

ENHANCED REACTIVE MAGNESIA CEMENT-BASED CONCRETE MIXES

Cross-Reference To Related Application

[0001] This application claims the benefit of priority of Singapore Patent Application
5 No. 10201700636V, filed 25 January 2017, the content of it being hereby
incorporated by reference in its entirety for all purposes.

Technical Field

[0002] The present disclosure relates to a method of producing a hydrated magnesium
10 carbonate based cement composite. The present disclosure also relates to a hydrated
magnesium carbonate based cement composite.

Background

[0003] The increasing concentration of carbon dioxide (CO₂) emitted by the
15 combustion of fossil fuels is a significant environmental concern. The Portland
cement (PC) industry is considered as one of the major contributors to the increasing
emissions of CO₂ as the annual global PC production, which exceeds 4 billion tons,
results in 5% to 10% of global anthropogenic CO₂ emissions and a large amount of
resource consumption. The amount of energy consumed annually for this process is
20 about 2780 to 3050 terawatt hours, accounting for about 2% to 3% of global primary
energy use. This is mainly due to the high amount of energy required for the
clinkering of raw materials at 1450°C, and the high CO₂ emissions result from
calcination of limestone. This necessitates the implementation of certain innovations
that can enable the reduction of net CO₂ emissions. One of these is the sequestration
25 of CO₂, which facilitates a safe and permanent storage of CO₂ within a range of
building applications. Along this line of innovation, most existing technologies on
carbonated cement binders focus on improving diffusion of CO₂ through the cement
pore system. This is an inefficient approach as the diffusion mechanisms relied on
high CO₂ pressures and/or elevated temperatures, and results in an increased overall
30 cost due to the need for specialized curing infrastructure. Bearing this in mind, there
are two main issues regarding carbonation of cement mixes.

[0004] The first is the low reaction degree associated with the reactivity and availability of unreacted phases. The second is the low diffusion rate of CO₂ within the cement matrix. To address the latter, conventional carbonation mechanisms involve high CO₂ pressures and/or elevated temperatures to enable carbonation within cement-based mixes as mentioned above. One example is the use of “supercritical carbonation”, which requires both high temperatures and pressures to transform CO₂ into a dense gas that acts as a solvent for water without exhibiting surface tension, thereby enabling its penetration into very fine pores. This is not only unsafe and costly but also hard to scale up due to the use of specialized equipment to enable high carbonation degrees.

[0005] Another approach is the development of alternative cement binders with potentially lower carbon footprints, such as the use of alkaline earth metal oxides for generation of sustainable cement with the ability to absorb CO₂. As cement is used as a binder material in construction, it may also be called a cement binder. One example of such cement with lower carbon footprint may be reactive magnesium oxide (MgO) cement (RMC).

[0006] This is because RMC is produced at lower calcination temperatures compared to PC (700-1000°C versus (vs.) 1450°C) and can sequester CO₂ during setting and gain strength accordingly. RMC enables utilization of waste and industrial by-products due to low sensitivity of their hydration products to impurities, and has the potential to be fully recycled when MgO is used as the only binder. Apart from calcination of magnesite (MgCO₃), MgO can be synthesized from seawater or reject brine, which is obtained from the waste at the end of desalination processes.

[0007] The hydration and carbonation reactions are critical for strength development of RMC as they control the degree of HMC (hydrated magnesium carbonate) formation. The hydration mechanism of MgO involves a dissolution-precipitation process initially controlled by the dissolution of MgO. However, the hydration degree of MgO is quite low (limited to 40% to 80%) under ambient conditions due to its low rate and degree of dissolution, and the precipitation of hydration and carbonation products on the surface of unhydrated MgO particles inhibits further hydration. Besides this, the precipitation of carbonate phases on unreacted Mg(OH)_{2(aq,s)} prevents progress of the carbonation reaction. These limitations in the hydration and

carbonation of RMC result in its inefficient use as a binder and limit the strength development of concrete formulations that it is incorporated in.

[0008] There is thus a need to provide for a solution that resolves and/or ameliorates the issues mentioned above.

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Summary

[0009] In one aspect, there is provided for a method of producing a hydrated magnesium carbonate based cement composite, the method comprising:

10 providing an aqueous solution comprising a hydration agent and hydrated magnesium carbonate seed particles;

contacting the aqueous solution with a magnesium oxide based cement to form magnesium hydroxide (i) from the hydration agent and the magnesium oxide based cement, and (ii) on the hydrated magnesium carbonate seed particles; and

15 exposing the magnesium hydroxide to carbon dioxide to form the hydrated magnesium carbonate based cement composite.

[0010] In another aspect, there is provided for a hydrated magnesium carbonate based cement composite obtainable by the method as disclosed above, wherein the hydrated magnesium carbonate based cement composite comprises hydrated magnesium carbonate formed from a magnesium oxide based cement and hydrated magnesium carbonate seed particles, and wherein the hydrated magnesium carbonate seed particles used comprise an amount of up to 1 wt% of the magnesium oxide based cement and the hydrated magnesium carbonate seed particles.

Brief Description of the Drawings

25 [0011] The drawings are not necessarily to scale, emphasis instead generally being placed upon illustrating the principles of the invention. In the following description, various embodiments of the present disclosure are described with reference to the following drawings, in which:

[0012] FIG. 1 shows a scanning electron microscopy (SEM) image of hydromagnesite seeds (i.e. hydromagnesite seed particles). The scale bar represents 1 μm .

[0013] FIG. 2a is an isothermal calorimetry results of samples showing the heat flow according to one embodiment disclosed herein.

[0014] FIG. 2b is an isothermal calorimetry results of samples showing the cumulative heat according to one embodiment disclosed herein.

[0015] FIG. 3 shows the compressive strength of all samples cured for up to 28 days according to one embodiment disclosed herein.

5 [0016] FIG. 4 shows the X-ray diffraction (XRD) patterns of various samples after 14 days of curing according to one embodiment disclosed herein.

[0017] FIG. 5 shows the mass loss and heat flow of all samples after 14 days of curing based on thermogravimetric analysis (TGA) according to one embodiment disclosed herein.

10 [0018] FIG. 6a shows a back-scattered electron (BSE) image of a H₂O.S0 sample after 14 days of curing according to one embodiment disclosed herein. The scale bar represents 10 μ m.

[0019] FIG. 6b shows a BSE image of a H₂O.S0.5 sample after 14 days of curing according to one embodiment disclosed herein. The scale bar represents 10 μ m.

15 [0020] FIG. 6c shows a BSE image of a HA.S0 sample after 14 days of curing according to one embodiment disclosed herein. The scale bar represents 10 μ m.

[0021] FIG. 6d shows a BSE image of a HA.S0.5 sample after 14 days of curing according to one embodiment disclosed herein. The scale bar represents 10 μ m.

20 [0022] FIG. 7a shows a SEM image of a H₂O.S0 sample after 14 days of curing according to one embodiment disclosed herein. The scale bar represents 1 μ m.

[0023] FIG. 7b shows a SEM image of a H₂O.S0.5 sample after 14 days of curing according to one embodiment disclosed herein. The scale bar represents 1 μ m.

[0024] FIG. 7c shows a SEM image of a H₂O.S1.0 sample after 14 days of curing according to one embodiment disclosed herein. The scale bar represents 1 μ m.

25 [0025] FIG. 8a shows a SEM image of a HA.S0 sample after 14 days of curing according to one embodiment disclosed herein. The scale bar represents 1 μ m.

[0026] FIG. 8b shows a SEM image of a HA.S0.5 sample after 14 days of curing according to one embodiment disclosed herein. The scale bar represents 1 μ m.

30 [0027] FIG. 8c shows a SEM image of a HA.S1.0 sample after 14 days of curing according to one embodiment disclosed herein. The scale bar represents 1 μ m.

[0028] FIG. 9 shows the heat flow of samples under sealed conditions (i.e. without carbonation) according to one embodiment disclosed herein.

[0029] FIG. 10 shows the compressive strength of samples subjected to 28 days of carbonation according to one embodiment disclosed herein.

[0030] FIG. 11 shows the XRD patterns of samples after 14 days of carbonation according to one embodiment disclosed herein.

5 [0031] FIG. 12a shows the weight loss and heat flow of samples after 14 days of carbonation according to one embodiment disclosed herein.

[0032] FIG. 12b shows the thermal decomposition of hydrate and carbonate phases within reactive magnesium oxide cement (RMC) formulation in one embodiment disclosed herein.

10 [0033] FIG. 13a shows a SEM image of H₂O.S0 sample after 14 days of carbonation according to one embodiment disclosed herein. The scale bar represents 1 μm .

[0034] FIG. 13b shows a SEM image of H₂O.S0.5 sample after 14 days of carbonation according to one embodiment disclosed herein. The scale bar represents 1 μm .

15 [0035] FIG. 13c shows a SEM image of H₂O.S1.0 sample after 14 days of carbonation according to one embodiment disclosed herein. The scale bar represents 1 μm .

[0036] FIG. 13d shows a SEM image of H₂O.S1.5 sample after 14 days of carbonation according to one embodiment disclosed herein. The scale bar represents 1 μm .

20 [0037] FIG. 13e shows a SEM image of H₂O.S2.0 sample after 14 days of carbonation according to one embodiment disclosed herein. The scale bar represents 1 μm .

[0038] FIG. 14a is a schematic representation of the hydration and carbonation processes in unseeded pastes showing MgO grains before hydration, according to one embodiment disclosed herein.

[0039] FIG. 14b is a schematic representation of the hydration and carbonation processes in unseeded pastes showing hydration product (Mg(OH)₂) nucleating on MgO particle surfaces, according to one embodiment disclosed herein.

30 [0040] FIG. 14c is a schematic representation of the hydration and carbonation processes in unseeded pastes showing carbonation products (HMCs) nucleating on the

outer layer of $\text{Mg}(\text{OH})_2$ and limiting further carbonation, according to one embodiment disclosed herein.

[0041] FIG. 15a is a schematic representation of the hydration and carbonation processes in seeded pastes showing seeds introduced within the pore spaces to facilitate nucleation on their surfaces, according to one embodiment disclosed herein.

[0042] FIG. 15b is a schematic representation of the hydration and carbonation processes in seeded pastes showing $\text{Mg}(\text{OH})_2$ nucleating on both MgO and seed surfaces to enable a higher degree of carbonation, according to one embodiment disclosed herein.

[0043] FIG. 15c is a schematic representation of the hydration and carbonation processes in seeded pastes showing HMCs forming both on $\text{Mg}(\text{OH})_2$ and seed surfaces, thereby filling up the pore spaces and densifying the microstructure, according to one embodiment disclosed herein.

[0044] FIG. 16a is an isothermal calorimetry results showing the heat flow of samples according to one embodiment disclosed herein.

[0045] FIG. 16b is an isothermal calorimetry results showing the cumulative heat of samples according to one embodiment disclosed herein.

[0046] FIG. 17a shows the compressive strength of samples that have undergone curing in ambient condition according to one embodiment disclosed herein.

[0047] FIG. 17b shows the compressive strength of samples that have undergone curing with accelerated carbonation according to one embodiment disclosed herein.

[0048] FIG. 18a shows the XRD patterns of $\text{MgO} \cdot \text{H}_2\text{O}$, $\text{MgO} \cdot \text{HC}0.1$, $\text{MgO} \cdot \text{MC}0.1$ and $\text{MgO} \cdot \text{MA}0.1$ samples after 14 days of curing in ambient conditions according to one embodiment disclosed herein.

[0049] FIG. 18b shows the XRD patterns of $\text{MgO} \cdot \text{H}_2\text{O}$, $\text{MgO} \cdot \text{HC}0.1$, $\text{MgO} \cdot \text{MC}0.1$ and $\text{MgO} \cdot \text{MA}0.1$ samples after 14 days of curing under accelerated carbonation according to one embodiment disclosed herein.

[0050] FIG. 19a shows the weight loss and heat flow of $\text{MgO} \cdot \text{H}_2\text{O}$, $\text{MgO} \cdot \text{HC}0.1$, $\text{MgO} \cdot \text{MC}0.1$ and $\text{MgO} \cdot \text{MA}0.1$ after 14 days of curing in ambient conditions according to one embodiment disclosed herein.

[0051] FIG. 19b shows the the weight loss and heat flow of MgO.H₂O, MgO.HC0.1, MgO.MC0.1 and MgO.MA0.1 after 14 days of curing under accelerated carbonation according to one embodiment disclosed herein.

[0052] FIG. 20a shows the Fourier-transform infrared (FTIR) spectra of MgO.H₂O, MgO.HC0.1, MgO.MC0.1 and MgO.MA0.1 after 14 days of curing in ambient conditions according to one embodiment disclosed herein.

[0053] FIG. 20b shows the FTIR spectra of MgO.H₂O, MgO.HC0.1, MgO.MC0.1 and MgO.MA0.1 after 14 days of curing under accelerated carbonation according to one embodiment disclosed herein.

[0054] FIG. 21a shows a BSE image for a MgO.H₂O sample that has undergone 14 days of ambient carbonation according to one embodiment disclosed herein. The scale bar represents 1 μ m.

[0055] FIG. 21b shows a BSE image for a MgO.HC0.1 sample that has undergone 14 days of ambient carbonation according to one embodiment disclosed herein. The scale bar represents 1 μ m.

[0056] FIG. 21c shows a BSE image for a MgO.MC0.1 sample that has undergone 14 days of ambient carbonation according to one embodiment disclosed herein. The scale bar represents 1 μ m.

[0057] FIG. 21d shows a BSE image for a MgO.MA0.1 sample that has undergone 14 days of ambient carbonation according to one embodiment disclosed herein. The scale bar represents 1 μ m.

[0058] FIG. 22a shows a SEM image of a MgO.H₂O sample that has undergone 14 days of accelerated carbonation according to one embodiment disclosed herein. The scale bar represents 1 μ m.

[0059] FIG. 22b shows a SEM image of a MgO.HC0.1 sample that has undergone 14 days of accelerated carbonation according to one embodiment disclosed herein. The scale bar represents 1 μ m.

[0060] FIG. 22c shows a SEM image of a MgO.MC0.1 sample that has undergone 14 days of accelerated carbonation according to one embodiment disclosed herein. The scale bar represents 1 μ m.

[0061] FIG. 22d shows a SEM image of a MgO.MA0.1 sample that has undergone 14 days of accelerated carbonation according to one embodiment disclosed herein. The scale bar represents 1 μm .

[0062] FIG. 23a shows the isothermal calorimetry results indicating the heat flow of various samples according to one embodiment disclosed herein.

[0063] FIG. 23b shows the isothermal calorimetry results indicating the cumulative heat of various samples according to one embodiment disclosed herein.

[0064] FIG. 24 shows the hydration degree of H₂O and HA (under 30°C) and H₂Ot60 and HAt60 (under 60°C) samples at different durations according to one embodiment disclosed herein.

[0065] FIG. 25 shows the density of various samples subjected to accelerated carbonation until an age of 28 days according to one embodiment disclosed herein.

[0066] FIG. 26 shows the compressive strength of samples subjected to accelerated carbonation until an age of 28 days according to one embodiment disclosed herein.

[0067] FIG. 27 shows the XRD patterns of various samples at an age of 14 days that have undergone accelerated carbonation according to one embodiment disclosed herein.

[0068] FIG. 28 shows the mass loss and heat flow of all samples at an age of 14 days that have undergone accelerated carbonation according to one embodiment disclosed herein.

[0069] FIG. 29 shows the attenuated total reflectance-FTIR (ATR-FTIR) spectra of various samples at the age of 14 days under accelerated carbonation according to one embodiment disclosed herein.

[0070] FIG. 30a shows a SEM image of H₂O sample at the age of 14 days under accelerated carbonation according to one embodiment disclosed herein. The scale bar represents 1 μm .

[0071] FIG. 30b shows a SEM image of H₂Ot60d1 sample at the age of 14 days under accelerated carbonation according to one embodiment disclosed herein. The scale bar represents 1 μm .

[0072] FIG. 30c shows a SEM image of H₂Ot60d2 sample at the age of 14 days under accelerated carbonation according to one embodiment disclosed herein. The scale bar represents 1 μm .

[0073] FIG. 31a shows a SEM image of HA sample at the age of 14 days under accelerated carbonation according to one embodiment disclosed herein. The scale bar represents 1 μm .

[0074] FIG. 31b shows a SEM image of HAt60d1 sample at the age of 14 days under accelerated carbonation according to one embodiment disclosed herein. The scale bar represents 1 μm .

[0075] FIG. 31c shows a SEM image of HAt60d2 sample at the age of 14 days under accelerated carbonation according to one embodiment disclosed herein. The scale bar represents 1 μm .

Detailed Description

[0076] The following detailed description refers to the accompanying drawings that show, by way of illustration, specific details and embodiments in which the invention may be practised.

[0077] Features that are described in the context of an embodiment may correspondingly be applicable to the same or similar features in the other embodiments. Features that are described in the context of an embodiment may correspondingly be applicable to the other embodiments, even if not explicitly described in these other embodiments. Furthermore, additions and/or combinations and/or alternatives as described for a feature in the context of an embodiment may correspondingly be applicable to the same or similar feature in the other embodiments.

[0078] The present disclosure relates to a method of producing a hydrated magnesium carbonate (HMC) based cement composite. The present disclosure also relates to the hydrated magnesium carbonate based cement composite. The hydrated magnesium carbonate based cement composite may be derived from a magnesium oxide based cement (e.g. RMC).

[0079] The method advantageously utilizes RMC and a hydration agent, and hydrated magnesium carbonate seed particles, to produce the hydrated magnesium carbonate based cement composite. The hydration agent and seed particles provide two additional means for forming hydrated magnesium carbonate based cement composite. As discussed below, the hydration agent can increase the formation of

magnesium hydroxide. This magnesium hydroxide may undergo carbonation to form the hydrated magnesium carbonate based cement composite. As for the seed particles, they serve as nucleation sites for magnesium hydroxide to grow, which can then undergo carbonation to form the hydrated magnesium carbonate based cement composite. Hence, besides forming hydrated magnesium carbonate based cement from RMC, the hydration agent and seed particles lead to more hydrated magnesium carbonate based cement formed.

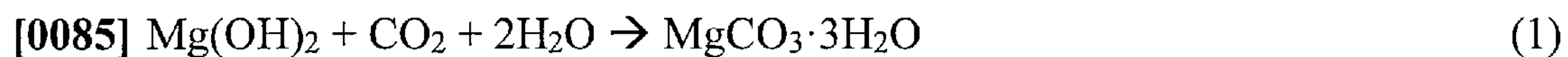
[0080] The hydration agent forms a magnesium ion complex with the magnesium that dissolves from the RMC. This complex migrates away from the original RMC grains so that when the complex converts to magnesium hydroxide, it does not precipitate on the RMC. Otherwise, the magnesium hydroxide may precipitate on the original RMC grains and this prevents further hydration of the original RMC grains. When magnesium hydroxide precipitates on the original RMC grains, it also prevents further carbonation to form the present hydrated magnesium carbonate cement based composite. This, however, is mitigated with the use of hydration agent since it forms a complex that converts to magnesium hydroxide away from the original RMC grains.

[0081] The use of hydrated magnesium carbonate seed particles serves to increase the available contact area for hydration and subsequent carbonation. The seed particles are disposed homogeneously in an aqueous solution during preparation. This advantageously enables their thorough dispersion in the pores of the original RMC, avoiding accumulation and/or agglomeration of seed particles on the original RMC. The seed particles then serve as nucleation sites for formation of magnesium hydroxide within the pores and away from the original RMC grains. This not only mitigates precipitation of magnesium hydroxide on the original RMC grains but also provides additional magnesium hydroxide available for carbonation to form the hydrated magnesium carbonate cement composite. As the pores are also utilized, the resultant cement composite attains a denser structure, which in turn translates to improved compressive strength.

[0082] Hence, the use of hydration agent and hydrated magnesium carbonate seed particles helps to form an improved hydrated magnesium carbonate cement composite. Further details of the specific mechanism are discussed below.

[0083] Overcoming the limitations associated with the low dissolution of MgO and the subsequent hydration and carbonation reactions not only increases formation of HMCs but also improves the mechanical performance of RMC based concrete formulations. As mentioned above, the present method overcomes the limitations via
 5 (i) the use of a hydration agent (HA) to improve the dissolution of MgO and increase the amount of $\text{Mg}(\text{OH})_{2(\text{aq},\text{s})}$ available for carbonation and (ii) the provision of additional nucleation sites dispersed into the pore spaces of the starting cement material to facilitate continuous hydration and carbonation by increasing the surface area for the nucleation and growth of carbonate phases away from the unhydrated
 10 MgO and uncarbonated $\text{Mg}(\text{OH})_2$.

