

On Sustainable Production of CaCO₃ via Monohydrocalcite—A Carbon Capture and **Mineralisation Product from Waste Brines**

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Abstract

This study investigated the conversion of monohydrocalcite (MHC) to anhydrous calcium carbonate. The primary material, MHC, was produced from waste brines containing Ca and Mg ions, reacted with sodium carbonate, which may serve in the carbon capture and mineralisation approach. Two different approaches to the conversion were studied: 1) the conversion of MHC conversion to anhydrous calcium carbonates in air (under ambient conditions); 2) the identification of conversion conditions which could be adapted for potential industrial application. The former focused on the effects of the synthesis system conditions of the primary material on the aragonite conversion process and the resulting aragonite morphology, whereas the latter covered the factors that accelerate conversion and influence the resulting morphology. The paper also discusses instances where MHC converts to the more stable polymorph, calcite. It was found that conditions leading to the polymorphic and morphological selection of converted minerals were temperature and humidity dependant.

Keywords

Morphology, Morphological Stability, Calcium Carbonates, Minerals, Salts

1. Introduction

Generally, the primary industrial source of calcium carbonate is limestone rock [1] [2] [3], which is extracted by mining or quarrying. The excavated mineral is then processed by crushing or grinding units; hence leading to the product being referred to as ground calcium carbonate (GCC) [4]. The rock is usually ground to a required particle size and comprised of irregular rhombohedral shapes reflecting the perfect cleavage of the calcite structure [5]. A purer synthesised product of CaCO₃, known as precipitated calcium carbonate (PCC), can be produced by precipitating the product under controlled conditions. While GCC dominates the market, PCC accounts for 18% of all calcium carbonate production and continues to grow [6]. Both precipitated and mined carbonates have a wide-range of commercial applications, which include but are not limited to paper, plastics, paints, coatings, cement and petroleum industries [7] [8]. Up to 72% of the total global produce of PCC is used in printing and writing paper production [9]; PCC improves the optical properties of the finished product by increasing the dispersion of light, enhancing impact resistance, oil absorption, strength, whiteness and so on [9] [10]. Furthermore, as long as the carbonate meets certain purity requirements, it can also be used as a direct food additive or in various pharmaceutical products, e.g. toothpaste [11].

While GCC is widely abundant, it is a natural product, and therefore, not very versatile due to the variety of aspects which influence carbonate precipitation and diagenesis. Some of the most significant environmental factors in carbonate formation include: the position of global sea level [12]; water temperature, latitudes [13] and changes in seawater chemistry (e.g. Mg/Ca ratio) [14]. The relationship between calcium carbonate polymorphs is made even more complex by the presence of rock building organisms, as they are known to use both calcite and aragonite in their skeletal structures [15]. Generally, in marine environments, calcite can be found as a primary constituent of shell debris or as a precipitated cement, however, it may also partially or fully replace aragonite in shells or other skeletal matter by dissolution and precipitation. Calcite minerals of different generations display textural geometry as well as elemental composition. The latter is influenced by the nature of the mineral diagenetic environment, e.g. calcites formed in reducing environments have high elemental Fe and recent carbonates have higher Sr content than ancient limestones, due to increased Sr levels in modern oceans [16].

Precipitation of carbonates is an alternative to carbonate mining and can be produced from waste [1] [2] [3]; the field has been widely studied for over a century and first commercially produced by John E. Sturge Ltd. in 1841 [17]. Due to its artificial synthesis, PCC gains several advantages including a reduced concentration of impurities such as silica, strontium, iron or lead. Furthermore, the particles of PCC are more uniform while their crystal morphologies can be adjusted to the desired product as per the specification of the relevant application; such as whiteness, which is an important product quality indicator (Cales de Llierca). There are many routes to precipitation, which employ various feedstocks. In the conventional synthesis of PCC, limestone is decarbonated into CaO and CO₂ calcination (at temperatures in excess of 900°C). After the calcined lime is slaked with water, the resultant Ca(OH)₂ product is purified by dissolution in water and then carbonated, ideally with the CO₂ recycled from the calcination process, thereby regenerating a pure CaCO₃ [18]. Other common PCC syntheses involve mixing soluble carbonate solutions with saline solutions containing Ca ions, e.g. Equation (1) [19] [20] [21], or heating a solution of calcium chloride and urea [22], or slow removal of CO_2 and water from Ca(HCO₃)₂ [23].

$$CaCl_{2} + Na_{2}CO_{3} \rightleftharpoons CaCO_{3} + 2NaCl$$
(1)

$$Ca(HCO_3)_2 \rightleftharpoons CaCO_3 + CO_2 + H_2O$$
 (2)

Overall, depending on the industry, the key properties of interest in carbonates are high purity, crystal colour/size/shape, powder density, surface area and oil absorption [24] [25]. In laboratory conditions, the particle formation can be controlled with adjustments to the reaction time, temperature, agitation rate, ion concentration in solution, system pressure, rate of carbon dioxide addition, pH and post-crystallization processing [26]; the exact conditions used for specific grades are proprietary. The control of particle properties is what makes PCC a more attractive and versatile process than the somewhat limited GCC.

