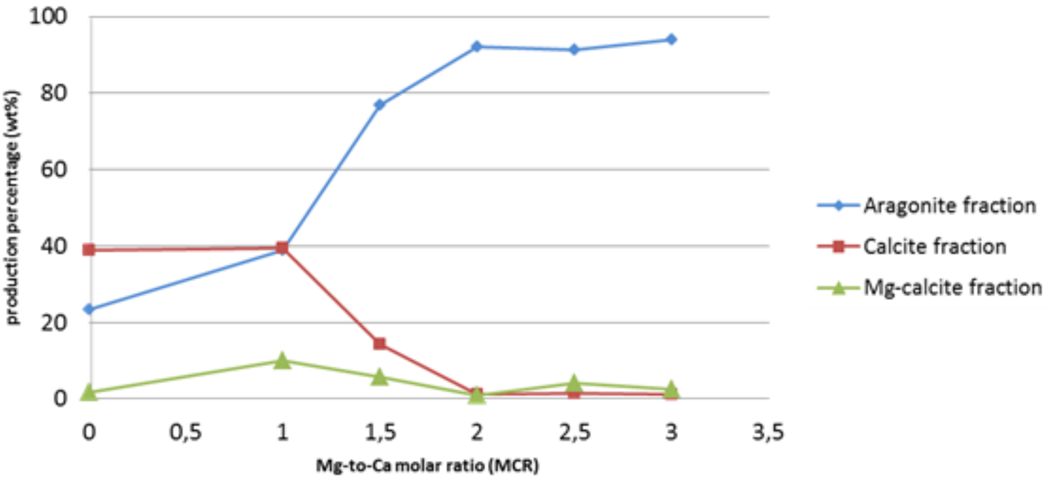


Figure 3: Mineral mass fractions as function of MCR (temperature = 30 °C, 18.5 g $Ca(OH)_2$, time = 100 min, reaction volume = 250 ml).