[0084] Referring to carbonation of RMC, it involves the absorption and permanent storage of CO_2 in the form of stable carbonates. In such systems, the hydration of MgO to form brucite (magnesium hydroxide, $\text{Mg}(\text{OH})_2$) is followed by its reaction with CO_2 to form hydrated magnesium carbonates (HMCs). Non-limiting examples of
 15 HMCs are nesquehonite ($\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$), hydromagnesite ($(\text{MgCO}_3)_4 \cdot \text{Mg}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$) and dypingite ($(\text{MgCO}_3)_4 \cdot \text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$). Their formation is shown in equations 1 to 3 below.

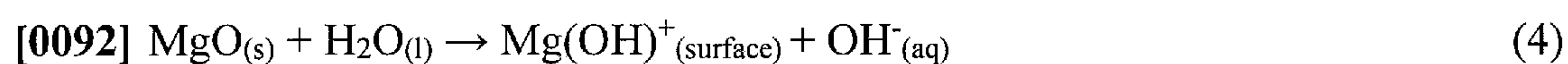


[0088] Carbonation is a critical process for RMC-based mixes as they harden and gain strength to form HMCs. Strength development of RMC formulations subjected to carbonation is related to (i) the increase in density as carbonation is an expansive process that reduces the overall pore volume (i.e. the formation of HMCs causes a
 25 significant expansion and increases the solid volume) and (ii) microstructure evolution as the morphology and binding strength of the carbonate crystals contribute to the network structure.

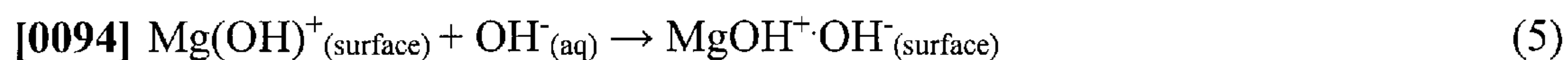
[0089] In carbonated RMC systems, the carbonation reaction is preceded by the hydration process, in which MgO is converted into brucite. Hence, the amount of
 30 brucite available to react with the diffused CO_2 affects the formation of strength providing HMCs. The hydration mechanism of MgO is based on the dissolution and precipitation processes shown in equations 4 to 7 below.

[0090] The degree of MgO conversion to brucite under ambient conditions is undesirably low and limited to 40% to 80%, hindering the subsequent formation of carbonation products. The conversion (i.e. progress of hydration) is further slowed down when subjected to carbonation because, apart from the slow dissolution of MgO, the hydration and carbonation products precipitate on the surface of MgO particles, thereby preventing the hydration and carbonation reactions from developing further.

[0091] MgO (alkaline oxide) plays an electron donator role in water:



10 [0093] OH^- anions are adsorbed on the positively charged surface:



[0095] OH^- anions are desorbed from the surface, releasing Mg^{2+} and OH^- ions into the solution:



15 [0097] Ion concentration reaches supersaturation, at which the hydroxide starts to precipitate as brucite on the oxide surface:



[0099] The improvement of hydration of RMC mixes is critical as it translates into a higher carbonation (i.e. CO_2 sequestration) degree and better mechanical performance with lower environmental impact. The improvement in all three aspects (i.e. reaction degrees, mechanical performance and sustainability) can be achieved through the use of (i) a hydration agent (HA) to increase the available $\text{Mg}(\text{OH})_2$ for the subsequent carbonation process and (ii) seeding to accelerate the nucleation and formation of HMCs in the pore spaces away from the MgO grains to facilitate further hydration and carbonation, as mentioned above.

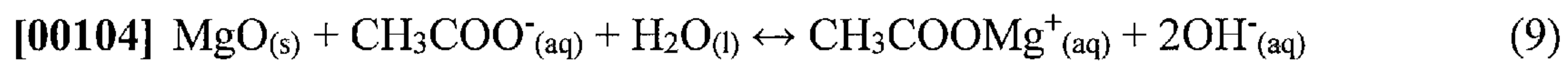
[00100] In some examples, magnesium acetate ($(\text{CH}_3\text{COO})_2\text{Mg}$), an effective HA, was used. $(\text{CH}_3\text{COO})_2\text{Mg}$ solution, with high pH, provides a higher potential to absorb and dissolve CO_2 compared to other hydration agents, such as MgCl_2 and HCl . In some examples, hydrochloric acid or magnesium chloride is used as the hydration agent. In cases where hydrochloric acid is used, it increases the amount of H^+ , which enhances the solubility of MgO and precipitation of $\text{Mg}(\text{OH})_2$ via the following steps: (a) diffusion of H^+ ions through the liquid film at the liquid-solid interface on the

surface of MgO solid particles, (b) surface chemical reaction between MgO and H^+ as depicted by $MgO_{(s)} + 2H^+_{(aq)} \rightarrow Mg^{2+}_{(aq)} + H_2O_{(l)}$, (c) diffusion of liquid products from the interface through the film to the bulk liquid, and (d) precipitation of $Mg(OH)_2$ away from the original MgO particles. The hydration of MgO in the presence of a hydration agent (e.g. $(CH_3COO)_2Mg$) occurs in a similar mechanism, and proceeds as shown in equations 8 to 11 below. The complex magnesia-acetate ions (CH_3COOMg^+) migrate away from their original particles to enable precipitation of $Mg(OH)_2$ within the bulk solution and provide for more contact surface between H_2O and unhydrated MgO for continuous dissolution of the latter. This mechanism increases the space available for the continuous hydration of MgO. Moreover, the Mg^{2+} dissociated from equation 10 enhances the precipitation of brucite, as shown in equation 11. The increased formation of brucite in the bulk system increases the amount of material available for carbonation.

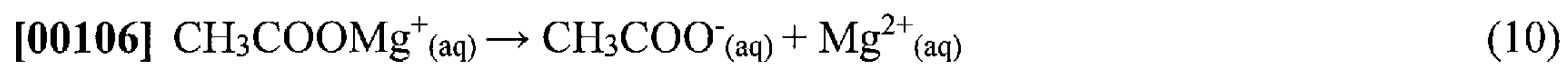
[00101] Dissociation of magnesium acetate:



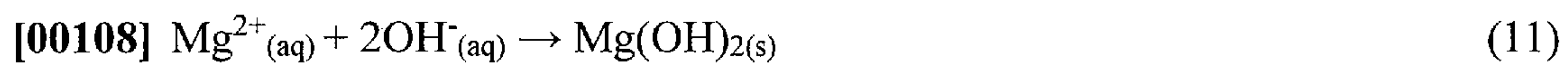
[00103] Dissolution of magnesia:



[00105] Dissociation of magnesium complexes:



20 [00107] Precipitation of magnesium hydroxide due to supersaturation:



[00109] In addition to the HAs, the addition of nucleation sites through the introduction of seed particles in the pore space enables the nucleation of brucite away from the original MgO grains. This dispersed formation of brucite into the pore spaces increases the contact surface of brucite with CO_2 to accelerate the carbonation process. This leads to an increase in the amount of carbonate phases that fill in the initially available pore space. The significant reduction in the porosity associated with these reactions as well as the strong binding network established by the dense formation of HMCs significantly improves the mechanical performance of carbonated RMC formulations.

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[00110] Having outlined various advantages of the present method and the present hydrated magnesium carbonate based cement composite, definitions of certain terms are first discussed before going into details of the various embodiments.

[00111] The word “substantially” does not exclude “completely” e.g. a composition which is “substantially free” from Y may be completely free from Y. Where necessary, the word “substantially” may be omitted from the definition of the invention.

[00112] In the context of various embodiments, the articles “a”, “an” and “the” as used with regard to a feature or element include a reference to one or more of the features or elements.

[00113] In the context of various embodiments, the term “about” or “approximately” as applied to a numeric value encompasses the exact value and a reasonable variance.

[00114] As used herein, the term “and/or” includes any and all combinations of one or more of the associated listed items.

[00115] As used herein, the phrase of the form of “at least one of A and B” may include A or B or both A and B. Correspondingly, the phrase of the form of “at least one of A and B and C”, or including further listed items, may include any and all combinations of one or more of the associated listed items.

[00116] Unless specified otherwise, the terms "comprising" and "comprise", and grammatical variants thereof, are intended to represent "open" or "inclusive" language such that they include recited elements but also permit inclusion of additional, unrecited elements.

[00117] Details of the various embodiments are now described below.

[00118] In the present disclosure, there is provided for a method of producing a hydrated magnesium carbonate based cement composite, the method comprising: providing an aqueous solution comprising a hydration agent and hydrated magnesium carbonate seed particles; contacting the aqueous solution with a magnesium oxide based cement to form magnesium hydroxide from the hydration agent and the magnesium oxide based cement, and on the hydrated magnesium carbonate seed particles; and exposing the magnesium hydroxide to carbon dioxide to form the hydrated magnesium carbonate based cement composite.

[00119] In various embodiments, providing the aqueous solution may comprise mixing the hydration agent with water before adding the hydrated magnesium carbonate seed particles. Adding the hydrated magnesium carbonate seed particles to the aqueous solution comprising the hydration agent allows for better distribution of the seed particles in the aqueous solution. The aqueous solution containing the hydration agent may be continuously stirred while adding the seed particles. The stirring may continue after the seed particles are added. According to various embodiments, providing the aqueous solution may therefore comprise stirring the aqueous solution in presence of the hydrated magnesium carbonate seed particles to disperse the hydrated magnesium carbonate seed particles throughout the aqueous solution. Such a step prevents accumulation and/or agglomeration of seed particles on the magnesium oxide based cement when the aqueous solution is contacted with the magnesium oxide based cement. Without a proper dispersion procedure, the accumulation and/or agglomeration that occurs inhibits the hydration and carbonation of MgO, even if a higher amount of seed particles is used (e.g. 20 wt% to 50 wt%), and this results in lower compressive strength. Hence, a proper dispersion of seeds particles helps to enhance formation of the hydrated magnesium carbonate phases and increase compressive strength. This, accordingly, sets out a procedure for better dispersion of the seed particles, and hydration of RMC is improved by adding the hydration agent.

[00120] In various embodiments, providing the aqueous solution may comprise mixing the hydration agent with water to form a concentration ranging from more than 0 M to 0.1 M. This means that the concentration of hydration agent is more than 0 M and at most 0.1 M. The hydration agent may have a concentration of 0.05 M according to some embodiments.

[00121] The hydration agent, in various embodiments, may comprise or consist of hydrochloric acid, magnesium acetate and/or magnesium chloride.

[00122] In the present method, providing the aqueous solution may comprise adding the hydrated magnesium carbonate seed particles in an amount ranging from more than 0 wt% to 1 wt%, wherein the wt% is based on the magnesium oxide based cement and the hydrated magnesium carbonate seed particles. This means that the seed particles constitute an amount more than 0 wt% but at most 1 wt%. The hydrated

magnesium carbonate seed particles may also be added in an amount ranging from more than 0 wt% to 0.5 wt% or 0.5 wt% to 1 wt%. The addition of more than 1 wt% of seed particles may reduce compressive strength. If an improper amount of seed particles is added, and the seed particles are not mixed uniformly in the aqueous solution, the compressive strength of the resultant cement may not improve or even adversely affected. The hydrated magnesium carbonate seed particles may, for example, comprise or consist of $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$, $\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 3\text{H}_2\text{O}$, $(\text{MgCO}_3)_4 \cdot \text{Mg}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ and/or $(\text{MgCO}_3)_4 \cdot \text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$.

[00123] Once the hydration agent and the seed particles are prepared in the form of an aqueous solution, they may be contacted with the magnesium oxide based cement. The magnesium oxide based cement may comprise or consist of magnesium oxide. The magnesium oxide based cement may comprise of magnesium oxide grains or crystals. The magnesium oxide based cement may be porous i.e. comprise a plurality of pores. Contacting the aqueous solution containing the hydration agent with the magnesium oxide based cement allows for reaction between the hydration agent and magnesium oxide to form magnesium hydroxide.

[00124] In various embodiments, contacting the aqueous solution with the magnesium oxide based cement may comprise contacting the hydration agent with the magnesium oxide based cement at a mass ratio from 0.55:1 to 0.7:1. The mass ratio may be any value from this range, for example, 0.55:1, 0.6:1 or 0.7:1. Such ratios can provide suitable concrete workability and high strength.

[00125] In various embodiments, contacting the aqueous solution with the magnesium oxide based cement may comprise disposing the hydrated magnesium carbonate seed particles within a plurality of pores of the magnesium oxide based cement. This means that the seed particles are dispersed in pore spaces within the magnesium oxide based cement but away from the grains (i.e. bulk) of the magnesium oxide based cement. Accordingly, when the magnesium oxide forms on the seed particles via nucleation and growth, the magnesium hydroxide would also be disposed within the plurality of pores and away from the bulk of the magnesium oxide based cement. According to various embodiments, the magnesium hydroxide formed on the hydrated magnesium carbonate seed particles is disposed within the plurality of pores and away from the magnesium oxide based cement. For the seed particles to be

distributed evenly in the magnesium oxide based cement, the preparation of the aqueous solution after adding the seed particles should involve stirring to obtain a homogeneous solution so that when the aqueous solution is contacted with the magnesium oxide based cement, it is distributed evenly throughout the magnesium oxide based cement.

[00126] After magnesium hydroxide is formed (i) from the reaction between the hydration agent and the magnesium oxide based cement, and (ii) on the seed particles, the magnesium hydroxide may be subjected to carbonation curing. The expression “carbonation” and “carbonation curing” are used interchangeably in the present disclosure.

[00127] In various embodiments, the carbonation may be carried out by exposing the magnesium hydroxide to carbon dioxide. This may comprise subjecting the magnesium hydroxide to 0.04 vol% to 10 vol% carbon dioxide at 25°C to 35°C and a relative humidity of 75% to 85% for 24 hours or more. The amount of carbon dioxide may be 0.04 vol% or 10 vol% according to some embodiments. The carbonation duration may be, for example, up to 1, up to 2, up to 3, up to 5, up to 7, up to 14, or up to 28 days according to various embodiments. In some embodiments, the carbonation may be carried out by subjecting the magnesium hydroxide to 0.04 vol% carbon dioxide at 60°C and a relative humidity of 75% to 85% for 1 to 2 days. As used herein, the term “ambient” when used in the context of CO₂ refers to 0.04 vol% of CO₂. The addition of more than 10 vol% of CO₂ may lead to cracks arising from expansion of the HMC at early stages of carbonation.

[00128] In other embodiments, a multi-step carbonation may be carried out. For such embodiments, exposing the magnesium hydroxide to carbon dioxide may first comprise subjecting the magnesium hydroxide to 0.04 vol% carbon dioxide at 60°C and a relative humidity of 75% to 85% for 1 to 2 days, 1 day or 2 days. Subsequently, the magnesium hydroxide may be subjected to 10 vol% carbon dioxide at 30°C and a relative humidity of 75% to 85% for a total carbon dioxide exposure period not exceeding 28 days. This means that the total carbonation duration for a multi-step carbonation may be 28 days or less. In this regard, for the multi-step carbonation embodiments, the present method may further comprise subjecting the magnesium

hydroxide to 10 vol% carbon dioxide at 30°C and a relative humidity of 75% to 85% for a total carbon dioxide exposure period not exceeding 28 days.

[00129] The present disclosure also provides for a hydrated magnesium carbonate based cement composite obtainable or obtained by the method as described above.

5 The hydrated magnesium carbonate based cement composite may comprise hydrated magnesium carbonate formed from a magnesium oxide based cement and hydrated magnesium carbonate seed particles, wherein the hydrated magnesium carbonate seed particles used may comprise an amount of up to 1 wt% of the magnesium oxide based cement and the hydrated magnesium carbonate seed particles. In other words, the
10 hydrated magnesium carbonate may comprise or consist of seed particles in the range of more than 0 wt% and up to 1 wt%, including 1 wt%. The magnesium oxide based cement may comprise RMC. The present disclosure further provides for a hydrated magnesium carbonate based cement composite comprising hydrated magnesium carbonate formed on the surface of one or more hydrated magnesium carbonate seed
15 particles.

[00130] Various embodiments of the present method, and advantages associated with various embodiments of the present method, as described above, may be applicable to the present hydrated magnesium carbonate based cement composite, and vice versa.

[00131] In various embodiments, the hydrated magnesium carbonate based cement
20 composite may comprise a plurality of pores. The hydrated magnesium carbonate seed particles may be disposed in the plurality of pores, within the hydrated magnesium carbonate based cement composite. Each of the pores in the resultant hydrated magnesium carbonate based cement has a pore size that is less than the starting magnesium oxide based cement material (RMC) because the seed particles
25 are added, which increase the density of the resultant cement composite as explained above.

[00132] In various embodiments, some of the hydrated magnesium carbonate may comprise an elongated shape. Such hydrated magnesium carbonate may be formed on the seed particles. In some embodiments, the hydrated magnesium carbonate may be
30 formed as particles comprising an elongated shape, and wherein the particles are disposed on the hydrated magnesium carbonate seed particles.

[00133] In various embodiments, each of the hydrated magnesium carbonate seed particles may comprise a diameter of 1 μm to 7 μm .

[00134] In various embodiments, the hydrated magnesium carbonate based cement composite may further comprise hydrated magnesium carbonate formed as a layered structure or a plated structure.

[00135] In various embodiments, the hydrated magnesium carbonate may comprise $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$, $\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 3\text{H}_2\text{O}$, $(\text{MgCO}_3)_4 \cdot \text{Mg}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ or $(\text{MgCO}_3)_4 \cdot \text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$. As for the hydrated magnesium carbonate seed particles, they may comprise $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$, $\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 3\text{H}_2\text{O}$, $(\text{MgCO}_3)_4 \cdot \text{Mg}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ or $(\text{MgCO}_3)_4 \cdot \text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$.

[00136] In summary, the improvements of the present method and hydrated magnesium carbonate based cement composite include (a) the thorough dispersion of seed particles within the cement's pore structure, (b) the use of an amount of seed particles that does not lead to accumulation and/or agglomeration while serving as nucleation sites for enhanced carbonation, (c) the improvement of MgO hydration via the use of HA, and (d) the improvement in hydration and carbonation of RMC which enhances strength of the cement composite by using HA and seed particles. In contrast, the use of poorly dispersed and/or undispersed seed particles, in an inappropriate amount (e.g. more than 20 wt%), unlikely provides the above improvement(s).

[00137] While the methods described above are illustrated and described as a series of steps or events, it will be appreciated that any ordering of such steps or events are not to be interpreted in a limiting sense. For example, some steps may occur in different orders and/or concurrently with other steps or events apart from those illustrated and/or described herein. In addition, not all illustrated steps may be required to implement one or more aspects or embodiments described herein. Also, one or more of the steps depicted herein may be carried out in one or more separate acts and/or phases.

Examples

[00138] The present disclosure provides for an efficient method that enables the significant improvement of formation of both hydrate and carbonate phases from

reactive magnesium oxide (MgO) cement (RMC) via enhancement of the hydration process and increasing the contact surface area between $\text{Mg}(\text{OH})_2$ and CO_2 . These facilitate denser microstructural development and higher strength gain for the resultant cement composite. The method also advantageously reduces the overall curing time and has a positive environmental impact from producing the resultant cement composite.

[00139] The hydration process is enhanced by the use of a hydration agent (HA), which significantly enhances dissolution of MgO and formation of brucite ($\text{Mg}(\text{OH})_2$). This is further supported with the use of seeds (i.e. the seed particles) that stimulates nucleation of brucite in the pore spaces, thereby increasing the amount (i.e. surface area) of brucite available for carbonation. These enhancements not only increase the amount of CO_2 sequestered within the present cement composite and therefore lower their overall environmental impact, but also lead to the production of dense cement composites with high strengths. The use of HA and seeding with RMC also lowers overall cost of the resultant cement composite by (1) reducing the amount of RMC required to achieve a certain strength, that is comparable or better than, conventional cement composite such as PC, (2) reducing the curing time as there are more dissolved RMC reacting with CO_2 to form higher content of hydrated magnesium carbonates, and (3) reducing the dependency on natural resources via the use of MgO from waste materials and industrial by-products to form the present cement composite.

[00140] Examples of the present method, and the present hydrated magnesium carbonate based cement composite, are described below. The examples demonstrate the use of a HA, and seeding, to enhance the hydration, subsequent carbonation and performance of the resultant cement composite. The examples demonstrate that the HA improves hydration of MgO. Non-limiting examples of the HA include, but not limited to, magnesium acetate, magnesium chloride and hydrochloric acid. The seeding particles for (1) providing additional nucleation sites that improve formation and growth of carbonate phases, and (2) improving availability of $\text{Mg}(\text{OH})_2$ for subsequent carbonation reaction include, without being limited to, various hydrated magnesium carbonates such as hydromagnesite ($(\text{MgCO}_3)_4 \cdot \text{Mg}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$), nesquehonite ($\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$) and other hydrated magnesium carbonates. As an

example of hydrated magnesium carbonate, FIG. 1 shows the microstructure of hydromagnesite seeds. FIG. 1 illustrates the round ball-like shape of the hydromagnesite seeds, each having a diameter of about 1 μm to 7 μm and composed of about 0.5 μm diameter disks (i.e. multiple disk-like hydromagnesites accumulate to form seeds having the ball-like shape). Saturated surface dry (SSD) gravel with a particle size of 4.74 mm to 9.5 mm can be used to form the coarse aggregate for a resultant concrete mix.