The most commonly used carbonate mineral, for both GCC and PCC, is calcite. Aragonite, although more difficult to produce, in some cases presents superior industry-specific physical and mechanical properties than calcite [27]. The value of aragonite is attributed to morphology, particle size, chemical purity and other properties; all of which depend on the synthesis conditions [28]. For example, aragonite has a slightly greater average index of refraction than calcite, therefore, aragonite performs better as filler in the paper and plastic industries when compared with calcite [29] [30]. Aragonite also has a higher specific gravity (2.95) than calcite (2.71) [28] and is more soluble. Plummer and Busenberg [31] reported the solubility products *(i.e.,* log K_{SP} values) of calcite (-8.48 at 25°C and -8.56 at 37°C), aragonite (-8.33 at 25°C and -8.40 at 37°C). However, calcite can incorporate Mg²⁺ within its lattice and form magnesian calcite [32], thereby increasing its solubility to be comparable to that of aragonite. Aragonite minerals, which are largely Mg-free, seldom contain as much as 1% MgCO₃ [33].

Reportedly, aragonite use in agriculture is one of the key drivers of the growth of global aragonite markets. Aragonite in its raw state helps to add biological benefits to soil and limits the amount of fertilizers used through the stimulation of the soil's microbial life which influence the availability of nutrients needed for plant utilization [34]. Precipitated aragonite is regularly used as a filler in rubbers, paper, plastics, composites and paints [35] [36] [37] [38]. The precipitate is also used in car bumpers and dashboards as filler incorporated into thermoplastic and polypropylene composites amongst many other applications [39]. Many reports have highlighted the benefits of needle-like aragonite enhancing the mechanical and physical properties of materials, such as the dimensional stability and strength [38] [40] [41] [42] [43]. Employing aragonites of different morphologies can aid in controlling material properties, including e.g. the rheology of sealants [44]. Aragonite applications are extended to the pharmaceutical industry, because of its accessibility, low cost, safety, bio-compatibility, pH-sensitive

properties, osteo-conductivity and slow biodegradability [45] [46] [47]. It plays many roles including acting as a phosphate buffer in haemodialysis patients which helps the patients to filter blood in order to remove waste, such as urea, and to eliminate excess fluids from the body [48]. Aragonite polymorph has also been used in the design of the cancer drug carriers, tissue engineering and bone repairs [49]: e.g. in one study both an orthophosphate layer and aragonite whiskers were implanted into bone defect sites [50]. Larger aragonite crystals can be used as filter aids in cosmetics, e.g. as a replacement for mineral powders [28].

Generally, aragonite for commercial purposes is synthesized by two methods: 1) the carbonation process which involves reacting $Ca(OH)_2$ slurry with CO_2 gas [35] [51] [52] [53] and 2) the solution process which uses sodium carbonate solution for the precipitation stage [53] [54]. The formation of aragonite is favoured at elevated temperatures of around 60°C - 70°C [55] and by the presence of Mg²⁺. Studies have shown that the adsorption of Mg²⁺ onto calcite nuclei prevents the transport and integration of Ca^{2+} into the calcite crystal lattice, hence promoting aragonite precipitation [56] [57] [58].

This paper suggests a low temperature synthesis of aragonite, which includes precipitation of monohydrocalcite (MHC) in the first stage, which may be a part of a carbon capture and mineralisation process. MHC is well known to be metastable with respect to anhydrous CaCO₃ polymorphs. It is usually reported to have formed from amorphous ACC precursor, as an intermediate phase, before it transformed to aragonite over hours or days [23] [59] [60] [61]. This study observes MHC conversion to aragonite at different humidities, as well as proposes an accelerated method involving gentle heating in solution. Furthermore, conversion to calcite in dry conditions is explored.

2. Methods

The experimental design was subdivided into two parts: 1) precipitation of monohydrocalcite (the precursor) and 2) the conversion of monohydrocalcite to anhydrous calcium carbonate (the product).

The MHC syntheses were all carried out under atmospheric pressure of 1 atm at room conditions in the laboratory, at approximately 20°C. A rapid addition (under constant and vigorous stirring) of a 100 mL of artificial waste brine (containing various concentrations of Ca and Mg/Cu/Co salts) to a carbonate solution (1 M, 100 mL) was conducted to achieve a $(Ca^{2+} + Me^{2+})/CO_3^{2-}$ ratio of 1 (stabilising ion concentration were 0.2 M). The solutions were subjected to stirring between 2 - 48 hours in an open container on the lab bench.

A summary of the main variables of the study is presented in **Table 1**. The experimental protocol was further divided between 1) synthesis variables of MHC precursor which may affect the resulting aragonite morphology and 2) conversion influencing factors *i.e.* the aragonite transformation conditions.