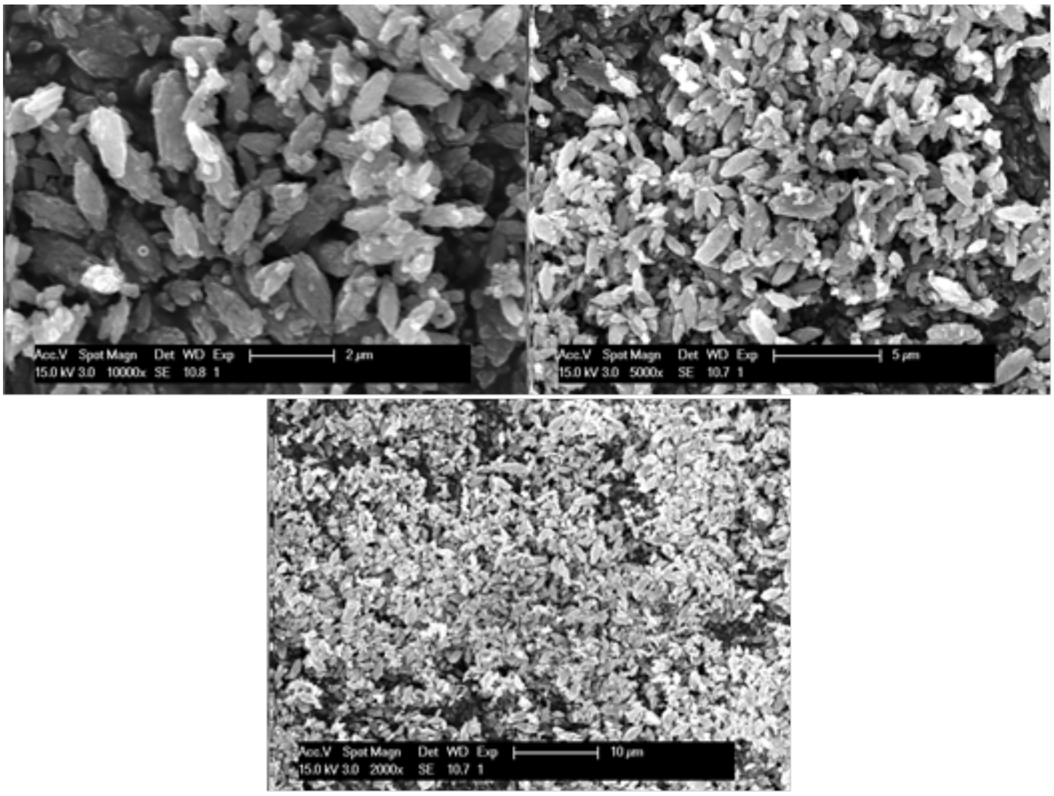
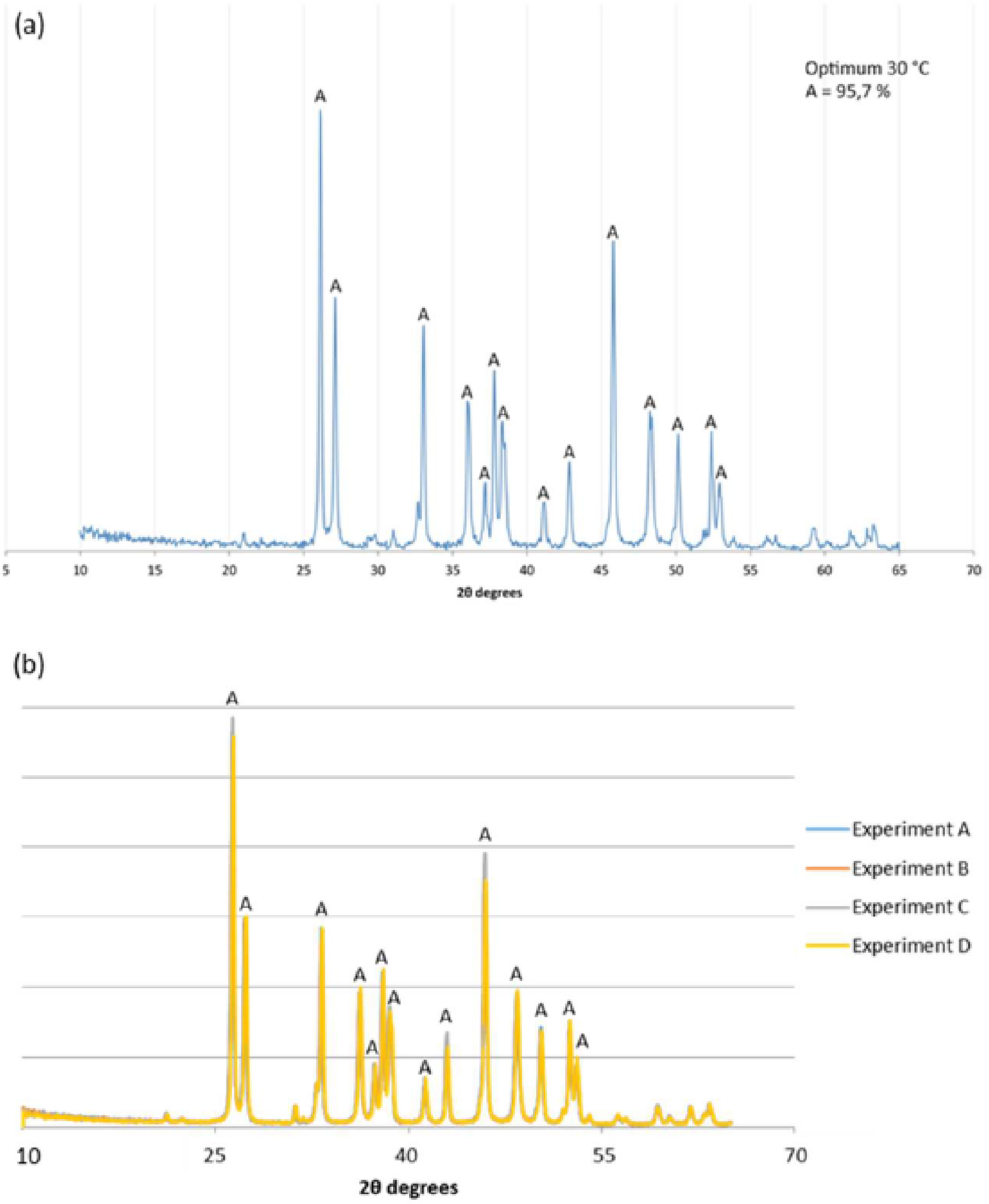


Figure 4: Particle morphology at optimal process conditions and different magnifications.



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List of Tables:

Table 1. Mineral mass fractions of carbonation precipitates as function of temperature (3.7 g $Ca(OH)_2$, MCR = 3, volume = 1 liter).