[00141] Example 1: Materials

[00142] The main cement binder used for various examples herein was RMC (commercial name “calcined magnesite 92/200”) obtained from Richard Baker Harrison (UK), that was produced at around 1000°C. The chemical and physical properties of RMC are shown in table 1 below.

[00143] Table 1 - Chemical Composition and Physical Properties of RMC

Chemical Composition (wt%)							Physical Properties	
MgO	SiO ₂	CaO	*R ₂ O ₃	K ₂ O	Na ₂ O	Loss on Ignition	Specific gravity (g/cm ³)	Specific surface area (m ² /g)
>91.5	2.0	1.6	1.0	-	-	4.0	3.0	16.3

*R₂O₃: Fe₂O₃ and Al₂O₃

[00144] The reactivity of RMC (i.e. measured by the time required for neutralization of 0.25 M of acetic acid by 5 grams of RMC) was recorded as 520 seconds. Magnesium acetate ((CH₃COO)₂Mg) obtained from VWR (Singapore) was used as the HA at a concentration of 0.05 M to promote the hydration process. Hydromagnesite seeds obtained from Fisher Scientific (UK) with a specific surface area of 43.5 m²/g were used to provide additional nucleation sites and to stimulate the nucleation and growth of HMCs in the pore space. FIG. 1 shows the microstructure of hydromagnesite seeds, which are spherical agglomerations as described above. Saturated surface dry (SSD) gravel with a particle size of 4.7 mm to 9.5 mm was used as the aggregates in the prepared concrete samples.

[00145] Example 2a: General Embodiment of Present Method

[00146] The present method was started with the preparation of a solution by dissolving a pre-determined amount of HA in water (e.g. concentration of 0 M to 0.1

M), followed by introduction of seeds (e.g. 0 weight percent (wt%) to 2 wt% of the magnesium oxide based cement and seeds) in the solution. The dispersion of seeds in the solution was enabled via use of a magnetic stirrer for 5 minutes at ambient temperatures (e.g. $30 \pm 3^\circ\text{C}$). The stirring of seeds in the solution enables homogenous dispersion within the pores of the RMC when subsequently added to the RMC. The thoroughly mixed solution can then be introduced into RMC to form a paste. This may be followed by, in some instances, the addition of coarse aggregates to the paste to finalize the production of the concrete mix. The cast samples were then consolidated and subjected to carbonation.

[00147] Example 2b: General Characterization

[00148] Isothermal calorimetry characterization was carried out for samples in the various examples below. The heat flow due to the hydration of each mixture was studied at 30°C by an I-Cal 8000 High Precision Calorimeter in accordance with ASTM C1702-15a. The preparation of pastes involved dispersion of seeds in H_2O or HA, which was previously heated to 30°C in order to produce samples at the same temperature as the measurement temperature. The seeded solution was then mixed with RMC. After around 15 seconds to 20 seconds of mixing, the prepared pastes were placed into the isothermal calorimeter channel to measure the heat of hydration.

[00149] For the water absorption test, each sample was measured after 14 and 28 days of carbonation. The initial mass of samples was recorded before they were immersed in a water tank. Their absorption mass was also measured when they reached a constant mass under water, which reflected their water absorption capacity. Water absorption (W_{ab}) was calculated as a percentage of the initial mass as shown in the equation below, where m_{ab} is the absorption mass of samples after reaching a constant mass when immersed in water and m_i is the initial mass.

$$W_{\text{ab}} = (m_{\text{ab}} - m_i)/m_i (\%)$$

[00150] The compressive strength of samples was measured by uni-axial loading in triplicates at 3, 7, 14 and 28 days. The equipment used was a Toni Technik Baustoffprüfsysteme machine, operated at a loading rate of 55 kN/min.

[00151] Samples extracted from the cubes crushed during strength testing were stored in acetone for at least 7 days to stop hydration, followed by vacuum drying for another 7 days in preparation for XRD, TGA, SEM and back-scattered electron (BSE)

analyses. The vacuum dried samples were ground down to pass through a 75 μm sieve before they were analyzed via XRD and TGA.

[00152] XRD was recorded on a Philips PW 1800 spectrometer using $\text{Cu K}\alpha$ radiation (40 kV, 30 mA) with a scanning rate of $0.04^\circ 2\theta/\text{step}$ from 5 to $80^\circ 2\theta$. The Reference Intensity Ratio (RIR) technique, which provides a comparison of the integrated intensity of a phase of interest (i.e. unhydrated MgO or uncarbonated $\text{Mg}(\text{OH})_2$) to that of a standard phase introduced in the sample in a known proportion, was applied for quantitative analysis of the phases present after the carbonation process. The internal standard used for quantification purposes was fluorite (CaF_2) included at 5 wt%. The RIR of the phases of interest was obtained by dividing the integrated intensity of the strongest line of each phase with that of the standard. As most HMC phases that form in carbonated RMC systems have overlapping peaks, their direct quantification presents a challenge. Therefore, the extent of hydration and carbonation within RMC samples can be calculated backwards by using the amounts of residual (i.e. unhydrated/uncarbonated) MgO and $\text{Mg}(\text{OH})_2$. Calibration curves for MgO and $\text{Mg}(\text{OH})_2$, the two main components used for quantitative analysis, are straight lines through the origin i.e. $y=kx$, where x is the RIR of the phase analyzed and y is the weight fraction of the component investigated. The value of k is 0.2886 for MgO and 0.3651 for $\text{Mg}(\text{OH})_2$.

[00153] TGA was conducted on a Perkin Elmer TGA 4000 equipment from 50 to 950°C with a heating rate of $10^\circ\text{C}/\text{min}$ under nitrogen flow. SEM was carried out with a Zeiss Evo 50 microscope to investigate morphologies of the hydration and carbonation products within the samples. The vacuum dried samples were mounted onto aluminum stubs using double-sided adhesive carbon disks and coated with gold before SEM analysis. Along with SEM, BSE images were used to provide a quantitative analysis of the hydration and carbonation products. In preparation for BSE, the vacuum dried samples were mounted in epoxy resin for 24 hours and then ground and polished to obtain smooth surfaces. Sand paper was used prior to final polishing by diamond slurry with sizes of 9, 3 and $0.3 \mu\text{m}$. Dust and diamond particles generated during the polishing process were removed by exposing the samples to an ultrasonic bath for 10 minutes, which was followed by 24 hours in vacuum and coating with gold prior to analysis.

[00154] Example 3a: Example of the Present Method and Hydrated Magnesium Carbonated Cement Composite for Investigation of CO₂ Sequestration

[00155] Unless specified otherwise, the materials used in this example have been described in example 1. Ordinary PC obtained from Lafarge cement Pte. Ltd. (Singapore) was used in the preparation of the PC-based control sample. Magnesium acetate (MA), magnesium chloride (MC) and hydrochloric acid (HC) obtained from VWR (Singapore) were used as HAs to improve the hydration of MgO. Saturated surface dry (SS) gravel with a particle size of 4.74 mm to 9.5 mm was used to form the aggregate profile in the prepared samples. The method used in this example is described below. Table 2 below shows the composition of the RMC and PC used.

[00156] Table 2 – Chemical Composition and Physical Properties of MgO and PC

Type	Chemical Composition (wt%)							Physical Properties	
	MgO	SiO ₂	CaO	*R ₂ O ₃	K ₂ O	Na ₂ O	Loss on Ignition	Specific gravity (g/cm ³)	Specific surface area (m ² /g)
RMC	> 91.5	2.0	1.6	1.0	-	-	4.0	3.0	16.3
PC	0.92	20.89	66.20	9.96	0.49	0.08	1.14	3.14	-

*R₂O₃: Fe₂O₃ and Al₂O₃

[00157] Before the casting of samples, the hydration mechanism of each sample was studied individually by preparing corresponding paste compositions containing different types (MA, MC and HC) and concentrations (0, 0.05 and 0.1 M) of HA. Water or HA solutions were mixed with MgO cement at a mass ratio of 0.6 to form pastes. This was followed with the preparation and analysis of samples with 7 different compositions involving MgO and 1 involving PC for comparison. The cement/aggregate ratio was kept constant at 0.67 for all samples. The compositions of the samples are listed in table 3.

[00158] Table 3 – Composition of Samples

Sample Number	Sample	Cement Type	HA Solution	
			Type	Concentration (M)
1	PC.H ₂ O	PC	H ₂ O	-
2	MgO.H ₂ O	MgO		-
3	MgO.HC0.05	MgO	HCl	0.05

4	MgO.HC0.1	MgO		0.1
5	MgO.MC0.05	MgO	MgCl ₂	0.05
6	MgO.MC0.1	MgO		0.1
7	MgO.MA0.05	MgO	(CH ₃ COO) ₂ Mg	0.05
8	MgO.MA0.1	MgO		0.1

[00159] 50×50×50 mm cubic specimens were cast for the determination of water absorption and compressive strength. Specimens were consolidated by using a vibrating table and trowel finished, after which they were kept in respective curing environments for 24 hours until de-moulding. The de-moulded samples were subjected to two curing environments for up to 28 days until testing: (i) ambient carbonation (28±2°C, 80±5% relative humidity, ambient carbon dioxide at 0.04 vol% CO₂) and (ii) accelerated carbonation (30°C, 80±5% relative humidity, 10 vol% CO₂) curing.

[00160] Example 3b: Characterization of the Samples of Example 3a

[00161] The samples were characterized in a similar manner as example 2b. Fourier-transform infrared spectroscopy (FTIR) characterization was carried out in this example. FTIR spectra of the samples were obtained by a Perkin Elmer FTIR Spectrometer Spectrum GX. Spectra were recorded in transmittance mode from 2400 to 400 cm⁻¹ at a resolution of 1 cm⁻¹.

[00162] In addition, the hydration degree was characterized based on the procedures as follows.

[00163] The hydration degree of MgO with and without HAs was evaluated by TGA. Before the analysis, MgO pastes were stored in acetone for at least 3 days to quench hydration and dried in a vacuum for at least 7 days to remove any remaining moisture. They were then ground to pass through a 75 µm sieve in preparation for TGA test, which was conducted on a Perkin Elmer TGA 4000 equipment. The samples were heated from 50 to 600°C with a heating rate of 10°C/min under nitrogen flow. The weight loss L (%) corresponding to the dehydration of brucite was used to calculate the hydration degree (HD) of MgO as shown in the equation below, where C is the actual MgO content in the cement component (%). 40 and 18 are the molecular weights of MgO and H₂O, respectively.

[00164] $HD = [L \times (40/18)] / [(1-0.01L) \times C] (\%)$

[00165] **Example 3c: Isothermal Calorimetry Results for Samples of Example 3a**

[00166] FIG. 16a and FIG. 16b show the heat flow and the cumulative heat of pastes over 72 hours of hydration, respectively. As seen in FIG. 16a, the dissolution occurred a few minutes after mixing for all samples. The dissolution of the control sample (MgO.H₂O) indicated the lowest heat flow, while this process was much more rapid for samples involving HAs. The significantly higher and sharper exothermic peaks of HA samples when compared to the control sample confirmed the role of HAs in enhancing the hydration of MgO. The cumulative heat curves in FIG. 16b clearly indicated a higher degree of hydration achieved by all the HA samples, whereas the control sample revealed the lowest heat. The degree of hydration increased with the concentration of HA for all samples. From the calorimetry results, MC and MA were identified as the most effective HAs. Samples containing MC outperformed those with MA at both concentrations (0.05 and 0.1 M) with their higher cumulative heat values at earlier stages. However, samples containing MA resulted in similar cumulative heat values as MC samples at the end of the analysis, indicating a steady progress of hydration.

[00167] **Example 3d: Hydration Degree Results for Samples of Example 3a**

[00168] Table 4 below shows the hydration degree of MgO in water and HA solutions at 3 and 14 days under sealed conditions (i.e. to prevent carbonation).

[00169] Table 4 – Hydration Degree of MgO Samples at 3 and 14 Days

Sample	3 Days (%)	14 Days (%)
MgO.H ₂ O	48.83	67.90
MgO.HC0.05	52.45	71.72
MgO.HC0.1	59.24	78.05
MgO.MC0.05	56.89	87.11
MgO.MC0.1	75.02	87.96
MgO.MA0.05	61.67	88.83
MgO.MA0.1	75.31	88.24

[00170] The results are consistent with the isothermal calorimetry results. The use of HAs resulted in an obvious increase in the hydration degree of MgO at all durations.

The concentration of HAs played an important role at earlier stages (3 days), during which the hydration degree increased with HA concentration. The effect of HA concentration was less obvious at 14 days. MC and MA were identified as the most effective HAs in terms of their contribution to the improvement of the hydration process. When compared to the control sample, whose hydration degree was limited to about 49%, the use of MC and MA enhanced the hydration process and increased the hydration degree to about 75% at the end of 3 days. A similar trend was observed at 14 days, at which the hydration degree of the control sample was increased from about 68% up to about 88% via the inclusion of HAs. Overall, the use of HAs led up to 54% and 30% increases in the hydration degree of the control sample at 3 and 14 days, respectively. This significant improvement resulted in the production of a higher amount of hydration products (brucite) readily available for carbonation.

[00171] Example 3e: Water Absorption Test Results for Samples of Example 3a

[00172] Table 5 below shows the water absorption of samples after 14 and 28 days under ambient and accelerated carbonation conditions.

[00173] Table 5 – Water Absorption of Samples After 14 and 28 Days of Curing

Sample	Ambient (wt%)		Accelerated (wt%)	
	14 Days	28 Days	14 Days	28 Days
MgO.H ₂ O	11.73	11.19	5.89	4.36
MgO.HC0.05	11.45	10.79	5.17	3.69
MgO.HC0.1	11.29	10.98	3.98	3.91
MgO.MC0.05	10.83	10.87	5.14	3.99
MgO.MC0.1	10.18	10.50	3.91	2.55
MgO.MA0.05	10.94	10.96	4.69	3.30
MgO.MA0.1	10.54	10.50	2.02	1.12

[00174] In both curing conditions, samples with HAs absorbed less water than the control sample (MgO.H₂O), which was more obvious at increased HA concentrations. This could be attributed to the higher degree of hydration within samples containing HAs, resulting in enhanced carbonation and HMC formation, which in turn led to denser microstructures. Accordingly, samples subjected to accelerated carbonation

absorbed much less water than those cured under ambient conditions. Generally, longer curing periods led to smaller amounts of water absorption.

[00175] The water absorption of the control sample was recorded as about 11.7% and 11.2% after 14 and 28 days of ambient curing, respectively. The inclusion of HAs such as MC and MA reduced the water absorption by up to about 13%, resulting in values as low as 10.2% under ambient curing. The water absorption of the control sample reduced to about 5.9% and about 4.4% after 14 and 28 days of accelerated carbonation, respectively. The inclusion of HAs at a concentration of 0.1 M led to a reduction in these values by up to about 65% and about 74% after 14 and 28 days of accelerated carbonation, respectively. The use of MA outperformed all the other HAs by resulting in water absorption values as low as about 2.0% and about 1.1% at the end of 14 and 28 days, respectively. This was due to the effective role of HAs in reducing pores available for water absorption, which was more obvious under accelerated carbonation than ambient curing. The increased amount of brucite formation attributed to the inclusion of HAs led to the dense formation of HMCs enabled by the accelerated carbonation conditions. Although all the HAs included in the designed formulations were effective in increasing the degree of hydration and lowering water absorption, samples containing MA led to better results than others, which were consistent with the hydration degree results.

[00176] **Example 3f: Compressive Strength Test Results for Samples of Example 3a**

[00177] The compressive strength of samples cured under ambient and accelerated carbonation conditions is presented in FIG. 17a and FIG. 17b, respectively. As expected, samples subjected to accelerated carbonation led to faster strength development and higher strength results than those cured under ambient conditions due to the rapid and more extensive formation of HMCs. When compared to the control sample, the inclusion of HAs led to an increase in the strength of all samples, which was much more apparent under accelerated curing conditions. As shown in FIG. 17b, the strength of all samples cured under ambient conditions slightly increased with age. The rate of strength gain was much higher for samples containing HAs than the control sample, which was in agreement with the isothermal calorimetry and hydration degree results. Samples MgO.MA0.05, MgO.MA0.1 and MgO.MC0.1

achieved strengths higher than 7 MPa at 7 days, which is the requirement for masonry blocks. Most samples containing HAs reached over 10 MPa at 28 days, while the control sample showed much smaller strengths of about 2.5 and 4.0 MPa at 7 and 28 days, respectively.

5 [00178] As seen in FIG. 17b, almost all samples containing HAs gained strengths of over 7 MPa at 3 days, at which the strength of the control sample was limited to 3 MPa. The strength generally increased as the concentration of HAs increased from 0.05 to 0.1 M. Samples MgO.HC0.05, MgO.MC0.05, and MgO.MA0.05 produced strengths up to about 60% higher than the control sample (28 MPa) at 28 days and
10 achieved 30, 34 and 44 MPa, respectively. Corresponding samples with a higher concentration of HAs, MgO.HC0.1, MgO.MC0.1, and MgO.MA0.1, reached strengths of 10, 17 and 26 MPa in only 3 days, respectively. These samples achieved strengths of up to 56 MPa in 14 days, which was 273% higher than the corresponding strength of the control sample (15 MPa). The same samples achieved strengths of up
15 to 58 MPa at 28 days, which was 107% higher than the control sample.

[00179] When the 28-day strengths were compared, samples MgO.MA0.05, MgO.HC0.1, MgO.MC0.1 and MgO.MA0.1 (39-58 MPa) outperformed the standard PC-based sample (38 MPa) prepared for comparison purposes. These results highlight that when the right type and content of HA are utilized under proper curing conditions,
20 samples containing MgO cements perform significantly better than control samples containing only MgO or PC as the main binder.

[00180] **Example 3g: XRD Test Results for Samples of Example 3a**

[00181] XRD patterns of MgO.H₂O, MgO.HC0.1, MgO.MC0.1 and MgO.MA0.1 after 14 days of curing under ambient and accelerated carbonation conditions are
25 depicted in FIG. 18a and FIG. 18b, respectively.

[00182] Amongst some minor peaks of other HMCs, peaks of nesquehonite, artinite, dypingite and hydromagnesite were observed. The intensities of these peaks increased with the presence of HAs and increased concentration of CO₂ (i.e. accelerated vs. ambient curing). In addition to HMCs, all samples indicated the presence of residual
30 MgO and brucite after both curing conditions.

[00183] Table 6 below shows the unhydrated MgO and uncarbonated brucite contents within samples after 14 days under ambient and accelerated carbonation curing.

[00184] Table 6 – MgO and Mg(OH)₂ Contents Obtained by XRD After 14 Days of Curing

Sample	Ambient (wt%)		Accelerated (wt%)	
	MgO	Mg(OH) ₂	MgO	Mg(OH) ₂
MgO.H ₂ O	34.23	56.35	31.18	42.14
MgO.HC0.1	27.05	62.61	25.16	44.16
MgO.MC0.1	20.37	67.75	18.58	55.09
MgO.MA0.1	23.34	65.66	18.00	28.65

[00185] The control sample indicated a higher unhydrated MgO content than samples containing HAs under both ambient and accelerated carbonation conditions. This finding was consistent with the hydration degree results and proved the active role of HAs in improving the conversion of MgO into Mg(OH)₂ under both curing conditions. The unhydrated MgO content of the control sample after 14 days of ambient and accelerated carbonation was around 34% and 31%, respectively. These figures were reduced to about 20% to 27% and 18% to 25% with the inclusion of HAs. Samples involving the use of MC and MA specifically outperformed all other samples, resulting in unhydrated MgO contents as low as about 20% and 18% under ambient and accelerated carbonation conditions, respectively.

[00186] The increased hydration degrees of samples containing HAs were reflected as higher brucite contents available for carbonation. Under ambient curing, carbonation was not as extensive as evident from the uncarbonated brucite contents of all mixes ranging between 56% to 66%. The higher brucite contents of samples containing HAs were due to their increased hydration degrees. A similar scenario was observed under accelerated carbonation for samples MgO.HC0.1 and MgO.MC0.1, which still indicated high brucite contents of 44% and 55% after 14 days of being subjected to 10 vol% CO₂ concentration, respectively. The main reason these results were higher than the brucite content of the control sample (about 42%) was mainly because of the increased hydration degrees of MgO.HC0.1 and MgO.MC0.1. Although these samples achieved higher hydration degrees evident by their smaller residual MgO contents than the control sample (19% to 25% vs. 31%), the conversion rate of brucite into strength providing HMCs via carbonation was relatively low.