As MHC reportedly decomposes to aragonite in air at ambient temperature

Aragonite m	orphology infl synthesis facto	uencing MHC ors	MHC – CaCO3 conversion			
Temperature	Time	Doping agent	Humidity	Accelerated aragonite conversion	Dry powder heating	
20°C standard MHC preparation 5°C for comparison purposes	2 h standard MHC preparation 24, 48 h for comparison purposes	Mg ²⁺ standard MHC preparation Cu ²⁺ and Co ²⁺ for comparison purposes	0, 42, 100 RH% at 20°C MHC storage in varied humidity environments	60°C, 80°C and 100°C heating in water baths	Thermal Analysis DTA/TG	

Table 1. A summary of the main variables of the study.

and pressure, the experiments which concentrated on observing this degradation process did not involve any treatment of the MHC precursor in order to influence the conversion and were deemed as "naturally converting". Conversely, studies where MHC conversion to aragonite took place in conversion favouring environments in order to hasten the process were classed as "accelerated conversion". Natural conversion was achieved using three different humidity-controlled environments: 1) low at approx. 0 RH%; 2) moderate at approx. 43 RH%; 3) high at approx. 100 RH%; all at 20°C. Six grams of synthesised MHC powder was divided into three equal parts (by weight) and stored in desiccators that were sealed with high vacuum grease. Silica gel and distilled water were selected to obtain conditions of extremely dry and wet environments, respectively. A saturated solution with an excess of potassium carbonate was used to achieve an approximate mid-range point of 43 RH%. A hygrometer was used to check whether the set arrangements were sufficient to maintain the chosen humidity.

Three sets of tests, in which the MHC product samples were immersed in water, were conducted in ovens set at different temperatures, to measure their respective conversions to aragonite. The experiments were carried out at 60°C, 80°C and 100°C over a 9 h period. A total of 27 samples containing 1 g MHC in 150 ml of water were placed in the three ovens. A detailed study was conducted using dry MHC powders upon which heat was applied in the absence of any liquid, with the aim of converting MHC to calcite at temperatures of 150°C - 250°C.

Obtained samples were dried at 30°C in a fan-assisted Carbolite AX1200ven overnight. Ground samples were analysed by powder X-Ray Diffraction (XRD) using an X'Pert Diffractometer (PANalytical, NL) employing Cu ka radiation (not monochromatic) at 45 kV/40mA. Data were collected over the range 5° - 60° in 2 θ , with a step size of 0.013° and a 16.575 s per step. The data obtained from the XRD scans was analysed using the Rietveld method using the EXPGUI application (a graphical user interface for General Structure Analysis System

software) for quantitative analysis. DTA/TG were carried out on an STA 780 (STANTON REDCROFT, UK) in a flowing N2 atmosphere (50 (\pm 5) mL·min⁻¹). Samples were dried and ground prior to analysis. The heating rate was set at 10°C per minute, up to the required temperature (400°C - 800°C) in a platinum crucible. The sample sizes were approximately 30 mg. MP-AES analysis was carried out on monohydrocalcite and aragonite samples. Both, the dissolved solid samples and supernatant retrieved after filtration were examined. 1 g of powder was dissolved in a 100 ml solution containing deionised water and 5 ml of nitric acid. Calibration curves were prepared using multi-element standards (Ca, Mg, Cu and Co). Scanning Electron Microscopy (SEM) images were collected on an MA-10 electron microscope (Zeiss, DE) equipped with an energy dispersive X-ray analyser (Oxford Instruments, UK). The analytical instrument used a 10 kV accelerating voltage. Prior to scanning, samples were ground and dispersed on a double-sided sticky carbon disc that was adhered to an aluminium stub and sputter-coated with gold under argon gas atmosphere using SC-500A sputter (EmScope, UK).

3. Results and Discussion

3.1. Monohydrocalcite (Precursor)

Initial microstructural analyses (**Figure 1**) were conducted in order to observe the morphology of the primary material (MHC) used throughout the conversion studies.

Powder XRD analyses confirmed the sample composition to be phase-pure. The SEM analyses revealed that MHC crystallites were rice-like, up to 2 - 3 μ m



Figure 1. SEM of MHC prior to accelerated aragonite conversion. MHC precipitated from a brine containing 0.2 M Mg; ageing in mother solution for 2 hours at 20°C (left and right images show the same image at different magnification).

long and about 0.5 μ m wide. Helical ridges were observed along the length of the grain surfaces, as shown in the inset of **Figure 1**. To test the range of temperatures which may cause MHC conversion, the same sample was analysed by DTA/TG (**Figure 2**).