Temperature (°C)	Aragonite (wt%)	Calcite (wt%)	Magnesian Calcite (wt%)
30	24,3	15,4	56,5
50	67,9	5,9	24,3
70	89,2	1,0	2,7

Table 2. Mineral mass fractions of carbonation precipitates as a function of Mg-to-Ca ratio (MCR) (3.7 g $Ca(OH)_2$, temperature = 30 °C, volume = 1 liter).

MCR	Aragonite (wt%)	Calcite (wt%)	Magnesian Calcite (wt%)
0	1,4	94,9	0,1
3	24,3	15,4	56,8
6	49,5	9,1	8,2

Table 3. Magnesium and calcium initial concentrations and mineral mass fractions of carbonation precipitates as a function of reaction volume (3.7 g $Ca(OH)_2$, MCR = 3, temperature = 30 °C).

Volume (L)	Ca-Conc. (M)	Mg-conc. (M)	Aragonite (wt%)	Calcite (wt%)	Magnesian calcite (wt%)	Brucite (wt%)
0,25	0.200	0.400	19.3	9.4	61.9	0,0
1	0.050	0.100	24.3	15.4	56.5	0,6
2	0.025	0.050	39.4	35.7	18.5	1,0

Notes: the Mg concentration discounts the MCH amount added the amount of magnesium that initially precipitates as brucite when the chloride ion of MCH is transferred to the Ca in $Ca(OH)_2$; the Ca concentration assumes all $Ca(OH)_2$ added is dissolved into aqueous $CaCl_2$.

Table 4: Mineral mass fractions of carbonation precipitates as a function of reaction volume (18.5 g $Ca(OH)_2$, MCR = 3, temperature = 30 °C).

Volume (L)	Aragonite (wt%)	Calcite (wt%)	Magnesian calcite (wt%)	Brucite (wt%)
0,25	91,2	1,5	4,2	0,3
1	76,5	2,6	11,9	6,5
2	59,0	10,3	7,1	19,1

Table 5: Mineral mass fractions of carbonation precipitates as a function of temperature (18.5 g $Ca(OH)_2$, MCR = 3, reaction volume = 250 ml).

Temperature (°C)	Aragonite (wt%)	Calcite (wt%)	Magnesian calcite (wt%)	Brucite (wt%)
30	95.7	1.4	1.2	0.1
50	96.4	0.4	1.5	0.1
70	89.9	1.7	3.0	1.3

Table 6: Average particle sizes of carbonation precipitates as a function of temperature (18.5 g $Ca(OH)_2$, MCR = 3, reaction volume = 250 ml).

Temperature (°C)	D[3,2] (µm)	D[4,3] (µm)	Aragonite fraction (wt%)
30	0,53	2,17	95.7
50	0,55	3,10	96,4
70	0,58	1,73	90,0

Table 7: Mineral mass fractions of carbonation precipitates as a function of reaction time (temperature = 30 °C, 18.5 g $Ca(OH)_2$, MCR = 3, reaction volume = 250 ml).

Time (min)	Aragonite (wt%)	Brucite (wt%)
100	93,4	0,3
75	92,6	0,3
50	35,1	6,6
25	34,0	10,3

Table 8: Influence of the re-use of magnesium chloride on the mineral mass fractions of carbonation precipitates (temperature = 30 °C, 18.5 g $Ca(OH)_2$, MCR = 3, time = 100 min, reaction volume = 250 ml).

MCR	Aragonite (wt%)	Calcite (wt%)	Magnesian calcite (wt%)	Brucite (wt%)
3 (Initial)	94,1	1,2	3,4	0,1
Re-use 1	94,5	1,0	0,5	2,3
Re-use 2	76,6	12,5	2,4	5,0
Re-use 3	0,8	25,4	3,1	56,3

Table 9: Chemical analysis of filtrate solutions utilized in recycling experiments, determined by ICPMS.

MCR	Mg^{2+} concentration (g/L)	Ca^{2+} concentration (g/L)
Re-use 1	28.4	5.4
Re-use 2	21.1	12.1
Re-use 3	1.2	34.0

Table 10: Overview of the optimal process conditions for intensified sonochemical synthesis of precipitated aragonite, and resulting yield rate and material properties. Present study and authors' previous study are compared.