Different from these two samples, MgO.MA0.1 outperformed all samples by revealing brucite contents as low as about 29% at the end of 14 days under accelerated carbonation. Combined with its high degree of hydration (i.e. conversion of MgO into brucite, shown by the low residual MgO content after curing), the extensive carbonation (i.e. conversion of brucite into HMCs, shown by the low residual brucite content after curing) of MgO.MA0.1 is the main reason behind its significant strength development which outperformed all other samples. Although they both achieved almost the same hydration degrees shown by their similar residual MgO contents of about 18%, samples MgO.MA0.1 and MgO.MC0.1 mainly differed by their carbonation capabilities (residual brucite contents of 29% vs. 55%). The higher carbonation of MgO.MA0.1 led to an enhanced mechanical performance, highlighting the importance of carbonation in strength development.

[00187] Example 3h: TGA Test Results for Samples of Example 3a

[00188] The TGA and heat flow data of MgO.H₂O, MgO.HC0.1, MgO.MC0.1 and MgO.MA0.1 after 14 days of curing under ambient and accelerated carbonation conditions are presented in FIG. 19a and FIG. 19b, respectively. In addition to a strong endothermic peak at about 380°C and a broader beak at about 700°C clearly visible in both figures, samples exposed to accelerated carbonation indicated two endothermic peaks at 120°C and 220°C, as seen in FIG. 19b. In addition to the weight losses associated with the decomposition of HAs that resulted in minor weight losses, the three main decomposition steps have been discussed below in example 4g, and summarized in FIG. 12b.

[00189] Table 7 below summarizes the weight loss of samples at each step along with the total weight loss.

[00190] Table 7 – Weight Loss of Samples Obtained by TGA After 14 Days of Curing

Curing Solution	Sample	Weight Loss (wt%)					
		50-300°C	300-500°C	500-900°C	Mg(OH) ₂	HMCs	Total
Ambient	MgO.H ₂ O	1.83	18.73	4.30	17.49	7.37	24.86
	MgO.HC0.1	2.47	21.33	3.45	19.43	7.82	27.25

	MgO.MC0.1	2.41	22.27	4.10	21.03	7.75	28.78
	MgO.MA0.1	3.19	21.47	4.46	20.38	8.74	29.12
Accelerated	MgO.H ₂ O	4.40	22.85	4.49	13.08	18.66	31.75
	MgO.HC0.1	10.37	27.33	4.02	13.70	28.02	41.72
	MgO.MC0.1	8.56	27.13	3.82	17.10	22.41	39.51
	MgO.MA0.1	12.28	26.05	4.00	8.89	33.44	42.33

[00191] The weight loss due to the decomposition of HMCs was calculated by subtracting the weight loss of brucite, whose content was determined by XRD analysis, from the total weight loss of samples. The findings listed in table 7 indicated that a majority of the weight loss is observed in the 300 to 500°C temperature range, which is associated with 3 main reactions attributed to the: (i) dehydroxylation of hydromagnesite and dypingite, (ii) decarbonation of nesquehonite and (iii) decomposition of uncarbonated brucite. Regardless of the curing conditions, samples containing HAs revealed higher HMC contents than the control sample. The TGA results were consistent with the strength results in general, showing an increase in the weight losses referring to the decomposition of HMCs with an increase in strength. The highest weight losses corresponding to the decomposition of HMCs were indicated by sample MgO.MA0.1, which also achieved the highest strengths of 56 and 10 MPa amongst all samples after 14 days of accelerated and ambient curing, respectively.

[00192] Although the use of MC led to higher hydration degrees than samples containing HC (i.e. 88% vs. 78%), the weight loss due to the decomposition of HMCs that formed under accelerated carbonation was much lower in MC samples when compared to HC samples (i.e. 22% vs. 28%). This was consistent with the strength and XRD results, indicating that the use of HC led to higher rates of brucite conversion into HMCs. The weight losses due to the decomposition of carbonation products within the control sample and samples containing HAs subjected to accelerated carbonation were 153% and 189% to 282% higher than the corresponding samples cured under ambient conditions, respectively. This proves the extended formation of HMCs under high CO₂ concentrations (10 vol% vs. 0.04 vol%) and the contribution of these HMCs to the overall strength gain. When compared to the

control sample, the use of HAs at a concentration of 0.1 M increased the amount of HMCs by 5% to 19% and 20% to 79% within samples cured under ambient and accelerated carbonation conditions, respectively. The HAs included within MgO cement formulations demonstrated a more influential role in the strength gain of samples under accelerated carbonation as opposed to ambient curing. This is because the accelerated carbonation conditions enabled the effective utilization of the increased amount of brucite produced, which reacted with CO_2 to result in the dense formation of a strong carbonate network.

[00193] Example 3i: FTIR Results of Samples of Example 3a

[00194] The FTIR spectra of $\text{MgO.H}_2\text{O}$, MgO.HC0.1 , MgO.MC0.1 and MgO.MA0.1 after 14 days of curing under ambient and accelerated carbonation conditions are presented in FIG. 20a and FIG. 20b, respectively. The FTIR results are consistent with the compressive strength, XRD and TGA results, showing carbonation bands with much higher intensities after accelerated carbonation. Regardless of the curing conditions, samples containing HAs indicated a much more obvious carbonation trend than the control sample.

[00195] In the case of ambient curing shown in FIG. 20a, the control sample showed a weak absorption band at 1447 cm^{-1} , assigned to CO_3^{2-} . This band had a much higher intensity in corresponding samples MgO.HC0.1 and MgO.MC0.1 , confirming the increase in the formation of HMCs and strength with the introduction of these HAs. An absorption band at 1420 cm^{-1} accompanied with a shoulder at 1642 cm^{-1} assigned to the formation of HMCs was obvious in the case of MgO.MA0.1 .

[00196] The accelerated carbonation results shown in FIG. 20b, showed a broad band between 1506 and 1411 cm^{-1} for the control sample, while all the other samples incorporating HAs showed a broader band between 1573 and 1411 cm^{-1} . The major difference between the results obtained under ambient and accelerated carbonation was the significant increase in the intensity of this broad band in the latter case, corresponding to the extensive formation of HMCs under the increased concentration of CO_2 .

[00197] These broad bands were ascribed to CO_3^{2-} within hydromagnesite/dypingite and nesquehonite, which contributed to the development of microstructural strength through their dense formation. The presence of HMCs was also shown by a shoulder

at 850 cm^{-1} in MgO.HC0.1 and MgO.MA0.1, which indicated the highest strengths at 14 days.

[00198] Example 3j: Results of Microstructural Analysis for Samples of Example 3a

5 [00199] FIG. 21a to FIG. 21d show the microstructure of the control sample and samples containing different HAs at a concentration of 0.1 M (MgO.HC0.1, MgO.MC0.1 and MgO.MA0.1) after 14 days under ambient curing. Unlike previous studies performed on MgO cement mixes, the formation of various HMCs were clearly observed after only 14 days under ambient curing conditions. Disk-like
10 formation of hydromagnesite/dypingite (diameter about $1\text{ }\mu\text{m}$, thickness less than $0.1\text{ }\mu\text{m}$) was observed after the carbonation of the control sample under ambient conditions (FIG. 21a). The presence of several uncarbonated particles was also observed in the microstructure of the control sample, revealing incomplete carbonation after 14 days of curing. This also explains the lower strengths obtained by
15 the control sample compared to samples incorporating HAs. Clusters of hydromagnesite/dypingite (diameter about $1\text{ }\mu\text{m}$, thickness less than $0.1\text{ }\mu\text{m}$) that agglomerated into a rose-like form as shown in FIG. 21b was observed in sample MgO.HC0.1. The abundant formation of hydromagnesite/dypingite (diameter about $0.3\text{ }\mu\text{m}$, thickness less than $0.1\text{ }\mu\text{m}$) led to a dense microstructure in MgO.MC0.1 (FIG.
20 21c), whereas a clear formation of nesquehonite (diameter about $0.4\text{ }\mu\text{m}$, length about $3\text{ }\mu\text{m}$) with a needle-like morphology was observed in sample MgO.MA0.1 (FIG. 21d), resulting in higher strengths than all other samples after 14 days under ambient curing.

[00200] FIG. 22a to FIG. 22d show the microstructure of the same samples presented
25 in FIG. 21a to FIG. 21d after 14 days of accelerated carbonation. When compared to those cured under ambient conditions, the main difference of samples shown in FIG. 22a to FIG. 22d is the CO_2 concentration (0.04 vol% vs. 10 vol%) used during the curing process. The carbonate phases formed under accelerated carbonation were significantly larger than those observed under ambient curing. Different from the
30 microstructures of samples subjected to ambient curing, in which the formation of either nesquehonite or hydromagnesite/dypingite was observed, the co-existence of both of these HMCs was seen in all samples subjected to accelerated carbonation. The

accelerated carbonation of the control sample led to the formation of needle-like nesquehonite (diameter about 0.5 μm) and disk-like hydromagnesite/dypingite (diameter about 1 to 1.5 μm , thickness less than 0.1 μm), as seen in FIG. 22a. Along with these HMCs, the presence of unhydrated MgO and uncarbonated brucite particles was observed, which could explain the lower strength results obtained when compared to samples containing HAs.

[00201] The formation of needle-like nesquehonite (diameter about 0.3 μm , length about 5 μm) along with hydromagnesite/dypingite (diameter about 2 μm , thickness less than 0.1 μm) was observed after the carbonation of MgO.HC0.1, as shown in FIG. 22b. The microstructure of MgO.MC0.1 revealed an abundant hydromagnesite/dypingite (diameter about 0.8 μm , thickness less than 0.1 μm) growth on the surface of nesquehonite (diameter about 0.3 μm), as seen in FIG. 22c. In line with the compressive strength, water absorption and TGA results, the carbonation of MgO.MA0.1 indicated the largest phase formations, leading to the densest microstructure amongst all the samples. Much larger needles of nesquehonite (diameter less than 1 μm , length about 8 to 9 μm) than those observed in other samples coupled with a few hydromagnesite/dypingite disks (diameter about 2 μm , thickness about 0.2 μm) was spotted in FIG. 22d. This extensive formation of large nesquehonite needles led to a higher increase in the density of MgO.MA0.1 after carbonation, providing higher strengths than all other samples presented in this example.

[00202] **Example 3k: General Discussion of the Results for Samples of Example 3a**

[00203] The samples of example 3a that were studied, demonstrated the use of different HAs in improving the hydration, carbonation and mechanical performance of reactive MgO cement formulations under ambient and accelerated carbonation conditions. The introduction of HC increased the H^+ concentration, which enhanced the solubility of MgO and the formation of brucite. The inclusion of MC and MA accelerated the dissolution of MgO and the precipitation of brucite via the additional Mg^{2+} available. The enhancement of hydration at initial and later stages was clearly identified by isothermal calorimetry and hydration degree results obtained by XRD and TGA. The extra brucite available led to a more extensive carbonation, thereby

improving the mechanical performance of the prepared samples. Some of the main findings are discussed below.

[00204] (i) Out of the three different HAs used in this study, MC and MA were confirmed to be the most effective for the enhancement of MgO hydration. Samples containing MC indicated the highest hydration rates during the first 3 days, after which they hydrated at a similar rate as samples containing MA. This increased hydration rate demonstrated by MC samples at early ages could be attributed to the stronger dissolution of magnesia by Cl^- than CH_3COO^- , while both MA and MC contributed by increasing the amount of dissociated Mg^{2+} for the enhanced precipitation of brucite. The hydration degree results obtained by TGA also confirmed the highest hydration rates produced by MC and MA at 3 days onwards.

[00205] (ii) As carbonation proceeded, the formation of HMCs may have presented a barrier on the progress of hydration as they precipitated on the surface of MgO particles. This has led to high residual/unhydrated MgO contents even after 14 days of curing. However, as shown by the XRD results, the inclusion of HAs effectively reduced the amount of unhydrated MgO by converting MgO into brucite.

[00206] (iii) The effect of HA concentration was obvious at early ages (i.e. initial 3 days), during which the rate and degree of hydration increased with HA concentration. This effect was less obvious at 14 days as the hydration degrees of almost all samples reached similar values regardless of the HA concentration. However, the introduction of carbonation may have hindered the continuous hydration progress via the formation of HMCs in the available space. Therefore, samples containing lower concentrations of HA could not achieve similar carbonation degrees and strengths as high as those with higher concentrations over the entire curing period.

[00207] (iv) The XRD, TGA and FTIR results confirmed that the inclusion of HAs not only increased brucite formation, but also enhanced the carbonation degree of samples they were incorporated in. Consistent with FTIR results, samples containing HAs led to higher weight losses corresponding to the decomposition of HMCs than the control sample. The extensive formation of HMCs within these samples resulted in denser microstructures and lower water absorption values, which translated into higher compressive strengths than the control sample.

[00208] (v) Despite their similar hydration degrees, samples containing MC carbonated less than those with HC and MA, which was also reflected by their lower compressive strengths after 14 days. This could be attributed to the high hydration rate of MC samples during the initial stages, which resulted in the quick precipitation
5 of a bulk amount of brucite rather than its even dispersion into the solution over a longer period. This dense formation of brucite around the MgO particles may have resulted in its agglomeration, reducing the surface area available for carbonation.

[00209] (vi) The CO₂ sequestration ability of all samples can be assessed and compared by the ratio of the weights associated with the decomposition of their
10 HMCs and unreacted brucite (H/B) obtained at the end of this study. While the H/B ratios of all samples showed minor variations within a narrow range of 0.11 to 0.13 under ambient curing conditions, the introduction of accelerated carbonation led to an increase in this ratio. The H/B ratios of samples containing MA reached up to 1.17, which was much higher than that of the control sample (0.44) and samples containing
15 HC (0.63) and MC (0.41). These were in line with the compressive strength results, which were dependent on the extent of carbonation and the associated formation of HMCs. Therefore, the introduction of HAs such as MA and HC not only improved the hydration process, but also enhanced the CO₂ sequestration ability by enabling the dispersion of brucite into the pores for the formation of a bulk structure and increasing
20 the surface area available for carbonation.

[00210] (vii) The positive effect of the introduction of MA into MgO formulations on the enhancement of carbonation was also visible by the improved morphology of the prepared samples. Compared to other samples, the extensive formation of larger nesquehonite particles along with hydromagnesite/dypingite was observed to present a
25 benefit in the creation of a denser microstructure. This contributed to the achievement of much higher strength results by samples containing MA than all other samples. The formation of various HMCs were clearly observed after only 14 days under ambient curing conditions, which has not been reported in any of conventional studies.

[00211] **Example 3l: Summary of Results for Samples of Example 3a**

[00212] All of the examples in example 3 aimed to improve the carbonation and
30 associated mechanical performance of reactive MgO cement formulations by enhancing the hydration process and enabling a higher amount of brucite available for

carbonation. Three different types of HAs (HC, MC and MA) were used at two different concentrations (0.05 and 0.1 M) to increase the conversion of MgO to brucite, which then reacted with CO₂ to form a range of strength providing HMCs. The hydration and carbonation mechanisms were investigated under ambient and accelerated carbonation curing conditions (0.04 vol% vs. 10 vol% CO₂ concentration). The degree and rate of MgO hydration were evaluated by isothermal calorimetry and TGA. Water absorption and compressive strength results were used to assess the mechanical performance of the prepared samples. The formation of HMCs along with the quantification of different components were performed via XRD, TGA and FTIR. The morphology of carbonate phases under different conditions was observed under SEM and BSE. The following conclusions can be drawn:

[00213] (i) The introduction of HAs improved the dissolution of reactive MgO and the precipitation of brucite, which in turn increased the rate and degree of reactive MgO hydration. MC and MA provided the highest hydration degrees which reached up to 75% and 89% at the end of 3 and 14 days, respectively. These values were up to 54% higher than the control sample.

[00214] (ii) Samples containing HAs led to a higher utilization of MgO, which not only increased the amount of brucite available for carbonation, but also enhanced the CO₂ sequestration ability of brucite. This resulted in the formation of a denser carbonate network composed of a higher amount of HMCs with larger particle sizes than the control sample.

[00215] (iii) The improvement in the quantity and morphology of HMCs translated into improved mechanical performance, reaching strengths as high as about 60 MPa at the end of 28 days under accelerated curing conditions. Samples incorporating MA outperformed all others in terms of their compressive strengths, which were 273% and 107% higher than the corresponding strengths of the control sample at 14 and 28 days, respectively. Strengths higher than 7 MPa were achieved by samples containing HAs after 7 days of ambient curing, which were more than 180% higher than the corresponding strengths of the control sample. The inclusion of HAs also led to up to 74% lower water absorption values than the control sample.

[00216] The findings of this study indicate the significant potential of MgO cement-based formulations in achieving high strengths based on the amount of CO₂

sequestered and the properties of the resulting carbonate system. The carbonation process was enhanced by improving the preceding hydration, which is usually the limiting step in MgO samples. The obtained results highlight the ability of MgO to carbonate and gain strength within a few days under ambient conditions, while demonstrating significant mechanical performance when the right conditions are provided.

[00217] Example 4a: Another Example of the Present Method and Hydrated Magnesium Carbonated Cement Composite for Investigation of the Influence of Nucleation Seeding

[00218] Unless specified otherwise, the materials used in this example have been described in example 1. The method used in this example is described below.

[00219] Before the casting of samples, the hydration mechanism of RMC with different seed contents was studied by preparing the samples corresponding to the sample compositions listed in table 8 below.

[00220] Table 8 – Composition of Samples for Example 4a

Sample	Seed (wt%)	Mix Proportion (kg)			
		RMC	Seed	Coarse Aggregate	Water
H ₂ O.S0	0	500	0	1100	350
H ₂ O.S0.5	0.5	497.5	2.5	1100	350
H ₂ O.S1.0	1.0	495	5	1100	350
H ₂ O.S1.5	1.5	492.5	7.5	1100	350
H ₂ O.S2.0	2.0	490	10	1100	350

[00221] The ratio of water to binder (i.e. RMC with or without seeds) was kept constant at 0.7 for all samples. The samples were tested under isothermal calorimetry to observe their hydration behaviour. This was followed by the preparation of samples according to the compositions listed in table 8. In addition to the control sample, H₂O.S0, whose binder component was only composed of RMC without any seed addition, samples with different seed contents were prepared to assess the influence of seeds on performance. The seed content of samples H₂O.S0.5, H₂O.S1.0, H₂O.S1.5 and H₂O.S2.0 was systematically increased to contain 0.5, 1, 1.5 and 2 wt% of seed,

respectively, with respect to RMC and seed particles. The method started with seeds dispersed in water with a magnetic stirrer before mixing with the rest of the components. After mixing, the concrete samples were cast into 50×50×50 mm cubic moulds, consolidated by a vibrating table and trowel finished. All samples were de-

5 moulded after 24 hours and subjected to carbonation curing under 10 vol% CO₂, 80±5% relative humidity and 30±1.5°C for up to 28 days.

[00222] Example 4b: Characterization of the Samples of Example 4a

[00223] The samples were characterized in a similar manner as example 2b.

[00224] Example 4c: Isothermal Calorimetry Results for Samples of Example 4a

10 **[00225]** FIG. 9 presents the heat flow of all samples over 24 hours of hydration. The dissolution-nucleation of MgO occurred a few minutes after mixing for all samples, which took place more rapidly in seeded samples (H₂O.S0.5, H₂O.S1.0, H₂O.S1.5 and H₂O.S2.0) than the control sample (H₂O.S0) at the initial stages (about 2 to 5 hours) of hydration. The higher and wider hydration peaks of the seeded samples

15 demonstrated the enhancement of hydration via the introduction of seeds. This could indicate the active role of seeds in facilitating the hydration of MgO at early stages through the provision of additional nucleation sites within the pore space. The additional nucleation sites stimulated the nucleation and growth of brucite away from the MgO grains and increased the contact surface of MgO with water at initial stages.

20 This was also evident from the initial peak, whose height increased with the seed content, indicating the acceleration of the hydration reaction. The influence of seed content on the acceleration of hydration was more obvious up until 1 wt% of seed addition. Any increase in the seed content beyond this value (i.e. within samples H₂O.S1.5 and H₂O.S2.0) did not have a noticeable effect on the acceleration of the

25 hydration reaction. The initial rapid hydration induced with the introduction of seeds was followed by a relatively slower reaction in comparison to the control sample.

[00226] Example 4d: Water Absorption Test Results for Samples of Example 4a

[00227] The water absorption values of all samples after 14 and 28 days of carbonation are listed in table 9 below.