DTA confirms the loss of water in two stages: the evaporation of free water is indicated at temperatures 50° C to 150° C, whereas, the higher temperature endotherm 180° C - 280° C is likely to be structural water loss. XRD analysis confirmed that the exothermic event at around 330° C is related to MHC to calcite



Figure 2. DTA graph showing three endothermic and one exothermic event upon heating MHC at 10°C min⁻¹ up to 800°C. The sharp spike of the exotherm suggests that MHC conversion to calcite is isothermal. TG graph showing the mass loss (in wt.%) of XRD phase-pure MHC with increasing temperature.

re-crystallisation. TG analysis of the MHC sample showed the release of water happening in stages, gradually between 70°C and 270°C. The first step took place between 70°C and 210°C, where a gentle continuous slope of mass loss was observed. The second step, attributed to the crystal-bound water loss, is marked by a significantly steeper slope, between 210°C and 270°C. The sample was thermally stable between 270°C and 650°C, after which it underwent carbonate decomposition.

3.2. MHC—Aragonite Conversion in Humidity, Controlled Environments

MHC prepared at 5 and 20°C (2 h aging duration) were used to assess the influence of MHC synthesis temperature on the resulting aragonite, also, 24 and 48 h reactions (at 20°C) were carried out in order to test whether prolonging the MHC crystallisation process affects the conversion. Although differently synthesised, these samples were left to transform to aragonite over 4 weeks in identical conditions to those described in the experimental section. XRD patterns in **Figure 3** displays partial MHC-aragonite conversion which depicted the said transformation.

Figure 4 shows the morphologies of partial MHC, aragonite conversion products, formed from naturally aged MHC samples which were synthesised at 5°C and 20°C. Ageing took place in a moderately humid environment (43 RH%), at 20°C over 4 weeks. It was observed that the 5°C sample converted the fastest and the opposite was true for the 24 h, 20°C sample.



Figure 3. Partial MHC, aragonite conversion XRD patterns obtained from 4 MHC samples prepared at different conditions: MHC prepared at 5 and 20°C (2 h ageing duration) and 24 and 48 h reactions (at 20°C). On the right, XRD phase-pure MHC (M) (102) and aragonite (A) (111), (021) peaks.



Figure 4. SEMs of partially converted samples highlights the contrast between the parent material (MHC) and the spherical product (aragonite). Precursor MHC was precipitated from 0.2 M Mg brine; ageing in mother solution for 2 hours at 20°C (left, 24% aragonite) and 5°C (right, 30% aragonite). The conversion took place over 4 weeks in moderate relative humidity environment at 20°C.

XRD phase identification was followed by the morphological assessment. The MHC loose needles seen in the reference image (Figure 1) were replaced by flakes and spherical clusters. The increase in the latter coincided with the observed XRD changes. Spherulites differed from those typically described in literature: reporting authors often observe aragonite products exhibiting a narrow-needle (acicular) shape, however flower, cauliflower and flake-like crystals are also common [62].

The resultant aragonite products were found to be between 20 - 30 μ m, in the cases where the precursor was synthesised at 20°C. In the experiments where MHC was synthesized at 5°C, the formed spheres were visibly smaller in size, with diameters ranging between 10 - 15 μ m. These findings indicated that colder MHC precipitation temperatures favoured smaller aragonite spheres.

Having noted that MHC formation temperature had a significant effect on crystallite morphology and conversion time, further studies were carried out in order to test the effects of the precursor reaction duration on the resulting aragonite morphology. **Figure 5** overviews the transition of an MHC sample, which was aged at 24 and 48 h in mother solution prior to the curing.

Although both samples were cured for the same duration of time and at the same conditions (over 4 weeks in a moderately humid (43 RH%) environment), the difference in size between the spherical aragonite products was clearly visible (**Figure 5**). The aragonite spheres that formed from a sample aged for 24 h, were between 50 - 70 μ m in diameter, more than twice as large as those converted from 2 h MHC (**Figure 4**). In the case of the 48 h aged samples, they were between 80 - 100 μ m across, further signifying the influence of MHC ageing



Figure 5. Natural Partial MHC to aragonite conversion. MHC precipitation conditions 0.2 (M) Mg concentration in mother solution; ageing in mother solution at 20°C for 24 hours (left 7% aragonite), and 48 hours (20% aragonite). The conversion also took place over 4 weeks in moderate relative humidity environment at 20°C.

duration prior to its natural conversion. The resulting large aragonite spheres also displayed a clear cohesion between the particles across the grain boundary. The grains contained both surface cracks, and deep fractures. The former were shallow microcracks on an otherwise smooth surface, and the latter, a uniaxial diametric crack up to $2 \mu m$ wide.

 Mg^{2+} used in the kinetic stabilisation of MHC were replaced by Co^{2+} and Cu^{2+} . To test whether this would lead to a change in morphology, a selected number of MHC samples were left to age in "moderate humidity" environments and analysed by XRD and SEM. Presented in **Figure 6** are their conversion products.