	Present study	Previous study (Santos et al., 2012)
Mass $MgCl_2.6H_2O$ (g)	152.5	61
Mass $Ca(OH)_2$ (g)	18.5	3.7
Solution volume (L)	0.25	1.0
CO_2 flow rate (NL/min)	0.4	0.24
Time (min)	100	150
Temperature (°C)	30	30
PCC production rate (g/(L·min)	1	0.033
Aragonite purity (wt%)	95.7	99.0
D[4,3] (μm)	7.02	1.23
D[3,2] (μm)	0.74	0.69

Table 11: Experimental conditions tested for sonochemical synthesis of precipitated-aragonite from calcium acetate solution ($Ca(CH_3COO)_2$ = 0.056 mol, NaOH = 0.102 mol, reaction volume = 200 ml).

Experiment	Temperature (°C)	Reaction Time (min)	CO_2 flow rate (NL/min)	MCR
EXPERIMENT A	36	95	0.4	3
EXPERIMENT B	36	105	0.24	3
EXPERIMENT C	49	80	0.4	3
EXPERIMENT D	36	112	0.4	6

Improving the Yield of Sonochemical Precipitated-Aragonite Synthesis by Scaling-up Intensified Conditions

Rafael M. Santos, Jolien Thijs, Evangelos Georgakopoulos, Yi Wai Chiang, Ann Creemers, Tom Van Gerven

Supplementary Materials:

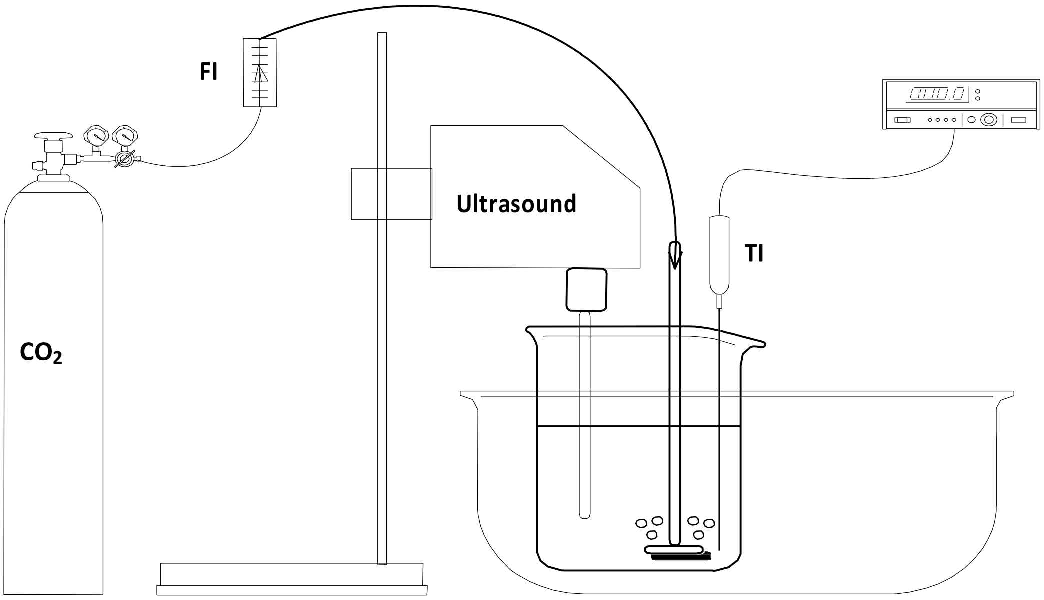

Figure S1. Schematic overview of the experimental set-up.