30 **[00228]** Table 9 – Water Absorption of Samples

Sample	Water Absorption (%)	
	14 Days	28 Days

H ₂ O.S0	4.12	1.95
H ₂ O.S0.5	3.29	1.84
H ₂ O.S1.0	2.53	1.66
H ₂ O.S1.5	2.37	1.24
H ₂ O.S2.0	1.94	1.25

[00229] Compared to the control sample (H₂O.S0), the seeded samples absorbed less water at both ages. The water absorption of S0 was recorded as 4.12% after 14 days of curing. The inclusion of 0.5 wt% to 2 wt% seeds reduced the water absorption by 20% to 53%, resulting in corresponding values as low as 1.94%. A similar trend was observed at 28 days, at which the water absorption of H₂O.S0 was 1.95%. The introduction of seeds led to up to 36% reduction in this value and revealed 28-day water absorption values as low as 1.25%. The amount of water absorbed generally decreased with increasing seed content at both ages. The significant reduction in the water absorption values of the seeded samples could be attributed to the reduction of sample porosities and generation of denser structures due to the increased formation of carbonate phases induced by the introduction of seeds within the pore spaces. The lower water absorption of all samples after longer curing durations (i.e. 14 vs. 28 days) was an indication of the continuous progress of carbonation and the formation of HMCs that led to the densification of samples over time, thereby reducing the amount of pore spaces initially available for water absorption.

[00230] Example 4e: Compressive Strength Test Results for Samples of Example 4a

[00231] FIG. 10 illustrates the compressive strength development of the control and seeded samples cured for up to 28 days. All samples demonstrated an increase in strength with time, which was due to the formation of carbonate phases within the pore structure. When compared to the control sample (H₂O.S0), the inclusion of up to 1 wt% seed in samples H₂O.S0.5 and H₂O.S1.0 led to an increase in strength, which was especially apparent after 7 days. The rate of strength gain of these two samples outperformed all others, revealing strengths as high as 64 MPa at 28 days. The positive contribution of the seeds to the strength development of H₂O.S0.5 and H₂O.S1.0 was obvious at as early as 3 days, leading to higher strengths than H₂O.S0 (i.e. 14 vs. 11 MPa). The difference in the strength of seeded and unseeded samples

became more obvious at later ages as samples H₂O.S0.5 and H₂O.S1.0 produced strengths about 33% to 36% higher than H₂O.S0 and achieved 49 MPa (vs. 36 MPa of H₂O.S0) and 64 MPa (vs. 48 MPa of H₂O.S0) at 14 and 28 days, respectively. The higher strengths of seeded samples could be attributed to the provision of additional nucleation sites, which stimulated the carbonation process by creating extra contact surface between brucite and CO₂. This enabled a more extensive formation of HMCs that filled up the pore spaces, which led to a higher strength gain than the control sample, whose phase formation was limited without the seed addition.

[00232] An opposite effect was observed when the seed content was increased beyond 1 wt% in samples H₂O.S1.5 and H₂O.S2.0. Sample H₂O.S1.5 containing 1.5 wt% seeds, revealed strengths of up to 37 MPa (vs. 36 MPa of H₂O.S0) and 39 MPa (vs. 48 MPa of H₂O.S0) at 14 and 28 days, respectively. A further reduction to 20 MPa at 14 days and 22 MPa at 28 days was observed as the seed content increased to 2 wt% in sample H₂O.S2.0. The reduction in strength at higher seed contents could be attributed to the loss of bonding strength between the aggregates and carbonate phases as the seeds did not directly contribute to the bonding structure. Instead, the increased seed usage could have led to the extra seeds forming an additional layer surrounding the aggregates. This additional layer around the aggregates could weaken the bond between the aggregates and the cement paste, which was more pronounced under excessive seed usage. These samples also did not demonstrate any strength development after 14 days as there was almost no increase in their strengths from 14 to 28 days. This could be an indication of limited carbonation due to slower diffusion of CO₂ through the highly seeded systems.

[00233] Example 4f: XRD Test Results for Samples of Example 4a

[00234] The XRD patterns of all samples after 14 days of carbonation are shown in FIG. 11. All samples demonstrated the formation of various HMC phases due to carbonation, namely nesquehonite, dypingite and hydromagnesite. Along with HMCs, the presence of unhydrated MgO (main peak at 42.9° 2θ) and uncarbonated brucite (main peak at 38.1° 2θ) was observed. When compared to the control sample (H₂O.S0), the inclusion of up to 1 wt% seed within samples H₂O.S0.5 and H₂O.S1.0 was beneficial for carbonation, which was obvious from the reduced intensity of the MgO and brucite peaks within these samples when compared to H₂O.S0. Increasing

the seed content to 1.5 wt% and 2 wt% within samples H₂O.S1.5 and H₂O.S2.0 had an opposite effect on the phase transformation and led to higher residual MgO contents than H₂O.S0.

[00235] The contents of unhydrated MgO and uncarbonated brucite within all samples after 14 days of carbonation are presented in table 10 below.

[00236] Table 10 – MgO and Mg(OH)₂ Contents Obtained by XRD after 14 Days of Curing

Sample	MgO (wt%)	Mg(OH) ₂ (wt%)
H ₂ O.S0	42	53
H ₂ O.S0.5	37	44
H ₂ O.S1.0	34	30
H ₂ O.S1.5	46	42
H ₂ O.S2.0	46	37

[00237] Samples with 1 wt% or less seed content showed higher hydration degrees than the control sample. This was evident from the lower residual MgO contents of samples H₂O.S0.5 (37%) and H₂O.S1.0 (34%) when compared to H₂O.S0 (42%). The difference in the hydration capacity of H₂O.S0 in the presence of carbonation could be attributed to the formation of carbonate phases that limited further access to the unhydrated MgO grains. The introduction of seeds partially enabled the nucleation of HMCs on the surface of the seeds, whose dispersion in the pore spaces away from the MgO grains could have enhanced further hydration and resulted in a higher utilization rate of MgO. However, increasing the seed content beyond 1 wt% could have led to the agglomeration of seeds on the surface of MgO grains due to their higher content, which could prevent the continuation of the hydration process and result in a lower utilization of MgO than the control sample.

[00238] The introduction of seeds within the pore spaces enabled the partial formation of brucite on seed surfaces in addition to the surface of MgO grains. Therefore, the nucleation process increased the surface area of brucite available to react with the diffused CO₂. As a result, the uncarbonated brucite contents of seeded samples were significantly lower than that of the control sample (i.e. 30% to 44% vs. 53%). This was reflected by the higher carbonation capacities of the seeded samples, in which sample H₂O.S1.0 outperformed all others. The combination of the lowest

unhydrated MgO and uncarbonated brucite achieved by H₂O.S1.0 in comparison to all other samples was generally in line with the trend observed in the compressive strength results, where H₂O.S1.0 demonstrated the highest strength gain. This could explain the relationship between the degree of carbonation and the strength development of RMC formulations, whose final mechanical performance is dependent on the seed content incorporated within the initial mix design.

[00239] Example 4g: TGA Test Results for Samples of Example 4a

[00240] The weight loss and heat flow results of all samples after 14 days of carbonation are shown in FIG. 12a. The decomposition behaviour demonstrated by all samples, which are summarized in FIG. 12b, was consistent with reported studies. The three main decomposition steps were identified as:

[00241] 50 to 300°C: Dehydration of water bonded to HMCs (e.g. nesquehonite, hydromagnesite and dypingite).

[00242] 300 to 500°C: Dehydroxylation of HMCs (e.g. hydromagnesite and dypingite), decarbonation of HMCs (e.g. nesquehonite) and decomposition of uncarbonated brucite.

[00243] 500 to 900°C: Decarbonation of HMCs (e.g. nesquehonite, hydromagnesite and dypingite).

[00244] The two endothermic peaks corresponding to the dehydration of water bonded to HMCs were observed at 120°C and 220°C. A strong endothermic peak responsible for the decomposition of uncarbonated brucite, accompanied with the dehydroxylation of HMCs (e.g. hydromagnesite) was observed at around 370°C to 410°C. This was followed by a broader peak corresponding to the decarbonation of HMCs at about 720°C.

[00245] The weight loss observed within the samples at each step, along with the total weight loss, which represented the content of hydrate and carbonate phases within each sample, are listed in table 11 below.

[00246] Table 11 – Weight Loss and Carbonation Ratio of Samples Obtained by TGA After 14 Days of Curing

Sample	Weight Loss (wt%)						R _{CO2} (x10 ⁻²)
	50- 300°C	300- 500°C	500- 900°C	Mg(OH) ₂	HMCs	Total	
H ₂ O.S0	8.13	27.41	2.79	16.41	21.92	38.33	8.19

H ₂ O.S0.5	10.89	28.16	2.66	13.52	28.19	41.71	13.39
H ₂ O.S1.0	11.13	27.22	2.68	9.28	31.75	41.03	16.05
H ₂ O.S1.5	6.99	23.93	3.06	13.10	20.88	33.98	7.22
H ₂ O.S2.0	7.45	23.39	3.13	11.38	22.59	33.97	9.23

[00247] A majority of the weight loss in all samples was recorded in the 300°C to 500°C temperature range, which was associated with 3 main reactions attributed to the dehydroxylation of hydromagnesite and dypingite, decarbonation of nesquehonite and decomposition of uncarbonated brucite. The weight loss due to the decomposition of HMCs was calculated by subtracting the weight loss due to the decomposition of uncarbonated brucite from the total weight loss.

[00248] When compared to the control sample (H₂O.S0), samples H₂O.S0.5 and H₂O.S1.0 revealed higher total weight loss values (41% to 42% vs. 38% of H₂O.S0), which was associated with their higher HMC contents (28% to 32% vs. 22% of H₂O.S0). This was reflected as up to 45% increase in the HMC content with the inclusion of 1 wt% seed within the initial mix design. In addition to their higher HMC contents, samples H₂O.S0.5 and H₂O.S1.0 also demonstrated lower uncarbonated brucite contents than H₂O.S0, which confirmed the active role of seeds in improving the carbonation capability of RMC formulations.

[00249] The decomposition results of samples H₂O.S0.5 and H₂O.S1.0 in comparison to H₂O.S0 were in line with their mechanical performance, in which the higher total weight loss values of H₂O.S0.5 and H₂O.S1.0 corresponded to their higher compressive strength and lower water absorption than H₂O.S0. Consistent with the above examples, an increase in the seed content to 1.5 wt% or more led to lower total weight loss values than all other samples. Despite their similar HMC contents, the amount of water loss demonstrated by samples H₂O.S1.5 and H₂O.S2.0 within the range of 50 to 300°C was less than that of the control sample. The reduced weight losses of these samples demonstrated their limited hydration and carbonation in comparison to other samples, which agreed with their inferior mechanical performance.

[00250] Example 4h: Carbonation Ratio Results for Samples of Example 4a

[00251] A more in-depth comparison of the carbonation potential of seeded and unseeded samples could be facilitated through the quantification of the carbonation

ratio (i.e. CO₂ sequestration ratio, R_{CO2}). This value was calculated as shown in the equation below, where P_{CO2} is the percentage of CO₂ sequestered (i.e. obtained by subtracting the weight loss associated with the loss of H₂O from the total weight loss between 300°C and 900°C) and P_{PMC} is the percentage of final mass at 900°C (i.e. residual MgO).

[00252] $R_{CO2} = P_{CO2}/P_{PMC}$

[00253] The results listed in table 11 showed that the increase in the carbonation capabilities of samples containing up to 1 wt% seed, which achieved up to 96% higher carbonation than the unseeded control sample. The increased carbonation of these seeded samples enabled a more extensive formation of HMCs that filled up the pore space. This was evident from the formation of much denser structures as revealed by the significantly reduced water absorption values of the seeded samples. Furthermore, the seed particles could have contributed to the overall microstructural development by functioning as micro-aggregates in between the carbonate crystals. These improvements observed within the seeded samples translated to up to 36% higher strengths than the control sample, whose phase formation was limited without the seed addition.

[00254] **Example 4i: Results of Microstructural Analysis for Samples of Example 4a**

[00255] FIG. 13a to FIG. 13e show the microstructure of all samples after 14 days of carbonation. Needle-like nesquehonite and disk/rose-like hydromagnesite/dypingite, whose formation led to strength gain, were the main carbonate phases observed. The disk- or rose-like hydromagnesite/dypingite crystals that formed due to the carbonation process could be distinguished from the hydromagnesite seeds included within the initial mix, which possessed a round ball-like morphology, as indicated earlier in FIG. 1. As seen in FIG. 13a, the carbonation of the control sample (H₂O.S0) revealed hydromagnesite/dypingite disks with a diameter of about 1.5 to 2 μm, which gathered to form a rose-like morphology that grew on the surface of nesquehonite needles with a diameter of about 1 μm. The morphologies of these HMCs observed after the carbonation of H₂O.S0 differed from those of the seeded samples.

[00256] The use of seeds led to variations in the microstructure of samples, in which the morphology of the carbonation products differed with the introduced seed content.

In addition to the carbonate phases that formed as a result of the curing process, round ball-like hydromagnesite seeds with a diameter of about 1 to 7 μm (FIG. 1), were observed within the seeded samples. Sample H₂O.S0.5 revealed the formation of disk-like hydromagnesite/dypingite (diameter about 1.5 to 2 μm) along with the presence of seed particles within the pores, as shown in FIG. 13b. Increasing the seed content to 1 wt% in sample H₂O.S1.0 enabled the dense formation of nesquehonite by acting as potential nucleation sites. This was obvious from the presence of a seed particle with a diameter of about 6 μm amongst the nesquehonite needles in FIG. 13c. Besides their role as nucleation sites, the introduction of seeds in the pore spaces provided a filling effect and increased the overall density by reducing the initial porosity. Therefore, the increased carbonation capabilities of samples H₂O.S0.5 and H₂O.S1.0, coupled with their denser microstructures facilitated with the moderate use of seeds, could explain their favourable mechanical performance when compared to the control sample.

[00257] The effects of increasing the seed content to 1.5 wt% and 2 wt% were evident from the microstructures of samples H₂O.S1.5 and H₂O.S2.0, in which the presence of the seed particles were highly visible throughout FIG. 13d and FIG. 13e. Although the formation of nesquehonite needles was seen in both cases, they were covered by the excessive presence of the seed particles. The high inclusion rate of seeds within these samples may have led to the reduction of the bonding strength between the other solid phases, thereby explaining the undesirable mechanical performance of samples H₂O.S1.5 and H₂O.S2.0 in comparison to other samples. These observations were consistent with the strength results, as well as the findings revealed by XRD and TGA, which highlighted the role of nucleation seeding in enhancing the carbonation and the associated mechanical performance of RMC formulations.

[00258] Example 4j: Summary of Results for Samples of Example 4a

[00259] In unseeded systems, MgO grains are surrounded by solid Mg(OH)₂ particles, whose carbonation leads to the formation of an encapsulating dense layer of HMCs, thereby limiting further access to the unhydrated MgO and uncarbonated Mg(OH)₂ particles, as shown in FIG. 14a to FIG. 14c. The introduction of seeds can provide additional nucleation sites within the pore spaces and allow hydrate and carbonate

phases to grow on seed surfaces away from the original MgO grains, thereby facilitating further access to the unhydrated MgO and uncarbonated Mg(OH)₂ particles, as shown in FIG. 15a to FIG. 15c. As carbonation proceeds, the nuclei of carbonation products do not only form on the surface of the MgO/Mg(OH)₂ grains, but also around the seeds dispersed within the pore spaces. This dispersed formation of hydration products into the pore spaces can enhance the carbonation process, leading to an increase in the amount of carbonate phases that fill in the initially available pore space. The significant reduction in the porosity associated with these reactions as well as the strong binding network established by the dense formation of HMCs improve the mechanical performance of RMC-based formulations.

[00260] Nevertheless, this example aimed to improve the hydration and carbonation of RMC-based concrete formulations with the introduction of nucleation seeding that provided extra contact area to stimulate these reactions. The developed formulations included different amounts (i.e. 0 wt% to 2 wt% of RMC) of hydromagnesite seeds that were included in the initial mix to increase the contact surface of the solid phases with water and CO₂. The results indicated the advantages of using 1 wt% or less seeds in enhancing the hydration and carbonation potential of the developed samples, which demonstrated higher utilization rates of MgO than the unseeded control sample. The introduction of seeds within the pore spaces enabled the formation of brucite on seed surfaces in addition to the surface of MgO grains. This led to a higher brucite content that was dispersed throughout the pore spaces instead of solely agglomerating on the original MgO grains, thereby increasing the contact surface area available for further hydration and carbonation and resulting in up to 20% lower unhydrated MgO contents.

[00261] As they benefitted from a larger contact surface area of brucite available to react with the diffused CO₂, the seeded samples achieved up to 96% higher carbonation than the control sample, resulting in significantly lower uncarbonated brucite contents. The improved hydration and carbonation were reflected in the extensive formation of carbonate phases that filled up the pore spaces and facilitated dense microstructures, which led to a continuous strength development. Samples containing up to 1 wt% seed achieved 36% higher strengths than the control sample due to the provision of additional nucleation sites, which stimulated the continuation of the carbonation processes by creating extra space away from the original MgO

particles within the pore system. The findings of this study indicated the importance of determining the optimum amount of seeds to be introduced into a specific mix to fully harvest the benefits of nucleation seeding on the final performance of RMC based formulations.

5 **[00262] Example 5a: Another Example of the Present Method and Hydrated Magnesium Carbonate Cement Composite for Further Characterization**

[00263] Unless specified otherwise, the materials used in this example have been described in example 1. The method for this example is described as follows.

10 [00264] Two sets of samples (i.e. with and without HA) were used to investigate the influence of HA and seeding on the hydration and carbonation of RMC formulations. table 12 below lists the compositions of the concrete samples prepared under this study.

[00265] Table 12 - Compositions of Concrete Samples Investigated

Sample	Seed (wt%)	Mix Proportion (kg)				
		RMC	Seed	Coarse Aggregates	H ₂ O	HA
H ₂ O.S0	0	500	0	1100	350	-
H ₂ O.S0.5	0.5	497.5	2.5	1100	350	-
H ₂ O.S1.0	1.0	495	5	1100	350	-
HA.S0	0	500	0	1100	-	350
HA.S0.5	0.5	497.5	2.5	1100	-	350
HA.S1.0	1.0	495	5	1100	-	350

15 [00266] Each set included seed contents of 0 wt% (samples H₂O.S0 and HA.S0), 0.5 wt% (samples H₂O.S0.5 and HA.S0.5) and 1 wt% (samples H₂O.S1.0 and HA.S1.0) of the RMC and seeds. The ratio of water or HA solution to RMC was kept constant at 0.7 for all samples. Before casting the concrete samples, corresponding pastes were prepared to study the effects of HA and seeding on the hydration of MgO via
20 isothermal calorimetry.

[00267] To prepare the concrete samples, seeds were dispersed in water or HA solution by a magnetic stirrer and were then added to a dry mix of the RMC. The concrete compositions prepared in this example did not include any fine aggregates (particles with size of less than 4.95 mm) to enable the extraction of carbonated paste
25 from the concrete samples without any contamination and to ensure accurate quantification of the hydrate and carbonate phases via X-ray diffraction (XRD) and

thermogravimetric analysis (TGA). After mixing, the concrete samples were cast into 50×50×50 mm cubic moulds, consolidated by a vibrating table and trowel finished. All samples were de-moulded after 24 hours and subjected to carbonation curing under 10 vol% CO₂, 80±5% relative humidity and 30±1.5°C up to 28 days for water absorption testing, compressive strength measurements and microstructural analysis.

[00268] Example 5b: Characterization of the Samples of Example 5a

[00269] Unless specified otherwise, the methods for characterization of the samples of example 5a are described in example 2b.

[00270] Example 5c: Isothermal Calorimetry Results for Samples of Example 5a

[00271] FIG. 2a and FIG. 2b present the heat flow and cumulative heat of the samples during the first 24 hours of hydration, respectively. The results indicated that the dissolution-nucleation of MgO occurred a few minutes after mixing for all samples. The higher exothermal peaks and increased total heat outputs demonstrated by HA samples in comparison to the corresponding H₂O samples confirmed the active role of HA (e.g. (CH₃COO)₂Mg) in promoting the dissolution of MgO.

[00272] The introduction of seeds in both the H₂O and HA samples was effective in facilitating the hydration of MgO at early stages (about 2 to 5 hours) through the provision of additional nucleation sites within the pores. The higher and wider hydration peaks of the seeded samples demonstrated the enhancement of hydration via the introduction of seeds. As the use of HA also promoted hydration by leading to the precipitation of brucite away from the original MgO grains, the effect of seeding on early hydration was more obvious in H₂O than HA samples. The initial rapid hydration in seeded samples was followed by a relatively slower reaction when compared to the corresponding unseeded samples.

[00273] Example 5d: Water Absorption Test Results for Samples of Example 5a

[00274] Table 13 below lists the water absorption values of all samples after 14 and 28 days of carbonation curing.

[00275] Table 13 – Water Absorption of Samples of Example 5a after 14 and 28 Days of Curing

Sample	Water Absorption (%)	
	14 days	28 days
H ₂ O.S0	4.12	1.95

H ₂ O.S0.5	3.29	1.84
H ₂ O.S1.0	2.53	1.66
HA.S0	2.01	0.83
HA.S0.5	1.75	0.85
HA.S1.0	1.41	0.86

[00276] The significant decrease in the water absorption of all samples from 14 to 28 days of curing indicated reduction in the amount of connected pores, which were filled by hydration and carbonation products. HA samples achieved 44% to 57% lower water absorption than the corresponding H₂O samples at both ages. The lower water absorption of HA samples could be attributed to the enhancement of hydration, which led to an improvement in HMC formation and sample microstructures via the increased availability of Mg(OH)_{2(aq,s)} for carbonation.