Post-synthesis, the samples were held in a moderately humid (43 RH%) environment; over 4 weeks. The micrographs showed that the samples had a varying degree of conversion, but nevertheless, all exhibited a resemblance to the spherical morphology observed in the Mg-stabilised MHC conversion products. Both of the 2 h MHC samples displayed a significant amount of flaky, poorly defined flocculants, whereas, the cases with increased ageing duration led to well-formed spheres. Cu-MHC formed aragonite aggregates of crystals up to 30 - 40 μ m, while Co-MHC converted to slightly sintered, large and fractured spheres. Comparable to the Mg²⁺ doped samples, only the largest grains showed evidence of cracking. Co-MHC conversion grains were up to 70 μ m across, larger than any previously described in this study. Thus, it could be concluded that, Mg²⁺ was not responsible for the shape of aragonite products, as Cu²⁺ and Co²⁺ products exhibited similar habits.

When it came to natural MHC to aragonite conversion, none of the tested MHC synthesis variables (reaction temperature, time and stabilising ion) affected



Figure 6. The aragonites formed from MHC samples precipitated after 2 h (top) and 48 hour (bottom) reactions. MHC precipitation conditions 0.2 M Cu²⁺ and Co²⁺ concentration in both mother solutions; ageing in mother solution for 2 hour at 20°C (top left 35% aragonite, top right 50% aragonite) for 48 hours at 20°C (bottom left 40% aragonite, bottom right 90% aragonite). The Cu and Co monohydrocalcite samples were cured in moderate humidity environments for 4 weeks prior to SEM analysis.

the shape of the product (*i.e.* the spherical habit), however, they did affect the size of individual grains (Figure 7). It must be noted that none of the experiments described thus far led to calcite formation, with aragonite being the only observed conversion phase with exception to minor unidentified peaks in Mg-MHC (most likely hydromagnesite) and malachite in Cu-MHC.

Whilst still concentrating on the natural conversion aspect, it was necessary to investigate the influence of the environmental humidity on the persistence of the MHC powder precursor. Assuming that, in a commercial setting, MHC would be stored in a warehouse or laboratory storage with minor temperature variations, the humidity aspect may be less predictable and more difficult to manage. It is very unlikely that industrially produced MHC would be stored at strictly humidity-controlled facilities, therefore knowing the implications it may have on the product is very important.

Low humidity experiments displayed a successful case of well-preserved, loose MHC powder, even after 2 months of curing. There were no significant differences between the resultant MHC grains and the benchmark reference (Figure 1). Aragonite was absent in both XRD and SEM analyses, suggesting that low humidity environments significantly increased MHC persistence. The X-ray



Figure 7. Spherical aragonite crystallite sizes resulting from MHC prepared at different conditions (BC, bicarbonate used instead of carbonate, 20° C), based on n = 10 particles measured per sample.

diffractograms confirmed the purity of the specimen, the only observed difference between the reference sample and the aged specimen were noted in the peak intensity (**Figure 1**). A partial conversion to aragonite was observed in the MHC sample held in a low humid environment (0 RH%) for 6 months. The micrographs in **Figure 8** display the changes observed at the onset of aragonite conversion.

The MHC rice-like crystals appeared in agglomerated clusters, with interconnecting web-like bridges in between them. Some pseudo-spherical shapes were also identified amongst the MHC agglomerates. MHC was additionally kept in a system with a 100 RH% where a more advanced MHC conversion was observed to have taken place (**Figure 9**).

The MHC sample which was kept in a very humid environment (100 RH%) for 2 months had fully converted and MHC could no longer be detected via XRD. The initial conversion signs appeared after 2 weeks, when grains began to form webbed clusters, similar to those seen in **Figure 8**. After two months, the recovered sample was a paste and no longer a powder: the solid was suspended in water, adsorbed from the environment, as 100 RH% was used. The aragonite spheres were between 15 - 20 μ m across and fully connected by a sheet-like layer. One may note that the spheres exhibited a uniform size throughout, which is an advantage for calcium carbonate applications which often rely on a specific grain size.

The humidity in the air encouraged the MHC conversion to aragonite, confirming the hypothesis regarding the importance of water in MHC conversion to aragonite. It must be noted that the very humid environment (100 RH%) accelerated the conversion with a very high efficiency comparing to the moderate humidity environment (43 RH%) described in the previous subsections. XRD



Figure 8. The morphology of monohydrocalcite stored in a desiccator where equilibrium relative humidity was maintained at approx. 0%. Around 5% of the sample had converted to aragonite, the image on the right shows the main changes observed to have taken place after 6 months.



Figure 9. The morphology of fully converted, XRD phase-pure aragonite formed from MHC in a system where the equilibrium relative humidity was maintained at 100%.

identified aragonite and small quantities of hydromagnesite; considering that aragonite does not incorporate Mg into its lattice, it's not surprising that a Mg phase is present. An unidentified peak may belong to MHC (Figure 10).