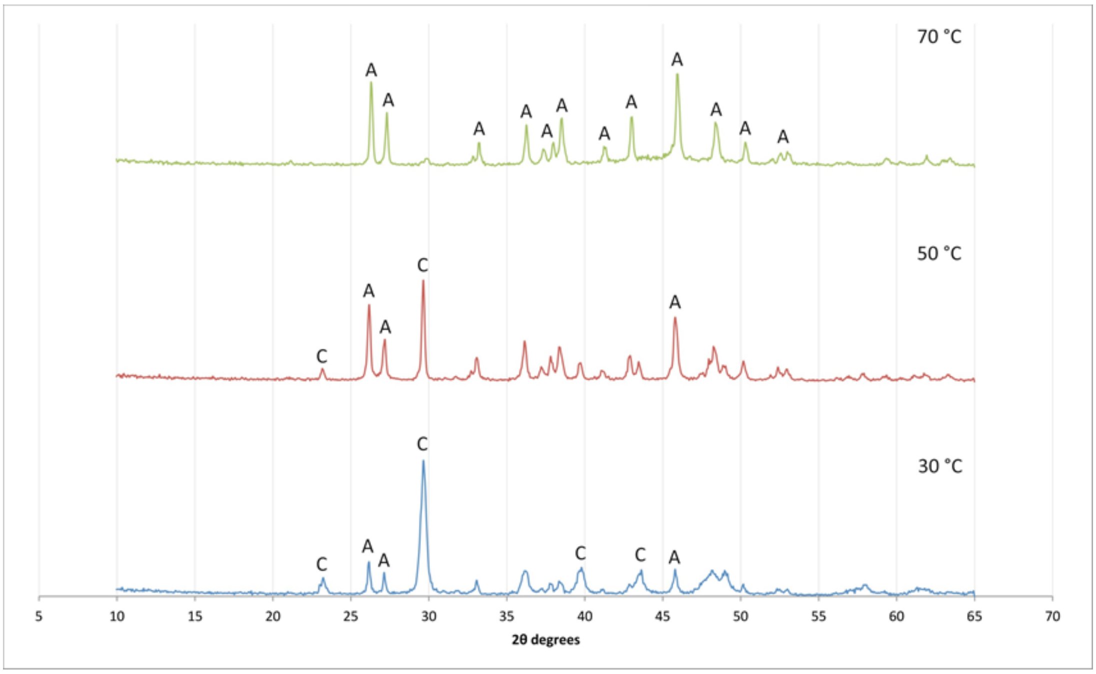

Figure S2. Calcium carbonate polymorphism of carbonation precipitates as function of temperature (3.7 g $Ca(OH)_2$, MCR = 3, volume = 1 liter). A = aragonite, C = calcite

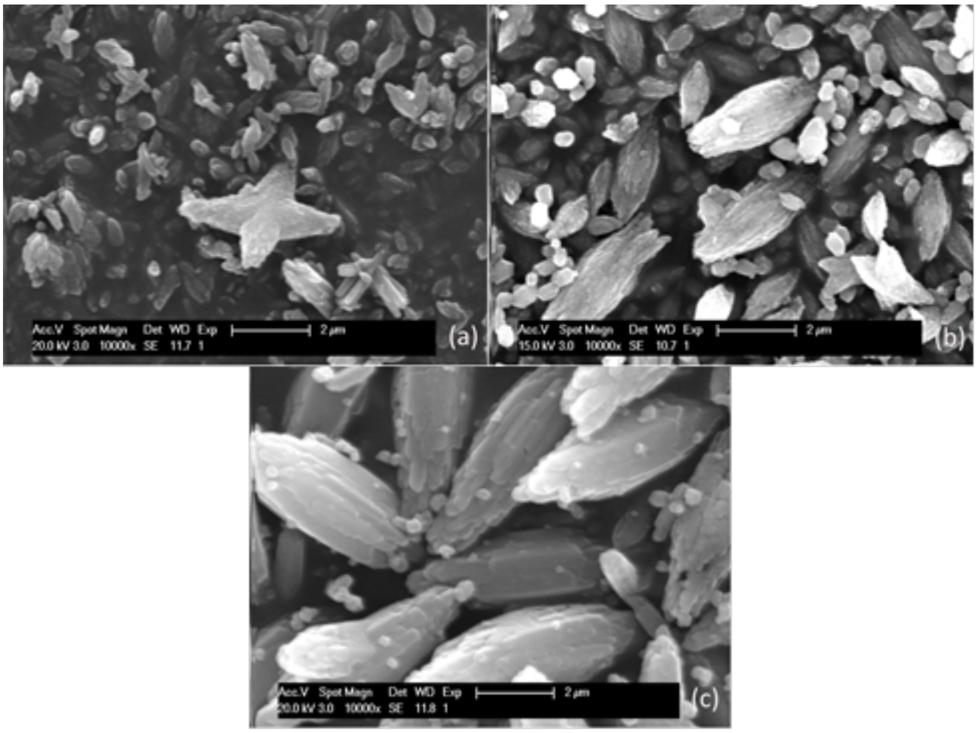

Figure S3. Comparison of carbonation precipitate crystal morphology as a function of temperature (3.7 g $Ca(OH)_2$, MCR = 3, volume = 1 liter): (a) 30 °C, (b) 50 °C and (c) 70 °C.