[00277] Compared to H₂O.S0 sample, introduction of seeds reduced the water absorption by up to 39%. Amongst the H₂O samples that did not include any HA, water absorption decreased with an increase in seed content. The reduction in the water absorption of the seeded samples was linked with the decrease in porosities via the enhanced nucleation and growth of hydrate and carbonate phases enabled by the introduction of seeds within the pores. A similar trend was observed in seeded HA samples after 14 days of carbonation as introduction of seeds reduced the amount of absorbed water by up to 30%. However, the use of seeds did not have any influence in reducing the water absorption values recorded at 28 days. The reduction of water absorption with seeded HA samples at 14 days could be attributed to the role of seeds in accelerating the nucleation and growth of brucite, and the subsequent formation of carbonate phases at early ages.

[00278] Example 5c: Compressive Strength Test Results for Samples of Example 5a

[00279] The compressive strength of all samples of example 5a cured for up to 28 days is shown in FIG. 3. All samples demonstrated an increase in strength with time, which was an indication of the continuous formation of HMCs over the 28 days of curing. The initial rapid strength gain observed during the first 14 days was followed by a slower rate associated with the reduction in the rates of the hydration and

carbonation reactions over time. Amongst all the samples, the samples with seeds and/or HA have significantly improved compressive strength, which was especially notable at 14 days of curing or more.

[00280] When compared to the control sample (H₂O.S0), the sample HA.S0 experienced 119% and 48% increase in compressive strength after 3 and 7 days of curing, respectively. As carbonation proceeded, the compressive strength of HA.S0 reached 68 MPa at 28 days, which was 42% higher than the corresponding strength of H₂O.S0. The improvement of compressive strength in the presence of HA was attributed to the active role of HA in the enhancement of the hydration process, which led to the production of higher amounts of Mg(OH)_{2(aq,s)} available for subsequent carbonation and thus the higher extent of HMC formation.

[00281] The use of seeds without HA also led to improved performance as demonstrated by the compressive strengths of the H₂O.S0.5 and H₂O.S1.0 samples, which were 36% and 33% higher than the corresponding strengths of H₂O.S0 at 14 and 28 days, respectively. The positive contribution of seeds to the strength development of H₂O.S0.5 and H₂O.S1.0 was an indication of the active role of seeding in stimulating the nucleation of hydration and carbonation products away from the original MgO particles within the pores. This improved arrangement of particles facilitated the creation of extra contact surface area for further hydration and carbonation within these samples. Unlike the introduction of seeds in PC and alkali-activated slag systems, which demonstrated accelerated hydration and strength gain, the use of seeds improved the performance of RMC formulations after 14 days of curing. In PC and alkali-activated slag systems, cement is dissolved at an early stage when contacting with water, thus, the introduction of seeds in PC and alkali-activated slag systems accelerated the nucleation and growth of hydration products, and accordingly, strength gained at early ages. On the other hand, in MgO cement system, the slow solubility of MgO cement leads to slow hydration and carbonation. The introduction of seeds in carbonated MgO systems increases the contact surface of Mg(OH)₂ for carbonation but cannot accelerate the hydration of MgO. Therefore, the effectiveness of strength gain was observed after 14 days when a sufficient level of carbonation is achieved.

[00282] The simultaneous inclusion of HA and seeding (HA.S0.5 sample) outperformed all other samples after 7 days of curing. The plateau observed in the strength development of HA.S0 and HA.S1.0 between 7 and 14 days was replaced by a continuous strength gain in HA.S0.5. The compressive strengths of HA.S0.5 were 5 64% (59 vs. 36 MPa) and 46% (70 vs. 48 MPa) higher than those of the control sample at 14 and 28 days, respectively. The improvement in the performance of HA.S0.5 clearly proved the important roles of HA in enhancing the hydration of MgO and seeds in (i) stimulating the nucleation of the hydration and carbonation products away from the original grains to facilitate the further continuation of these reactions 10 and (ii) acting as micro-aggregates that filled in the pores. As shown by the differences in the strength development of all samples presented in FIG. 3, the use of HA and seeding in HA.S0.5 led to significant improvements in mechanical performance and reduced the total curing time required to achieve a certain strength, thereby reducing the overall costs associated with sample preparation. Increasing the 15 seed content from 0.5 wt% to 1 wt% (HA.S1.0 sample) led to similar strengths as other HA samples at 28 days, showing that seed usage of up to 0.5 wt% already provides the improved mechanical performance.

[00283] Example 5f: XRD Test Results for Samples of Example 5a

[00284] The XRD patterns of samples of example 5a after 14 days of carbonation are 20 shown in FIG. 4. All samples demonstrated formation of various HMC phases due to carbonation, namely nesquehonite, dypingite and hydromagnesite. Along with HMCs, the presence of unhydrated MgO (main peak at $42.9^\circ 2\theta$) and uncarbonated brucite (main peak at $38.1^\circ 2\theta$) was observed in all samples with or without HA and/or seeds. The quantification of unhydrated MgO and uncarbonated brucite within all samples 25 after 14 days of carbonation, as reported in table 14, was performed with respect to the introduced fluorite (main peak at $28.2^\circ 2\theta$).

[00285] Table 14 – MgO and $\text{Mg}(\text{OH})_2$ Contents of all Samples Obtained by XRD after 14 Days of Curing

Sample	MgO (wt%)	Brucite (wt%)
H ₂ O.S0	43	53
H ₂ O.S0.5	37	44

H ₂ O.S1.0	34	30
HA.S0	34	33
HA.S0.5	33	34
HA.S1.0	31	35

[00286] When compared to the control sample (H₂O.S0), the use of HA in HA.S0 reduced the unhydrated MgO content from 43% to 34%. A similar trend reflecting a decrease in the MgO content was also seen with the introduction of seeds. These samples revealed higher hydration degrees than the control sample, which was reflected by the lower residual MgO contents of H₂O.S0.5 (37%) and H₂O.S1.0 (34%) when compared to H₂O.S0 (43%). Similar to the introduction of HA, the use of seeds increased the utilization of RMC by up to 19%. Furthermore, the simultaneous inclusion of HA and seeds resulted in the lowest residual MgO contents as revealed by samples HA.S0.5 (33%) and HA.S1.0 (31%), which translated into an increase in the utilization of RMC by up to 26%.

[00287] The inclusion of HA and/or seeds not only reduced the amount of residual MgO and therefore achieved higher hydration degrees, but also significantly reduced the uncarbonated brucite content when compared to the control sample. Accordingly, the use of HA in the HA.S0 sample reduced the uncarbonated brucite content of the control sample (H₂O.S0) from 53% to 33%, while the inclusion of seeds within the samples H₂O.S0.5 and H₂O.S1.0 led to values as low as 30%. The lower brucite contents revealed by samples containing HA and/or seeds indicated the role of these additives in improving carbonation, which could explain the higher compressive strengths of these samples than those of the control sample. While the presence of HA produced a bulk brucite structure to facilitate the diffusion of CO₂ and its reaction with Mg-bearing phases, the dispersion of seeds in the pore spaces enabled the formation of brucite on seed surfaces in addition to the surface of the MgO grains, thereby increasing the reactive surface area of brucite for carbonation. A slightly different scenario was observed in HA samples that incorporated seeds. As the use of HA led to the migration of complex (e.g. magnesia-acetate) ions away from their original particles to form a bulk brucite structure in the pore spaces regardless of the presence of seeds, the introduction of seeds stimulated the nucleation process rather

than extend the surface area of the bulk brucite for carbonation. As a result, seeds were not influential in reducing the uncarbonated brucite contents within HA.S0.5 and HA.S1.0 and led to similar values to those of HA.S0.

[00288] Example 5g: TGA Test Results for Samples of Example 5a

5 **[00289]** The mass loss and heat flow results of all samples after 14 days of carbonation are shown in FIG. 5. The two endothermic peaks corresponding to the dehydration of water bonded to HMCs were observed at 120°C and 220°C. A strong endothermic peak responsible for the decomposition of uncarbonated brucite, accompanied by the dehydroxylation (e.g. hydromagnesite) and decarbonation (e.g. nesquehonite) of HMCs was observed at around 370°C to 420°C. This was followed by a broader peak corresponding to the decarbonation of HMCs at about 720°C. The three main decomposition steps of all samples were consistent with the patterns as presented and summarized below.

15 **[00290]** 50 to 300°C: Dehydration of water bonded to HMCs (e.g. nesquehonite, hydromagnesite and dypingite), as shown in equation (i).



[00292] 300 to 500°C: Decomposition of uncarbonated brucite (equation (ii)), dehydroxylation of HMCs such as hydromagnesite and dypingite (equation (iii)) and decarbonation of HMCs such as nesquehonite (equation (iv)).



[00296] 500 to 900°C: Decarbonation of HMCs, as shown in equation (iv).

25 **[00297]** The mass loss values observed at each step, along with the total mass loss, which represented the content of hydrate and carbonate phases within each sample, are listed in table 15 below.

[00298] Table 15 - Mass Loss and Carbonation Ratios of All Samples Obtained by TGA after 14 days of Curing

Sample	Mass Loss (wt%)						R _{CO2}
	50°C to 300°C	300°C to 500°C	500°C to 900°C	Brucite	HMCs	Total	
H ₂ O.S0	8.13	27.41	2.79	16.41	21.92	38.33	0.082

H ₂ O.S0.5	10.89	28.16	2.66	13.52	28.19	41.71	0.134
H ₂ O.S1.0	11.13	27.22	2.68	9.28	31.75	41.03	0.161
HA.S0	8.44	27.87	2.62	10.35	28.58	38.93	0.126
HA.S0.5	10.16	27.52	2.37	10.52	29.53	40.05	0.133
HA.S1.0	10.54	27.68	2.77	10.84	30.15	40.99	0.125

[00299] A majority of the mass loss in all samples was recorded in the 300°C to 500°C temperature range, which was associated with several reactions involving the decomposition of uncarbonated brucite, and the dehydroxylation and decarbonation of various HMCs. Differentiation between the mass loss due to the decomposition of HMCs and that of brucite was made by subtracting the mass loss due to the decomposition of uncarbonated brucite (i.e. calculated from the brucite content in table 14) from the total mass loss.

[00300] In line with the XRD results, the introduction of HA led to improvements in the carbonation of RMC samples, which could be observed via a comparison of HA.S0 with the control sample (H₂O.S0). The mass loss due to the decomposition of HMCs within these samples increased by 31% with the use of HA. The inclusion of 0.5 wt% and 1 wt% seeds also led to enhanced carbonation within H₂O.S0.5 and H₂O.S1.0 samples, which was reflected by an up to 45% increase in the mass loss due to HMCs within these samples when compared to the control sample. These mass loss values included the decomposition of small amount of seeds in addition to the carbonate phases that formed during the curing process. These findings were consistent with the uncarbonated brucite contents calculated via XRD analysis as described above, showing variations in the role of seeds depending on the presence of HA. In general, the lower unhydrated MgO contents, coupled with the higher degree of carbonate formation demonstrated by the phase quantification results, confirmed the contribution of HA and seeds in improving the hydration and carbonation capability of RMC formulations.

[00301] **Example 5h: CO₂ Sequestration Test Results for Samples of Example 5a**

[00302] The improvements in the amount of CO₂ absorbed by each sample incorporating the use of HA and/or seeds were demonstrated through the quantification of the CO₂ sequestration ratio (R_{CO2}), which was calculated as shown in

the equation below, where P_{CO_2} is the percentage of CO_2 sequestered (i.e. obtained by subtracting the mass loss associated with the loss of H_2O from the total mass loss between $300^\circ C$ and $900^\circ C$) and P_{RMC} is the percentage of final mass at $900^\circ C$ (i.e. residual MgO). These figures involved the slight mass loss due to the decomposition of seeds during thermal analysis.

[00303] $R_{CO_2} = P_{CO_2} / P_{RMC}$

[00304] The results listed in table 15 indicated that the addition of seeds increased the CO_2 sequestration ratio of the control sample by up to 96%, which increased with increasing seed content. Similar to the use of seeds, the inclusion of HA without any seeds in sample HA.S0 improved the CO_2 sequestration of the control sample by 54%. The increased CO_2 sequestration of samples including HA and/or seeds enabled a more extensive formation of HMCs that filled up the pore spaces and established a strong network, which was also evident from the significantly reduced water absorption values (table 13) and higher compressive strength results (FIG. 3).

[00305] **Example 5i: Results of Microstructural Analysis for Samples of Example 5a**

[00306] FIG. 6a to FIG. 6d show the BSE images of selected samples after 14 days of carbonation. As observed from the images, the hydration and carbonation products mostly formed on the surface of MgO particles (about 30 to 40 μm). The porous structure of the control sample ($H_2O.S0$), in which large pore spaces (more than 10 μm) were observed (FIG. 6a), differed from the other samples. In contrast, the inclusion of seeds and HA individually led to denser microstructures with smaller pore spaces (less than 4 μm) in samples $H_2O.S0.5$ (FIG. 6b) and HA.S0 (FIG. 6c), respectively. The hydration and carbonation products surrounding the spherical seeds (diameter of about 2 to 5 μm) of sample $H_2O.S0.5$ shown in FIG. 6b proved the role of seeds in enabling the nucleation of brucite away from the original MgO particles and extending the amount of contact surface area between brucite and the diffused CO_2 . On the other hand, when compared to the control sample, the increased formation of hydrate and carbonate phases within the pore spaces in addition to the surface of MgO particles confirmed the role of HA in promoting the dissolution of MgO and leading to the formation of hydration products with a bulk structure within sample HA.S0 shown in FIG. 6c. The increase in the extent of hydration and

carbonation associated with the use of seeds and HA led to unhydrated MgO particles with smaller sizes (less than 10 μm) as well as diminished pore spaces (less than 4 μm). The simultaneous use of seeds and HA within sample HA.S0.5 shown in FIG. 6d revealed the densest microstructure amongst all samples, which contained the smallest amount of pores (less than 3 μm). This reduction in the amount of pore spaces for sample HA.S0.5 was in line with its mechanical performance and phase quantification results presented earlier.

[00307] FIG. 7a to FIG. 7c and FIG. 8a to FIG. 8c show the morphology of H₂O and HA samples after 14 days of carbonation, respectively. Needle-like nesquehonite and disk/rose-like hydromagnesite/dypingite, which were the main sources of strength development in RMC formulations, were observed in all samples. The disk- or rose-like hydromagnesite/dypingite crystals that formed due to the carbonation process could be distinguished from the hydromagnesite seeds included within the initial mix, which possessed a round ball-like morphology, as indicated earlier in FIG. 1. HA samples generally presented dense microstructures with firmly blended nesquehonite layers, whereas a mix of hydromagnesite/dypingite along with nesquehonite needles were observed within H₂O samples. The dense microstructures generated by the use of HA could be associated with the role of HA in enhancing the hydration and subsequent carbonation reactions, thereby increasing the formation of carbonate phases.

[00308] The unseeded samples H₂O.S0 and HA.S0 (FIG. 7a and FIG. 8a) showed similar microstructures composed of carbonates with identical morphologies. In these samples, agglomeration of hydromagnesite/dypingite disks in a rose-like form with a diameter of about 1.5 to 2 μm was observed to grow on the surface of nesquehonite needles with a diameter of about 1 μm . The use of HA enabled the formation of firmly bonded nesquehonite needles that led to the densification of the microstructure. The inclusion of seeds to provide additional nucleation sites for the formation of carbonate phases resulted in variations in the morphologies of HMCs and the overall microstructures of H₂O and HA samples when compared to those of the unseeded samples. The role of seeds in providing nucleation sites for the formation of HMCs was observed in H₂O.S0.5, H₂O.S1.0, HA.S0.5 and HA.S1.0 samples including 0.5 wt% to 1 wt% of seeds. In addition to the carbonate phases that formed as a result of

the curing process, round hydromagnesite seeds with a diameter of about 1 to 7 μm (FIG. 1) were observed within the seeded samples.

[00309] While the absence of HA in sample H₂O.S0.5 revealed the formation of disk-like hydromagnesite/dypingite with a diameter of about 1.5 to 2 μm along with nesquehonite needles surrounding the seed particles (FIG. 7b), the introduction of HA in sample HA.S0.5 (i.e. involving the simultaneous use of HA and seeds) led to the formation of large nesquehonite needles that nucleated and grew on the seed surfaces dispersed within the pore spaces (FIG. 8b). The vast formation of large nesquehonite crystals within this sample was facilitated via the use of seeds that established a bond between these carbonates, thereby enabling the densification of the microstructure via the formation of nesquehonite “plates”, which were a combination of individual needles. In addition to their active role in stimulating the formation of HMCs by providing additional nucleation sites, the seed particles served as micro-aggregates that filled in the initially available pore space. These improvements in the microstructure could explain the improved mechanical performance of samples involving the use of HA and seeds.

[00310] Increasing the seed content to 1 wt% in sample H₂O.S1.0 led to the dense formation of nesquehonite, which reduced the overall porosity. The presence of seeds was obvious from the widely observed seed particles, with diameters of about 6 μm , on top of the nesquehonite needles (FIG. 7c). As observed earlier, the introduction of seeds in the pore spaces enhanced the overall carbonation process by providing extra surface for the continuation of the reaction and induced a filling effect that increased the overall density via their functioning as micro-aggregates amongst the carbonate crystals. These observations were in line with the reduction in the water absorption values and increase in the strength of H₂O samples with the introduction of seeding. Alternatively, increasing the seed content to 1 wt% in sample HA.S1.0 demonstrated an excessive presence of seeds, with diameters of about 1 to 2 μm , partially covering the nesquehonite needles (FIG. 8c). This could be due to the reduction in the available pore spaces via the higher degree of brucite formation within HA samples, thereby leaving a limited area for the dispersion of seeds throughout the sample microstructure. Within these constraints, the excessive usage of seeds, which themselves have limited bonding properties, may have led to the reduction of the

bonding strength between the carbonate phases and aggregates, thereby explaining the lower strengths of HA.S1.0 when compared to HA.S0.5 after 14 days of carbonation.

[00311] Example 5j: Summary of Results for Samples of Example 5a

[00312] In RMC-based concrete formulations, the formation of an initial layer of hydrates and/or carbonates can slow down the continuation of hydration and carbonation by establishing a physical barrier that prevents further contact between unreacted $\text{MgO}/\text{Mg}(\text{OH})_2$ with $\text{H}_2\text{O}/\text{CO}_2$. These limitations can result in large amounts of unreacted MgO and $\text{Mg}(\text{OH})_2$, which translate into relatively low strength gain and porous microstructures. Example 5a aimed to improve the hydration, carbonation and associated mechanical performance of RMC-based concrete formulations. This was achieved via the enhancement of the hydration process through the use of a HA (e.g. magnesium acetate, $(\text{CH}_3\text{COO})_2\text{Mg}$ at a concentration of 0.05 M) and the improvement of carbonation through the inclusion of carbonate seeds. The samples were subjected to carbonation under a CO_2 concentration of 10 wt% for up to 28 days and tested for their water absorption, compressive strength, reaction degree, phase formations as well as microstructural development. The overall results indicated that the addition of HA and/or seeds significantly improved the hydration, carbonation and strength of the samples.

[00313] The main contribution of the presence of HA was its role in promoting the dissolution of MgO and increasing the formation of hydration products with a bulk structure. This improvement in the hydration process translated into higher amounts of well dispersed brucite available for carbonation within the pore space. The introduction of seeds not only enabled the nucleation of brucite away from the original MgO particles, but also extended the amount of contact surface area between the Mg-phases and diffused CO_2 . Moreover, seeds acted as micro-aggregates that filled the pore spaces and enabled the vast formation of firmly bonded large nesquehonite crystals, whose combination established dense carbonate clusters. The carbonate clusters derived from, e.g. the nesquehonite crystals, may comprise strong networks of interconnected and well-developed crystals. The nesquehonite crystals may be, for example, particles comprising an elongated shape. The particles may be disposed on the hydrated magnesium carbonate seed particles. These improvements

led to an increased utilization rate of RMC via enhanced hydration and carbonation reactions.

[00314] The increase in the carbonation, coupled with the densification of the microstructure via the formation of a strong network composed of large carbonate crystals, e.g. the nesquehonite crystals mentioned above, having improved morphologies, facilitated the strength development of RMC formulations involving the use of HA and/or seeds. The enhancement of the reaction degrees was reflected as 28-day water absorption values as low as 0.85% (i.e. 56% lower than the control sample) and strengths as high as 70 MPa (i.e. 46% higher than the control sample). Therefore, introduction of HA and seeding not only significantly increased the compressive strength of samples by increasing their CO₂ sequestration capabilities, but also enabled reduced material usage and shorter curing durations by improving the utilization degree of RMC and facilitating early strength development.