Assuming that aragonite does not incorporate Mg^{2+} into its crystal lattice as per previously published studies [33], and that Mg^{2+} is indeed responsible for the



Figure 10. XRD pattern of an MHC conversion product obtained at 100 RH% over 2 months.

stabilisation of MHC [63], then the loss of Mg^{2+} is a key factor in the conversion mechanism. Equation (3) shows MHC dissolution and Equation (4) aragonite recrystallisation.

$$Ca_{1-x}Mg_{x}CO_{3} \cdot H_{2}O \rightleftharpoons Ca^{2+} + Mg^{2+} + CO_{3}^{2-} + H_{2}O$$
(3)

$$Ca^{2+} + Mg^{2+}CO_3^{2-} + H_2O \rightleftharpoons CaCO_3 + Mg^{2+} + H_2O$$
(4)

As seen so far, humidity favours the conversion, turning the dry and loose MHC powder into aragonite paste, it can be concluded that moisture plays a crucial part in both, the loss of Mg^{2+} during the dissolution of MHC and the consequent reprecipitation of aragonite. Following that thought, it was hypothesised that in order to design an accelerated conversion method and ensure the availability of water molecules even at elevated temperatures, the powder could be submerged in water baths. A series of experiments testing the hypothesis are discussed below.

3.3. Accelerated MHC—CaCO₃ Conversion

Three sets of tests, in which the MHC product was immersed in water, were conducted in ovens set at different temperatures to observe their respective conversions to aragonite. The first experiment was carried out at 60°C (Figure 11), followed by an identical protocol for temperatures 80°C and 100°C. An additional test was carried out at room temperature (20°C), however, no conversion was observed over 9 hours.

The aragonite conversion tests conducted at 60°C did not show any change in the phase composition within the first 2 h, a period which may be classed as the dissolution-dominated stage. After 3 h approximately 10% of the MHC content was observed to have converted to aragonite. After 6 h of heat treatment the



Figure 11. A comparison of the formation of aragonite, in its conversion from monohydrocalcite, over time at 60°C. The stacked histograms show the percentage yields of aragonite and MHC (left axis) whereas the line plots show the development of the intensities of peak [111] for both of aragonite and monohydrocalcite (right axis).

aragonite content overtook MHC as the major phase; both semi-quant XRD and peak intensity data displayed this change.

After 9 h in the heated water bath MHC had fully converted to aragonite. No additional phase or impurity was observed in the XRD pattern. The findings of this process proved to be an encouraging sign, as it decreased the conversion time from weeks to just hours.

AES, which was carried out on the solids recovered from the accelerated conversion experiments conducted at 60°C, showed that Mg content within the powder decreased with increasing aragonite precipitation. Even within the first 2 hours a 2.7% decrease in Mg was observed, this was attributed to partial MHC dissolution. The final aragonite product contained around 20% less Mg than the MHC precursor. Although AES helps to identify patterns of decreasing Mg content, the data should not be interpreted as indication of the absolute aragonite elemental composition-aragonites are largely Mg-free, seldom containing as much as 1% MgCO₃ [33], hence Mg detected by AES could have also been present elsewhere, e.g. an amorphous phase not detected by XRD.

Following the successful accelerated aragonite conversion, further experiments were conducted at 80°C (Figure 12).

The aragonite conversion tests conducted at 80°C showed a 10% drop in MHC content within the 1st hour; further reduction in MHC over time followed a moreorless linear trend. Aragonite as the prevailing phase appeared in the experiments heated for over 3 hours. The final 30% of MHC converted at the highest rate. From the 5th hour of reaction and onwards, there was no MHC detected by XRD. A 20°C increase in the reaction temperature (from 60°C to 80°C), as shown, allowed for a significant reduction in the conversion time (up to 50%).

AES from the accelerated conversion experiments conducted at 80°C showed



Figure 12. A comparison of the formation of aragonite, in its conversion from monohydrocalcite, over time at 80°C. The stacked histograms show the percentage yields of aragonite and MHC (left axis) whereas the line plots show the development of the intensities of peak [111] for both of aragonite and monohydrocalcite (right axis).

that Mg content within the powder decreased with increasing aragonite precipitation. The same pattern was observed for the conversion products at lower temperatures. During the 1st hour the powder had lost around 2.6% of the Mg. After 5 hours, the resulting aragonite product contained only 10% of the initial Mg.

To complement the above data, further experiments were conducted at an additional 20° C increase (reaching 100° C) (**Figure 13**).

A sudden 70% drop in MHC is observed within the first hour of the experiment, followed by a steady, near-linear decrease over the next hours. This strongly contrasts the linear trend, followed by a drop observed 80°C experiment (**Figure 6**).