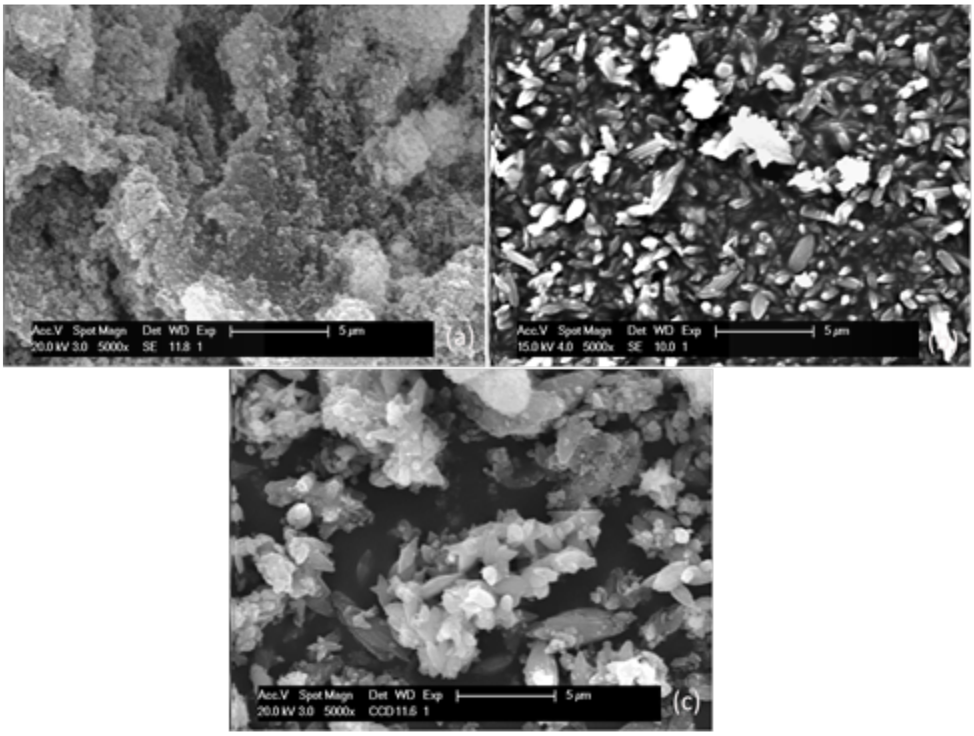

Figure S4. Comparison of carbonation precipitate crystal morphology as a function of MCR (3.7 g $Ca(OH)_2$, temperature = =30 °C, reaction volume = 1 liter): (a) MCR = 0, (b) MCR = 3 and (c) MCR = 6.

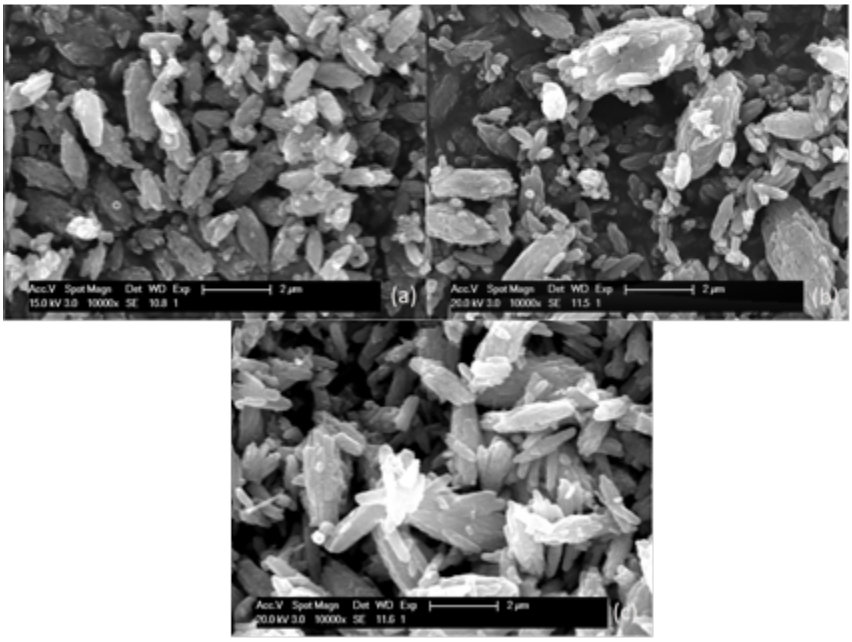

Figure S5: Particle morphology of carbonation precipitate as a function of temperature (3.7 g $Ca(OH)_2$, MCR = 3, volume = 250 ml): (a) 30 °C, (b) 50 °C and (c) 70 °C.