[00315] **Example 6a: Effect of HA and High Temperature Pre-curing**

[00316] The effects of high temperature pre-curing (HTPC) were investigated. For this example, the RMC of example 1 was used. Magnesium acetate was used as the HA. The samples were prepared by mixing the solutions (with or without HA) and RMC at a mass ratio of 0.55. The samples were subjected to 30°C (labelled as “H₂O” and “HA”) and 60°C (labelled as “H₂Ot60” and “HA_t60”). The prepared samples were then cast into 50x50x50 mm cubic moulds, consolidated by a vibrating table and trowel finished. All samples were de-moulded after 24 hours. Seeds were not used in this example.

[00317] HTPC was applied for 1 day (samples labelled as “H₂Ot60d1” and “HA_t60d1”) or 2 days (samples labelled as “H₂Ot60d2” and “HA_t60d2”) under 60°C, 75% to 85% relative humidity and ambient (0.04 vol%) CO₂. This was followed by accelerated carbonation under 30°C, 75% to 85% relative humidity and 10 vol% CO₂ until all samples reached 28 days of age (i.e. the time spent under HTPC was counted as a part of the total curing age). Meanwhile, a set of control samples that were not subjected to HTPC (samples labelled as “H₂O” and “HA”) were directly exposed to accelerated carbonation to assess the influence of HTPC conditions on the samples. The samples’ design and curing conditions are listed in table 16 below.

[00318] Table 16 – Samples for Investigation of under HTPC

Sample	Solution	HTPC Conditions		Carbonation Conditions	
		Temperature (°C)	Duration (Days)	Temperature (°C)	Duration (Days)
H ₂ O	H ₂ O	-	0	30	28
H ₂ Ot60d1		60	1		27
H ₂ Ot60d2			2		26
HA	HA (0.05 M)	-	0		28
HAt60d1		60	1		27
HAt60d2			2		26

[00319] Example 6b: Effect of HA and High Temperature Pre-curing (Isothermal Calorimetry Results)

[00320] FIG. 23a and FIG. 23b show the heat flow and the cumulative heat of samples over 48 hours of hydration, respectively. As seen in FIG. 23a, dissolution occurred a few minutes after mixing for all samples. The dissolution of samples hydrated at 60°C (H₂Ot60 and HAt60) was much more rapid than that of the corresponding pastes hydrated at 30°C (H₂O and HA). The heat flow curves also indicated the acceleration in the hydration of MgO with the use of HA, regardless of the temperature of hydration. The significantly higher exothermic peaks of samples HA, H₂Ot60 and HAt60 when compared to the control sample (H₂O) confirmed the role of HA and curing temperature in enhancing the hydration of MgO. Amongst these improvements, increasing the temperature from 30 to 60°C led to much sharper and higher initial hydration peak than the use of HA. This was an indication of the higher rate of MgO dissolution within samples subjected to slightly elevated temperatures during the initial stages of hydration.

[00321] The cumulative heat curves in FIG. 23b clearly indicated that the lowest hydration degree was revealed by the control sample (H₂O). The introduction of HA and/or the elevation of hydration temperature significantly accelerated the overall hydration process. Despite its lower hydration degree at initial stages, the HA sample achieved a slightly higher degree of hydration than the H₂Ot60 sample after 40 hours. This is a clear indication that although increasing the temperature accelerates the initial rate of hydration, the addition of HA provides a gradual and continuous

increase in hydration, thereby leading to similar or higher hydration degrees in the longer periods. This was reinforced by the simultaneous inclusion of the HA and temperature increase within the HAt60 sample, which achieved the highest cumulate heat amongst all samples during the entire course of hydration.

5 **[00322] Example 6c: Effect of HA and High Temperature Pre-curing (Hydration Degree)**

[00323] FIG. 24 demonstrates the hydration degree of all samples at 30°C and 60°C under sealed conditions (i.e. to prevent carbonation) over a period of 7 days. The results were consistent with those of the isothermal calorimetry analysis. The use of
10 HA and the increase of temperature both resulted in an obvious increase in the hydration degree of the prepared samples at all durations. The control sample (H₂O) revealed a hydration degree of 52% at 1 day, at which the corresponding hydration degrees of the HA, H₂Ot60 and HAt60 samples were 62%, 73% and 80%, respectively. Similar to the isothermal calorimetry results, although it started lower,
15 the HA sample achieved a similar hydration degree as the H₂Ot60 sample at 3 days (76%), after which it even revealed a slightly higher hydration degree than H₂Ot60 at 7 days (80% vs. 78%). The simultaneous inclusion of the HA at elevated temperatures (60°C) within the HAt60 sample promoted the hydration process and increased the hydration degree of the control sample by about 52% just after 1 day of hydration,
20 reaching a maximum value of 80%. A continuous trend was observed at 3 and 7 days, at which the hydration degree of the control sample was increased by up to 21% (from 67 to 81%) and 13% (from 73 to 83%) via the inclusion of HA and HTPC, respectively. The introduction of HA ((CH₃COO)₂Mg) improved the hydration of MgO as the presence of CH₃COO⁻ promoted the dissolution of MgO while the
25 additional Mg²⁺ favoured the increased precipitation of brucite. The precipitation of brucite within the bulk solution was also supported by the migration of the complex magnesia-acetate ions (CH₃COOMg⁺), which formed at the intermediate stage, away from their original locations. This resulted in an increase in the amount of space available for the continuous hydration of MgO, which can be inhibited in the control
30 sample by the initial precipitation of brucite. On the other hand, the increased temperature used during HTPC enhanced the diffusion of water into inner MgO grains, enabling its further and more rapid dissolution. The simultaneous inclusion of HA and

HTPC improved the diffusion rate and extent of HA, thereby significantly enhancing the dissolution and precipitation of brucite. This significant improvement resulted in the formation of a higher amount of brucite available for carbonation.

[00324] Example 6d: Effect of HA and High Temperature Pre-curing (Density and Water Absorption)

[00325] FIG. 25 shows the density development of concrete samples subjected to accelerated carbonation under a CO₂ concentration of 10 vol% up to the age of 28 days. The initial densities of all samples ranged between 2.12 and 2.15 g/cm³. Those samples subjected to HTPC showed lower densities within the first 3 days due to the low ambient CO₂ concentration used during the HTPC (0.04 vol%) for 1 or 2 days as opposed to the other samples that were directly subjected to accelerated carbonation at 10 vol% CO₂ right after casting. The inclusion of HA, along with the use of HTPC led to higher densities than the control sample at 7 days onwards. Samples including HA (HA, HAt60d1 and HAt60d2) achieved higher densities than corresponding samples without HA (H₂O, H₂Ot60d1 and H₂Ot60d2) regardless of age, which was consistent with the isothermal calorimetry and hydration degree results. HAt60d1 and HAt60d2 samples achieved the highest densities of 2.32 g/cm³ at the end of 28 days, which was 5% higher than the density of the corresponding control sample (2.22 g/cm³). This increase in density could be attributed to the higher degree of hydration within these samples.

[00326] The increased amount of Mg(OH)_{2(aq,s)} formation was followed by the enhanced carbonation process, which led to the dense formation of a range of HMCs that filled in the available pore spaces. This reduction in porosity via the expansive formation of HMCs can explain the increase in density observed.

[00327] Table 17 below shows the water absorption and corresponding standard deviation values of concrete samples at 14 days.

[00328] Table 17 – Water Absorption of Samples at 14 Days

Sample	Water Absorption (%)	Standard Deviation (%)
H ₂ O	4.01	0.16
H ₂ Ot60d1	3.21	0.20
H ₂ Ot60d2	2.35	0.25

HA	2.32	0.23
HAt60d1	1.76	0.19
HAt60d2	2.01	0.20

[00329] The inclusion of HA or the use of HTPC led to lower water absorption values than the control sample, whose absorption was recorded as 4.01% after 14 days of accelerated carbonation. Subjecting the samples to 1 and 2 days of HTPC led to a
5 reduction of about 20% and about 41% in the water absorption values, respectively. The inclusion of HA also reduced the water absorption by up to about 42%, resulting in a low value of 2.32%. The inclusion of HA alone without HTPC had a similar effect as subjecting the H₂O samples to HTPC for 2 days. This was attributed to the increase in the density of samples enabled by the enhanced hydration of MgO with the
10 introduction of HA and/or HTPC. The increased amount of Mg(OH)_{2(aq,s)} formation promoted carbonation and associated HMC formation, which in turn led to denser microstructures.

[00330] Regardless of the initial curing conditions, samples containing HA absorbed less water than corresponding H₂O samples. Although the implementation of HTPC
15 also reduced the water absorption of samples with and without HA, the use of HA demonstrated to be more effective on decreasing water absorption. Consistent with the isothermal calorimetry and hydration degree results, the simultaneous use of HA and HTPC reduced the water absorption of the control sample by up to about 56% and led to the smallest value of 1.76%, which could be explained by the corresponding
20 increase in the density of these samples.

[00331] Example 6e: Effect of HA and High Temperature Pre-curing (Compressive Strength)

[00332] The compressive strength of samples cured for up to 28 days is presented in FIG. 26. An increase in the compressive strength of all samples with age was
25 observed. Samples including HA (HA, HAt60d1 and HAt60d2) achieved higher strengths than corresponding samples without HA (H₂O, H₂Ot60d1 and H₂Ot60d2) at all ages. Inclusion of HA led to 28-day strengths of about 48 MPa and 56 MPa, with and without HTPC, respectively. These values were up to 40% higher than the corresponding strength of the control sample (40 MPa). Samples subjected to HTPC

(H₂Ot60d1, H₂Ot60d2, HAt60d1 and HAt60d2) generally indicated lower initial (3-day) strengths, which was due to the low CO₂ concentration (0.04 vol%) they were exposed to during the 1 to 2 days of HTPC. However, these samples more than made up for this initial low strength within 7 days of curing, at which they achieved similar or higher strengths than the corresponding H₂O and HA samples. Samples containing HA and/or subjected to HTPC indicated a continuous increase in strength after the first 7 days, which was slower for the control sample. This continuous strength gain was attributed to the increased rate and degree of hydration that enabled the higher availability of Mg(OH)_{2(aq,s)} for subsequent carbonation reaction.

[00333] The compressive strength of the control sample (H₂O) was recorded as 26 MPa, 29 MPa and 40 MPa after 7, 14 and 28 days, respectively. The use of HTPC resulted in an increase in the strength of the control sample by up to about 41% and 35% at 14 and 28 days, achieving 41 MPa and 54 MPa, respectively. The inclusion of HA without HTPC produced up to about 31%, 59% and 20% higher strengths than the control sample at 7 days (34 MPa vs. 26 MPa), 14 days (46 MPa vs. 29 MPa) and 28 days (48 MPa vs. 40 MPa), respectively. The simultaneous use of HA and HTPC for HAt60d1 and HAt60d2 samples led to strengths as high as 45 MPa and 50 MPa at 14 days, which were about 55% and about 70% higher than the corresponding strengths of the control sample (H₂O), respectively. These samples demonstrated a continuous increase in strength up to 28 days, leading up to 56 MPa in strength, which corresponded to a 40% increase in comparison to the control sample.

[00334] Among samples subjected to HTPC (H₂Ot60d1, H₂Ot60d2, HAt60d1 and HAt60d2), the use of HA showed a considerable improvement in strength at the age of 14 days as the compressive strengths of HAt60d1 (45 MPa) and HAt60d2 (50 MPa) samples were up to about 30% higher than those of H₂Ot60d1 (35 MPa) and H₂Ot60d2 (41 MPa) samples. The rate of this improvement slowed down at the age of 28 days at which the compressive strengths of HAt60d1 (52 MPa) and HAt60d2 (56 MPa) samples were slightly higher than those of H₂Ot60d1 (49 MPa) and H₂Ot60d2 (54 MPa) samples.

[00335] These results clearly indicated the high strength gain capacity of RMC-based samples when subjected to the appropriate curing conditions. The use of HA or HTPC independently provided equivalent strengths to the 28-day strength of the control

sample after only 7 days of curing, thereby shortening the curing period by up to 75%. The simultaneous use of HA and HTPC not only achieved 28-day strengths as high as 56 MPa, but also enabled fast strength gain by revealing 21 MPa only after 2 days of curing under 10 vol% CO₂. These results highlighted the ability of these formulations to be used in a range of applications without necessitating any long curing periods.

[00336] Example 6f: Effect of HA and High Temperature Pre-curing (XRD Results)

[00337] XRD patterns of all samples at the age of 14 days are presented in FIG. 27. Peaks of HMCs such as nesquehonite, dypingite and hydromagnesite were observed as a result of the carbonation process. In addition to HMCs, all samples indicated the presence of residual MgO (main peak at 42.9° 2θ) and brucite (main peak at 38.1° 2θ). The use of HTPC led to the increased hydration of MgO and the extensive formation of brucite in all samples, which was in agreement with the hydration degree results. The contents of unhydrated MgO and uncarbonated brucite were calculated in reference to the fluorite that was included as a standard in all samples.

[00338] Table 18 below shows the unhydrated MgO and uncarbonated Mg(OH)₂ contents within all samples after 14 days of curing.

[00339] Table 18 – MgO and Mg(OH)₂ Contents Obtained by XRD at 14 Days

Sample	MgO (wt%)	Mg(OH) ₂ (wt%)
H ₂ O	18.26	57.13
H ₂ Ot60d1	10.42	59.08
H ₂ Ot60d2	8.91	50.07
HA	16.65	44.21
HA _t 60d1	8.01	55.94
HA _t 60d2	6.09	63.13

[00340] The control sample revealed a higher unhydrated MgO content (18.3%) than all other samples with HA and/or HTPC. This high unutilized MgO content can explain the lower strengths obtained by the control sample. This was consistent with the hydration degree results and proved the active role of HA and HTPC in improving the conversion of MgO into Mg(OH)_{2(aq,s)}. Subjecting the samples to HTPC for 1 or 2 days resulted in the further utilization of MgO and revealed uncarbonated MgO

contents as low as 8.9%. The amount of residual MgO reduced as the HTPC duration increased from 1 to 2 days for all samples, indicating the effective role HTPC played on the progression of the hydration process. A similar trend was observed with the use of HA, which reduced the amount of residual MgO more than those observed within the corresponding H₂O samples. The simultaneous use of HA and HTPC proved to be the most efficient method of utilizing MgO, revealing the lowest MgO content of 6.1% amongst all samples.

[00341] The increased hydration of MgO was reflected as a higher brucite content available for carbonation within the HA and HTPC samples. All samples revealed relatively high residual brucite contents ranging between 44% and 63%. Most HA and HTPC samples indicated lower brucite contents than the control sample, which could be an indication of increased carbonation. Regardless of their composition, the conversion rate of brucite into strength providing HMCs via carbonation could be higher in all samples. This highlights the potential of these samples to reveal even higher strength results if their design and curing conditions were further developed to enable higher carbonation.

[00342] Example 6g: Effect of HA and High Temperature Pre-curing (TGA Results)

[00343] The mass loss and heat flow data of all samples at the age of 14 days after accelerated carbonation are presented in FIG. 28. In addition to the decomposition of HA that may have resulted in minor mass losses, the three main decomposition steps are summarized in FIG. 12b.

[00344] According to the heat flow data, the two endothermic peaks corresponding to the dehydration of water bonded to HMCs were observed at 120°C and 220°C. A strong endothermic peak responsible for the decomposition of uncarbonated brucite, accompanied with the dehydroxylation of HMCs (e.g. hydromagnesite) was observed at about 380°C. This was followed by a broader peak corresponding to the decarbonation of HMCs at about 700°C. The quantification of hydrate and carbonate phases within each sample was enabled by the calculation of mass losses at each of these peaks.

[00345] Table 19 summarizes the mass loss observed within the samples at each step, along with the total mass loss.

[00346] Table 19 – Mass loss and CO₂ Sequestration Capacity of Samples Obtained by TGA at 14 Days

Sample	Mass Loss (wt%)						Seq _{CO2} (%)
	50-300°C	300-500°C	500-900°C	Brucite	HMCs	Total	
H ₂ O	7.60	26.97	4.87	17.73	21.71	39.44	23.30
H ₂ Ot60d1	10.59	29.16	4.53	18.34	25.94	44.28	27.55
H ₂ Ot60d2	10.83	28.98	4.73	15.54	29.00	44.54	32.76
HA	11.56	27.90	4.56	13.72	30.30	44.02	33.48
HAt60d1	8.51	28.90	4.47	17.36	24.52	41.88	27.54
HAt60d2	7.16	28.50	4.72	19.59	20.79	40.38	22.86

[00347] The mass loss due to the decomposition of HMCs was calculated by subtracting the mass loss of brucite, whose content was determined by XRD analysis, from the total mass loss of each sample. These results indicate that a majority of the mass loss is observed in the 300 to 500°C temperature range, which is associated with 3 main reactions attributed to the: (i) dehydroxylation of hydromagnesite and dypingite, (ii) decarbonation of nesquehonite and (iii) decomposition of uncarbonated brucite. When compared to the control sample (H₂O), HA and HTPC samples generally revealed higher HMC contents. The approximate 22% mass loss corresponding to the HMC content within the control sample was increased by up to 40% with the inclusion of the HA. A similar effect was observed with most of the HTPC samples. The increase in the HMC contents can be attributed to the enhancement of MgO hydration with the introduction of HA or HTPC, resulting in the increased precipitation of Mg(OH)_{2(aq,s)} available for carbonation. The higher total mass losses associated with the decomposition of HMCs and brucite demonstrated by the HA and HTPC samples can also explain their higher strengths. These samples achieved higher total mass losses, proving the active role of HA and HTPC in improving hydration and carbonation.

[00348] Although the elevated temperatures used during HTPC increased the brucite content of the HA sample as observed by the hydration degree results, the mass loss due to the decomposition of HMCs within the HAt60d1 and HAt60d2 samples was less than that of the HA sample (i.e. about 21 to 25% vs. about 30%). This may be due to the accelerated dissolution and precipitation of brucite with the introduction of HTPC to the HA sample, leading to the rapid crystallization of brucite at 60°C. The

carbonation of $\text{Mg}(\text{OH})_{2(\text{aq})}$ takes place more readily than crystalline brucite, which is inhibited by the surface reaction. This can explain the higher HMC content within the HA sample, where the carbonation reaction took place in aqueous media rather than the crystalline brucite within the HAt60d1 and HAt60d2 samples, which revealed hydration degrees higher than 80% (FIG. 24). This phenomenon was not observed in the H₂Ot60d1, H₂Ot60d2 and H₂O samples because of their relatively lower hydration rates.

[00349] Example 6h: Effect of HA and High Temperature Pre-curing (Attenuated Total reflectance (ATR)-FTIR Results)

[00350] The ATR-FTIR spectra of all samples at the age of 14 days after accelerated carbonation are presented in FIG. 29. The results confirmed the formation of HMCs observed via the presence of the hydroxyl group and H₂O molecules at 3690 cm^{-1} (-OH stretching band) and CO_3^{2-} bands at 1420 to 1480, 1100, 850 and 792 cm^{-1} . A split band at 1420 to 1480 cm^{-1} was ascribed to CO_3^{2-} asymmetric stretching vibration (ν_3 mode). Absorption bands at 1100 and 850 cm^{-1} were assigned to CO_3^{2-} symmetric stretch (ν_1 mode) and CO_3^{2-} bending (ν_2 mode), respectively. A shift in the band corresponding to the antisymmetric bending (ν_4 mode) located at 780 cm^{-1} within the control sample to 792 cm^{-1} within the HA and HTPC samples was observed. The FTIR results were consistent with the XRD and TGA results, revealing carbonation bands with much higher intensities within H₂Ot60d1, H₂Ot60d2 and HA samples than the control sample.

[00351] Example 6i: Effect of HA and High Temperature Pre-curing (Microstructural Analysis)

[00352] FIG. 30a to FIG. 30c. and FIG. 31a to FIG. 31c show the microstructures of the H₂O (H₂O, H₂Ot60d1, H₂Ot60d2) and HA (HA, HAt60d1, HAt60d2) samples at the age of 14 days after accelerated carbonation, respectively. Needle-like nesquehonite and disk-like hydromagnesite/dypingite, whose formation led to strength gain, were the main carbonate phases observed. The presence of these carbonates in the HA and HTPC samples were more prominent than those observed in the control sample. This could be an indication of improvement of the morphology of RMC formulations with the introduction of HA and HTPC. Disk-like formation of hydromagnesite/dypingite (diameter about $0.6\text{ }\mu\text{m}$, thickness less than $0.1\text{ }\mu\text{m}$) was

observed after carbonation of the control sample (FIG. 30a). The use of HTPC resulted in an increase in the amount of $\text{Mg}(\text{OH})_2$, which promoted the carbonation process and led to denser microstructures within the $\text{H}_2\text{Ot60d1}$ and $\text{H}_2\text{Ot60d2}$ samples as seen in FIG. 30b and FIG. 30c, respectively. Along with the dense formation of hydromagnesite/dypingite (diameter about $1.3\ \mu\text{m}$, thickness less than $0.1\ \mu\text{m}$), the needle-like nesquehonite (diameter about $0.5\ \mu\text{m}$) was also observed in the $\text{H}_2\text{Ot60d1}$ sample (FIG. 30b). A similar morphology composed of nesquehonite (diameter about $0.6\ \mu\text{m}$, length about $2.5\ \mu\text{m}$) and hydromagnesite/dypingite (diameter about $1.5\ \mu\text{m}$, thickness less than $0.1\ \mu\text{m}$) was observed in the $\text{H}_2\text{Ot60d2}$ sample (FIG. 30c). The widespread formation of nesquehonite provided a connection between the hydrate and carbonate crystals to form a compact and interconnected network, resulting in a denser microstructure, which corresponded to higher strengths.