Although, in both 80°C and 100°C experiments, it took more than 4 h to completely dehydrate MHC and convert it to aragonite, the collected data suggested that the conversion kinetics were different in both cases. At 100°C, the dissolution dominating period appeared to be significantly shorter than those seen in the 60°C and 80°C conversions. Due to carbonates' unique characteristic of decreasing solubility with increasing temperature, it can be concluded that the aragonite reprecipitation stage was accelerated in higher temperatures and not the MHC dissolution.

The AES analysis suggested that after 1 h, as much as 3.1% percent of Mg was lost from the sample, more than observed at lower temperatures for the given time. Furthermore, approx. 1% of Mg was lost to solution each hour with increasing aragonite precipitation, the final product lost around 7% of the Mg from the precursor.

Aragonite formed using the accelerated conversion method had a very different morphology to the naturally converted spherical aragonites (Figure 14). The accelerated conversion grains took the shape of elliptical needles (between 15 -



Figure 13. A comparison of the formation of aragonite, in its conversion from monohydrocalcite, over time at 100°C. The stacked histograms show the percentage yields of aragonite and MHC (left axis) whereas the line plots show the development of the intensities of peak [111] for both of aragonite and monohydrocalcite (right axis).



Figure 14. Partial MHC to Aragonite conversion via accelerated conversion method. MHC precipitation conditions 0.2 M Mg concentration in mother solution; ageing in mother solution for 1 hour at 20°C. Conversion took place over 3 hours in an 80°C water bath.

20 μ m long and up to 5 μ m wide) and clusters thereof. The conversion temperature did not appear to have any significant effect on the morphology: the selected images (**Figure 14**) display partially converted MHC and aragonite mixtures resulting from the 80°C water bath over 3 hours, however, all of the aragonite products which were converted in heated water baths at temperatures of 60°C - 100°C resulted in similar grain sizes and morphologies (**Figure 15**).

Most of the aragonite crystallites were of uniform size, between 20 - 30 μ m



Figure 15. Complete MHC to Aragonite conversion. MHC precipitated from brines with initial 0.2 (M) Mg concentration; ageing in mother solution with carbonate for 2 hours at 20°C, washed and dried over 24 hours. Conversion took place in water baths over 9 hours at 60°C (left), 5 hours at 80°C (centre), and 8 hours at 100°C (right).

long and up to 15 μ m wide. Notably, the aragonite crystallites synthesised at 60°C were slightly larger (~2 μ m), elliptical needle shape, as opposed to crosses and stars as seen in the other temperature experiments. Although the XRD of the 60°C conversion product suggested a phase-pure aragonite, the small, flaky grains could suggest a secondary phase, *i.e.* hydromagnesite or small quantities of poorly crystalline MHC precursor. **Figure 16** shows that accelerated conversion produces aragonite of higher yield relative to natural conversion.

Most of the aragonites exhibited a single spindle-resembling shape, however, there was an obvious progression to the conjoining pairs and clusters. These were either forming an "X" shape by joining in the middle or joining at the ends to form a "V" shape and mostly abundant in the higher temperature studies. Some of the crystallites had a spherical, web-like growth surrounding the crystal; the web was either very loose (Figure 17, early rose), with visible porosity, or very closely packed, resembling a flower (Figure 17, rose). Often there were spindles and their clusters attached to the spherical formations. Figure 17 displays some of the more interesting interaction between the two morphologies.

There was an intermittent abundance of hierarchical microspheres, exclusive to the fully converted samples at the higher temperature range ($80^{\circ}C - 100^{\circ}C$). The particle shape somewhat resembled the spheres described in the natural conversion studies, however, on closer inspection proved to be very different: much more porous, and significantly larger than aragonite spheres described in the natural conversion studies (Figure 18).

Despite somewhat similar appearance it was evident that the sphere formation had taken place via different mechanism and the availability of water played the



Figure 16. XRD patterns comparing aragonite powders produced via MHC, by (a) natural conversion and (b) accelerated conversion methods.



Figure 17. The row of images proposes a potential particle evolution path from a single grain to clusters. All the images of crystallites were selectively picked from XRD-phase pure aragonite samples, transformed by the accelerated conversion method.

key role. In the natural conversion experiments, the powders could adsorb water due to the high relative atmospheric humidity. However, due to the absence of a suitable medium to disperse into, MHC dissolution may have caused locally saturated Mg environment around the reprecipitating crystallites. It could have been the reason for the formation a Mg-rich skin-like layer identified as hydromagnesite via XRD.

The XRD-amorphous spheres seen in the accelerated conversion studies (**Figure 17**) appeared as a visually distinct secondary phase. It exhibited morphological characteristics commonly associated with $Mg(OH)_2$ or Mg-carbonates e.g. hydromagnesite, dypingite [64] [65] [66] [67]. The locally saturated environments did not appear due to the significantly greater availability of water,



Figure 18. Micrographs displaying aragonite needles produced via MHC as well as secondary Mg-rich spheres. Crystallites with lower porosity/smoother surface (bottom left) and other spheres are thought to be the same minerals.





Figure 19. EDS analysis was carried out on a aragonite sample, where the conversion took place in an 80°C water bath. Three different colours were used to highlight the oxygen, Mg and Ca concentrated areas.

which acted as a medium for MHC dissolution and ion dispersion.

EDS elemental mapping showed that the largest Mg distribution coincided with the spheres, whilst the elliptical needle-clusters showed the highest Ca concentrations. These findings confirmed that Mg from MHC was lost during its conversion to aragonite, and eventually precipitated as Mg-minerals. Elemental mapping (**Figure 19**) validated the hypothesis that needles were a polymorph of very low-Mg CaCO₃ and spheres could potentially be identified as magnesite (MgCO₃).

3.4. Thermally Induced Decomposition to Calcite

Having evaluated the DTA data and the temperature range at which MHC lost

its structural water, 10 samples, from the same MHC batch, weighing 1 gram each, were gently heated over a range of temperatures (150°C - 250°C) in an oven.

The structure of MHC broke down gradually during the second stage of water loss, as identified in the DTA (Figure 20). With increasing temperature MHC converted to calcite, the XRD patterns of the heating products are seen in Figure 21.



	Weight %					Weight %			
	С	0	Mg	Ca		С	0	Mg	Ca
Max.	23.8	59.61	1.67	49.62	Max.	17.99	67.5	21.58	3.44
Min.	11.38	33.88	0.32	16.11	Min.	16.58	58.4	13.67	1
Aver.	18.69	49.9	0.72	30.67	Aver.	17.44	64.21	16.58	1.77

SPHERE (B)

FRACTURE



	Weight %					Weight %			
	С	0	Mg	Ca		С	0	Mg	Ca
Max.	24.29	65.55	18.62	1.06	Max.	23.5	64.4	24.89	4.27
Min.	18.92	60.21	11.44	0.39	Min.	11.68	54.02	17.24	0
Aver.	21.60	61.97	15.09	0.77	Aver.	16.88	59.96	20.77	2.39

Figure 20. Minimum, maximum and average weight % values derived from the selected spectrum points marked on images. Aragonite needles, sphere (A)—porous surface, sphere; (B)—smooth surface and fracture.



Figure 21. Thermally induced transformation of MHC to calcite. The zoomed in section (on the right) highlights the MHC and calcite peaks.



Figure 22. XRD patterns displaying regenerative behaviour of MHC.

MHC, calcite transition patterns pictured in the figure above highlighted that the conversion is gradual, first decreasing MHC peaks and resulting in largely amorphous phase, anhydrous ACC (between temperatures 200°C - 230°C). The anhydrous ACC was rehydrated in order to check for the potential regenerative properties, which were successful according to XRD (**Figure 22**). The steps taken involved the immersion of the dehydrated MHC powder into a vessel filled with double-distilled water, before mixing and filtration of the suspension, followed by acetone drying and XRD analysis. Two examples of MHC regeneration are presented: 1) where MHC is partially decomposed with minor calcite conversion at 190°C; 2) advanced MHC decomposition and conversion to calcite at 250°C. In both cases it was observed that MHC regenerates once the dehydrated powder is immersed in water. The dehydration of MHC could be compared to the conversion of gypsum (CaSO₄·2H₂O) into calcium sulfate hemihydrate (CaSO₄·0.5H₂O) and anhydrites (γ -CaSO₄ and β -CaSO₄) [68]. A loss of 3/2 molecules of water transforms gypsum into hemihydrate; whereas, in the case of MHC, the resulting amorphous CaCO₃ is assumed to be anhydrous due to the DTA/TG indicated water loss described in the previous sections.

4. Conclusions

The data presented in this paper documented a series of experiments during which monohydrocalcite was converted to aragonite and calcite. The key find-ings included:

MHC transformed to anhydrous polymorphs CaCO3 calcite or aragonite.

Four stages leading to aragonite production were identified: 1) MHC crystallisation from ACC precursor, 2) the dissolution of MHC, 3) the nucleation of aragonite and 4) the crystal growth of aragonite.

The simulated "natural" conversion in humid environments allowed the production of aragonite to take place in an eco-friendly and resource-saving manner, however, over an extended period of time (weeks and months). High relative humidity environments and elevated temperatures favoured the transformation.

In the natural conversion studies, Mg^{2+} was not responsible for the shape of the spherical aragonite, as Cu^{2+} and Co^{2+} MHC transformed into crystals with similar morphological habits.

Accelerated conversion took place over a number of hours. Results from 80°C tests showed the best potential in terms of the purity and conversion time.

Gentle heating led to the preservation of MHC, however, higher temperatures of 190° C - 250° C led to partial or full conversion to calcite.

MHC was found to have regenerative properties. When heated for a short amount of time, it first exhibited a poorly crystalline XRD pattern, later displaying MHC regeneration once immersed in water.

Conflicts of Interest

The author declares no conflicts of interest regarding the publication of this paper.

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