[00353] The inclusion of HA led to a significant improvement in the morphology of carbonate phases, as seen in FIG. 31a to FIG. 31c. Hydromagnesite/dypingite with a diameter of up to about $1.0\ \mu\text{m}$, almost twice as large as those forming after the carbonation of the control sample, was observed. The hydromagnesite/dypingite was accompanied by a dense cluster of nesquehonite crystals (diameter about $0.5\ \mu\text{m}$) firmly blended together, as seen in FIG. 31a. The use of HA and HTPC led to significant improvement in the morphology of the carbonate phases (FIG. 31a to FIG. 31c). The use of HTPC for HA samples led to morphologies primarily composed of long needle-like nesquehonite, as seen in FIG. 31b and FIG. 31c. The formation of nesquehonite with a diameter of about $0.5\ \mu\text{m}$ and a length up to about $10\ \mu\text{m}$ was observed in the HAt60d1 sample (FIG. 31b). In line with the strength results, the carbonation of HAt60d2 indicated the largest phase formations and interconnected network-like structures as opposed to the other samples. Much larger needles of nesquehonite (diameter about $1\ \mu\text{m}$, length about $10\ \mu\text{m}$) than those observed in other samples was revealed in FIG. 31c. The larger morphologies of HMCs within HA and HTPC samples could be attributed to the higher brucite concentrations within these samples, which enabled the linking of carbonate crystals to form larger clusters. This extensive formation of large nesquehonite needles explains for the higher strengths of HAt60d2 than all other samples.

[00354] The morphologies presented in this example clearly indicated the co-existence of different HMCs within the same samples. The formation of nesquehonite was observed within samples subjected to HTPC at 60°C. A much extended network of nesquehonite crystals was abundant within HA samples, in which firmly connected nesquehonite formed a compact and interlocked network structure. This explains for the improved mechanical performance of these samples when compared to the control sample, where the loose network structure of disk-like hydromagnesite/dypingite dominated. The elongated morphology of nesquehonite reduced the initial pore spaces by filling up the available pore structure. It also contributed to the enhancement of stiffness and strength gain by binding the carbonate network into a densely packed cluster. Overall, the development of the compact and interlocked network-like structure via the formation of interconnected and well-developed nesquehonite crystals played a key role in determining the mechanical performance of the developed formulations.

[00355] **Example 6j: Discussion on Effect of HA and High Temperature Pre-curing**

[00356] This study investigated the role of HA and HTPC in enhancing the hydration and subsequent carbonation processes within RMC based concrete formulations. The final results demonstrated by samples with a range of compositions cured under different conditions were reported and compared in terms of their microstructure and mechanical performance. Some of the main findings are discussed below.

[00357] The reaction of MgO with H₂O under ambient conditions is relatively limited due to its low dissolution (FIG. 23), resulting in a hydration degree of only 52% after 1 day (FIG. 24). The introduction of HA ((CH₃COO)₂Mg at a concentration of 0.05 M) or the use of HTPC (60°C for 1 to 2 days) individually led to an up to 40% rise in the hydration degree of MgO. This value was increased by 52% through the simultaneous implementation of HA and HTPC. The improvement in the hydration of MgO through the implementation of HTPC and/or the introduction of HA also resulted in a more extensive carbonation due to the extra Mg(OH)_{2(aq,s)} available. The CO₂ sequestration capability (SeqCO₂) of each sample listed in table 19 was calculated by the equation below, where m_{CO2} is the percentage of CO₂ sequestered and m_{RMC} is the percentage of the final mass at 900°C.

[00358] $\text{Seq}_{\text{CO}_2} = m_{\text{CO}_2}/m_{\text{RMC}} \times 100\%$

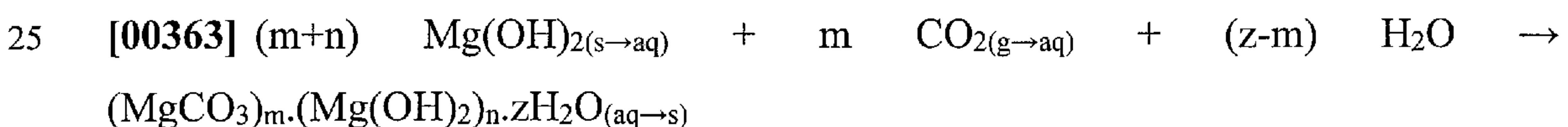
[00359] In the presence of HA, CH_3COO^- ions promoted the dissolution of MgO while the additional Mg^{2+} available favoured the increased precipitation of brucite. Furthermore, the precipitation of brucite within the bulk solution was also supported
5 by the migration of the complex magnesia-acetate ions ($\text{CH}_3\text{COOMg}^+$), which formed at the intermediate stage, away from their original locations. This increased the space available for the further hydration of MgO, which can otherwise be inhibited by the passivating layer formed by the previously precipitated brucite. The increased space enabled the dispersion of $\text{Mg}(\text{OH})_{2(\text{aq,s})}$ into the pores for the formation of the bulk
10 structure and increased the surface area available for carbonation and associated HMC formation.

[00360] While the introduction of HA significantly enhanced the hydration of MgO under sealed conditions (FIG. 24), it was not as influential within carbonated samples, as evident by the similar residual (unhydrated) MgO contents of H_2O and HA samples
15 listed in table 18 (18.3% vs. 16.7%). This could be associated with the formation of carbonate phases on the surface of MgO grains at early stages of hydration, which could prevent the further hydration of MgO. This could result in a diffusion controlled hydration process, thereby diminishing the role of HA in accelerating the dissolution of MgO. However, the extra contact surface area of the bulk structure of $\text{Mg}(\text{OH})_{2(\text{aq,s})}$
20 enabled by the introduction of HA increased the amount $\text{Mg}(\text{OH})_{2(\text{aq,s})}$ available for carbonation. This led to a reduction in the amount of uncarbonated brucite by increasing the carbonation capability of the HA sample. Additionally, the carbonation of aqueous $\text{Mg}(\text{OH})_2$ that formed within the HA sample could take place more readily than the carbonation of brucite crystals that formed within the samples subjected to
25 HTPC prior to the carbonation process. Therefore, samples in which HA was introduced achieved the highest CO_2 sequestration among all samples, which was 44% higher than the control sample (33.5% vs. 23.3%, as listed in table 19).

[00361] The implementation of HTPC enhanced the diffusion of water into inner MgO grains, enabling its rapid and further dissolution. Although samples subjected to
30 HTPC outperformed all others with their increased hydration within the first 3 days, those involving HA indicated a gradual increase in their hydration degree and demonstrated similarly high values at 3 days onwards. While the introduction of HA

increased the conversion rate and degree of MgO to Mg(OH)₂ when compared to the control sample, the increase of reaction temperature to 60°C with the implementation of HTPC for only 1 day significantly reduced the unhydrated MgO content, with and without the simultaneous use of HA (table 18). The implementation of HTPC without
 5 any HA reduced the unhydrated MgO content by up to 51% when compared to the control sample (i.e. 8.9% vs. 18.3%, as listed in table 18). This improvement in hydration could be associated with the expansion of brucite into the pore spaces and the increase in the surface area of brucite available for subsequent carbonation. Accordingly, the CO₂ sequestration ability of samples subjected to HTPC also
 10 increased by up to 41% compared to that of the control sample (i.e. 32.8% vs. 23.3%, as listed in table 19).

[00362] A similar trend regarding the promotion of hydration with the use of HTPC was observed in the presence of HA. The simultaneous inclusion of HA and HTPC in the HAt60d1 and HAt60d2 samples improved the diffusion rate and extent of
 15 hydration, thereby significantly enhancing the dissolution and precipitation of brucite. This led to the most efficient use of MgO by revealing the lowest unhydrated MgO contents among all samples. However, these samples could not maintain this performance during the carbonation process and revealed lower CO₂ sequestration capabilities than the HA sample. This was potentially attributed to the rapid
 20 precipitation and crystallization of the high brucite content in the presence of HA under the elevated temperatures used during HTPC. The additional Mg²⁺ in HA that was dissociated as shown in equation (8), could favour the rapid precipitation and crystallization of brucite. The carbonation of this rapidly crystallized brucite would take place slower than that of Mg(OH)_{2(aq)}, as described in the equation below.



[00364] Furthermore, the rapid precipitation of brucite would form an agglomerated structure rather than its bulk formation, leading to the lower diffusion of CO₂ in HAt60d1 and HAt60d2 samples when compared to the HA sample.

30 **[00365]** In RMC-based concrete formulations, the progress of hydration and carbonation is limited by the formation of hydrate and carbonate phases, which can present a physical barrier and inhibit the progress of these reactions by precipitating

on the surface of uncarbonated and unhydrated products. The high uncarbonated brucite contents revealed by all samples may suggest that the improvement of carbonation could be associated with the implementation of HA and HTPC, rather than purely by the increase of brucite content available for carbonation. The increase in the hydration degrees of samples involving the use HA was associated with the expansive formation of the bulk brucite structure that led to an increased contact surface area with the diffused CO₂, thereby promoting carbonation and HMC formation, as explained earlier. The improvement in hydration involving the use of HA and/or HTPC could also be associated with the expansion of brucite into the pore space and the increase in the surface area of brucite available for the subsequent carbonation. Furthermore, the accelerated hydration enabled by HTPC led to a higher volume expansion due to the extensive formation of brucite, which produced micro-cracks that could facilitate the diffusion of CO₂ and improve the carbonation process. The increased carbonation led to the expansive formation of HMCs within the pore space, thereby further densifying the microstructure and improving the performance of samples containing HA and/or HTPC more than the control sample.

[00366] In addition to the enhancement of hydration and carbonation mechanisms, the introduction of HA and/or HTPC into RMC formulations led to improvements in the morphologies of the prepared samples. Compared to the control sample (H₂O), larger hydromagnesite/dypingite crystals were observed in the HA sample. Dense networks of nesquehonite accompanied with large hydromagnesite/dypingite crystals resulted in the creation of denser microstructures when samples were subjected to HTPC. This was further improved with the simultaneous implementation of HA and HTPC, which revealed the formation of well-connected large needle-like nesquehonite crystals, establishing interlocked network structures. The elongated morphology of nesquehonite crystals with their 3D structures enabled the connection of the various phases and reduced the initially available pore spaces, thereby leading to higher strengths than samples in which disk-like hydromagnesite/dypingite dominated the microstructure. The morphology of carbonate phases played a key role in the determination of the final performance of the proposed formulations. The simultaneous implementation of HA and HTPC produced samples with the highest

density and strengths, which was also demonstrated by the formation of dense networks of interconnected and well-developed nesquehonite crystals.

[00367] The results clearly demonstrate that the mechanical performance of RMC-based concrete formulations is linked to the extent of the hydration and subsequent carbonation processes, as well as the morphology of the final hydrate and carbonate phases. Significant improvements in carbonation and the morphology of the resulting products were observed with the introduction of HA and/or HTPC. The formation of HMCs led to a reduction in the initial pore spaces, which was also demonstrated by the lower water absorption values and higher compressive strengths.

[00368] **Example 6k: Summary on Effect of HA and High Temperature Pre-curing**

[00369] Example 6 aimed to improve the hydration, carbonation and associated mechanical performance of RMC-based concrete formulations. This was achieved via the enhancement of the hydration process through the introduction of a HA (magnesium acetate, $(\text{CH}_3\text{COO})_2\text{Mg}$ at a concentration of 0.05 M) and HTPC (60°C for 1 to 2 days), which increased the conversion of MgO to $\text{Mg}(\text{OH})_{2(\text{aq},\text{s})}$. The prepared samples were subjected to carbonation under a CO_2 concentration of 10 vol% for up to 28 days. The rate and degree of hydration were evaluated by isothermal calorimetry and TGA. Density, water absorption and compressive strength results were used to assess the mechanical performance of the prepared concrete samples. The formation of HMCs along with the identification and quantification of various phases were performed via XRD, TGA and ATR-FTIR. The morphology of carbonate phases was observed under SEM. The following conclusions were drawn from the obtained results:

[00370] (i) The introduction of HA and/or HTPC significantly improved the dissolution of MgO and the amount of $\text{Mg}(\text{OH})_2$ precipitated. This led to an increase in the hydration degree of the prepared formulations by up to 52%.

[00371] (ii) The formation of higher amounts of $\text{Mg}(\text{OH})_{2(\text{aq},\text{s})}$ associated with volumetric expansion resulted in an increased contact surface area of $\text{Mg}(\text{OH})_{2(\text{aq},\text{s})}$ with CO_2 , leading to higher amounts of HMC formation and strength gain. The sole use of HA or HTPC increased the amount of CO_2 sequestered by up to about 44%. This was enabled by the extensive formation of brucite, which facilitated the

subsequent formation of HMCs, whose expansive formation filled in the available pore spaces and led to strength gain. Furthermore, the agglomerated formation of $\text{Mg}(\text{OH})_{2(\text{aq,s})}$ through the use of HTPC could have contributed to the formation of HMC phases with larger dimensions.

5 [00372] (iii) The incorporation of HA and HTPC led to the formation of carbonate phases with improved morphologies. The simultaneous implementation of HA and HTPC revealed the formation of well-connected large needle-like nesquehonite crystals, establishing interlocked network structures. The elongated morphology of nesquehonite crystals with their 3D structures enabled the connection of the various
10 phases and reduced the initially available pore space. This led to higher strengths than mixes in which disk-like hydromagnesite/dypingite dominated the microstructure.

[00373] (iv) The improvements in the quantity and morphology of HMCs with the introduction of HA and/or HTPC translated into a denser carbonate network, which led to enhanced mechanical performance. These samples revealed higher densities and
15 lower water absorption values than the control sample.

[00374] (v) These improvements were reflected as higher compressive strength values, which increased by up to 40% when compared to the control sample. 3-day strengths of more than 20 MPa and 28-day strengths as high as 56 MPa were achieved with the introduction of HA and HTPC, whose implementation provided equivalent
20 strengths to the 28-day strength of the control sample only after 7 days of curing, thereby shortening the curing period by up to 75%. These results highlighted the ability of the developed formulations to be used in a range of applications without necessitating any long curing periods.

[00375] The findings of example 6 indicated the significant potential of RMC-based
25 concrete samples in achieving high strengths within a few days. The strength gain of these formulations is based on the amount of CO_2 sequestered and the properties of the resulting carbonate system. As demonstrated, CO_2 sequestration and the morphology of the final carbonate phases can be enhanced through the inclusion of small amounts of HA and/or the implementation of short periods of HTPC, leading to
30 significant improvements in mechanical performance.

[00376] **Example 7: Commercial and Potential Applications**

[00377] The proposed method provides a feasible method to enhance hydration and CO₂ sequestration within RMC-based concrete formulations. The introduction of HA and seed particles significantly increases the compressive strength of concrete mixes and reduces material usage and curing durations while reaching high strengths at early
5 ages. The present method, therefore, is applicable for various building applications ranging from non-structural to structural uses, which can all benefit from efficient material usage, high performance and reduced environmental impacts.

[00378] While the invention has been particularly shown and described with reference to specific embodiments, it should be understood by those skilled in the art
10 that various changes in form and detail may be made therein without departing from the spirit and scope of the invention as defined by the appended claims. The scope of the invention is thus indicated by the appended claims and all changes which come within the meaning and range of equivalency of the claims are therefore intended to be embraced.

CLAIMS

1. A method of producing a hydrated magnesium carbonate based cement composite, the method comprising:

mixing an aqueous solution comprising a hydration agent with hydrated magnesium carbonate seed particles to disperse the hydrated magnesium carbonate seed particles throughout the aqueous solution, wherein the hydrated magnesium carbonate seed particles comprise an amount in the range of more than 0 wt% and up to 1 wt%, wherein the wt% is based on the hydrated magnesium carbonate seed particles and a magnesium oxide based cement to be contacted with the aqueous solution;

contacting the aqueous solution with the magnesium oxide based cement to form magnesium hydroxide (i) from the hydration agent and the magnesium oxide based cement, and (ii) on the hydrated magnesium carbonate seed particles; and

exposing the magnesium hydroxide to carbon dioxide to form the hydrated magnesium carbonate based cement composite.

2. The method according to claim 1, wherein mixing the aqueous solution comprises mixing the hydration agent with water before adding the hydrated magnesium carbonate seed particles.

3. The method according to claim 1 or 2, wherein mixing the aqueous solution comprises mixing the hydration agent with water to form a concentration ranging from more than 0 M to 0.1 M.

4. The method according to any one of claims 1 to 3, wherein the hydration agent comprises hydrochloric acid, magnesium acetate or magnesium chloride.

5. The method according to any one of claims 1 to 4, wherein the hydrated magnesium carbonate seed particles comprise $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$, $\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 3\text{H}_2\text{O}$, $(\text{MgCO}_3)_4 \cdot \text{Mg}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ or $(\text{MgCO}_3)_4 \cdot \text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$.
6. The method according to any one of claims 1 to 5, wherein contacting the aqueous solution with the magnesium oxide based cement comprises contacting the hydration agent with the magnesium oxide based cement at a mass ratio of 0.7:1.
7. The method according to any one of claims 1 to 6, wherein contacting the aqueous solution with the magnesium oxide based cement comprises disposing the hydrated magnesium carbonate seed particles within a plurality of pores of the magnesium oxide based cement.
8. The method according to any one of claims 1 to 7, wherein the magnesium hydroxide formed (ii) on the hydrated magnesium carbonate seed particles is disposed within the plurality of pores and away from the magnesium oxide based cement.
9. The method according to any one of claims 1 to 8, wherein exposing the magnesium hydroxide to carbon dioxide comprises subjecting the magnesium hydroxide to 10 vol% carbon dioxide at $30 \pm 1.5^\circ\text{C}$ and a relative humidity of 75% to 85% for up to 28 days.
10. The method according to any one of claims 1 to 9, wherein the hydrated magnesium carbonate based cement composite comprises magnesium oxide.
11. A hydrated magnesium carbonate based cement composite obtained by the method according to any one of claims 1 to 10, wherein the hydrated magnesium carbonate based cement composite comprises hydrated magnesium carbonate formed from a magnesium oxide based cement and hydrated magnesium carbonate seed particles, and wherein the hydrated magnesium carbonate seed particles comprise an amount of more than 0 wt% and up to 1 wt% of the magnesium oxide based cement

and the hydrated magnesium carbonate seed particles to render a denser microstructure in the hydrated magnesium carbonate based cement composite.

12. The hydrated magnesium carbonate based cement composite according to claim 11, wherein the hydrated magnesium carbonate seed particles are disposed in a plurality of pores within the hydrated magnesium carbonate based cement composite.

13. The hydrated magnesium carbonate based cement composite according to claim 11 or 12, wherein the hydrated magnesium carbonate is formed as particles comprising an elongated shape, and wherein the particles are disposed on the hydrated magnesium carbonate seed particles.

14. The hydrated magnesium carbonate based cement composite according to any one of claims 11 to 13, wherein each of the hydrated magnesium carbonate seed particles comprises a diameter of 1 μm to 7 μm .

15. The hydrated magnesium carbonate based cement composite according to any one of claims 11 to 14, further comprising hydrated magnesium carbonate formed as a layered structure or a plated structure.

16. The hydrated magnesium carbonate based cement composite according to any one of claims 11 to 15, wherein the hydrated magnesium carbonate comprises $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$, $\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 3\text{H}_2\text{O}$, $(\text{MgCO}_3)_4 \cdot \text{Mg}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ or $(\text{MgCO}_3)_4 \cdot \text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$.

17. The hydrated magnesium carbonate based cement composite according to any one of claims 11 to 16, wherein the hydrated magnesium carbonate seed particles comprise $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$, $\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 3\text{H}_2\text{O}$, $(\text{MgCO}_3)_4 \cdot \text{Mg}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ or $(\text{MgCO}_3)_4 \cdot \text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$.

18. The hydrated magnesium carbonate based cement composite according to any one of claims 11 to 17, wherein the hydrated magnesium carbonate based cement composite comprises magnesium oxide.