

CEMENTITIOUS COMPOSITION, CEMENT-BASED STRUCTURE, AND METHODS OF FORMING THE SAME

CROSS-REFERENCE TO RELATED APPLICATION

[0001] This application claims the benefit of priority of Singapore application No. 10201707698R filed on September 18, 2017, the contents of it being hereby incorporated by reference in its entirety for all purposes.

TECHNICAL FIELD

[0002] Various aspects of this disclosure may relate to a cementitious composition. Various aspects of this disclosure may relate to a cement-based structure. Various embodiments may relate to methods of forming the cementitious composition and/or the cement-based structure.

BACKGROUND

[0003] Strain hardening cementitious composites (SHCC) represent a group of construction materials with superior mechanical properties and environmental durability. SHCC can normally achieve at least 1% tensile strain capacity, which is about a hundred times that of conventional concrete. The extraordinary tensile properties are achieved by the addition of a small portion of fibers, which helps the formation of multiple microcracks with tight crack width, instead of few large cracks seen in conventional concrete. The superior tensile ductility, together with tight crack width, result in stronger corrosion resistance, and improve potential of self-healing of cracks in SHCC-based structures. While a wide range of fibers, such as metallic fibers, polymeric fibers, and natural fibers, have been used to manufacture SHCC, the selection of materials for matrix composition has been rather limited.

[0004] SHCC normally requires a high Portland cement (PC) content. Accordingly, the production of SHCC-based structures would consume large amount of energy, and would result in a high amount of carbon dioxide (CO₂).

SUMMARY

[0005] Various embodiments may provide a cementitious composition. The cementitious composition may include a mixture including a binder component including reactive magnesium oxide cement (RMC). The mixture may further include water. The cementitious composition may also include one or more fibers dispersed in the mixture.

[0006] Various embodiments may provide a cement-based structure. The cement-based structure may include a matrix including one or more hydrated magnesium carbonates. The cement-based structure may include one or more fibers embedded in the matrix.

[0007] Various embodiments may provide a method of forming a cementitious composition. The method may include forming a mixture. The mixture may include a binder component including reactive magnesium oxide cement. The mixture may also include water. The method may include dispersing one or more fibers in the mixture.

[0008] Various embodiments may provide a method of forming a cement-based structure. The method may include forming a matrix including one or more hydrated magnesium carbonates. One or more fibers may be embedded in the matrix.

BRIEF DESCRIPTION OF THE DRAWINGS

[0009] The invention will be better understood with reference to the detailed description when considered in conjunction with the non-limiting examples and the accompanying drawings, in which:

FIG. 1 shows a general illustration of a cementitious composition according to various embodiments.

FIG. 2 shows a general illustration of a cement-based structure according to various embodiments.

FIG. 3 is a schematic showing a method of forming a cementitious composition according to various embodiments.

FIG. 4 is a schematic showing a method of forming a cement-based structure according to various embodiments.

FIG. 5A is a plot of weight percentage (in percent or %) /heat flow (in milli-Watts or mW) as a function of temperature (in degrees Celsius or °C) showing the thermogravimetric analysis (TGA)

and differential thermal analysis (DTA) results of samples formed from Mix 1 and Mix 2 according to various embodiments.

FIG. 5B is a plot of tensile stress (in mega-Pascals or MPa) as a function of tensile strain (in percent or %) showing the uniaxial tensile stress-strain curves of samples formed from Mix 1 according to various embodiments.

FIG. 5C is a plot of tensile stress (in mega-Pascals or MPa) as a function of tensile strain (in percent or %) showing the uniaxial tensile stress-strain curves of samples formed from Mix 2 according to various embodiments.

FIG. 6 is a plot of fiber-bridging stress (σ) as a function of crack opening displacement (δ) showing the tensile stress-crack opening displacement curve and strain-hardening criteria, illustrating the fiber-bridging constitutive law.

FIG. 7 is a plot of cumulative fraction (in percent or %) as a function of particle diameter (in micrometers or μm) showing particle size distribution of reactive magnesium oxide cement (RMC) and fly ash (FA) used in compositions according to various embodiments.

FIG. 8A shows the rheometer used to measure the samples according to various embodiments.

FIG. 8B shows the test setup used to measure the samples according to various embodiments.

FIG. 9A shows the top view and side view of a dog-bone shaped mold according to various embodiments.

FIG. 9B shows the test setup for conducting the uniaxial tensile test for the samples according to various embodiments.

FIG. 10A is a plot of torque τ (in Pascals or Pa) as a function of shear rate N (per second or $1/\text{s}$) showing the torque-shear rate ($\tau - N$) of sample FA60-0.53 at 6 minutes (mins), 12 minutes (mins), and 18 minutes (mins) according to various embodiments.

FIG. 10B is a plot of torque τ (in Pascals or Pa) as a function of shear rate N (per second or $1/\text{s}$) showing the magnified plot of the box outlined in FIG. 10A according to various embodiments.

FIG. 11A shows a plot of plastic viscosity (in Pascals second or Pa s) as a function of fly ash / binder ratio (FA/b) (in percent or %) illustrating the effects of the water and fly ash contents on the plastic viscosity of the mixture according to various embodiments.

FIG. 11B shows a plot of yield stress (in Pascals or Pa) as a function of fly ash / binder ratio (FA/b) (in percent or %) illustrating the effects of the water and fly ash contents on the yield stress of the mixture according to various embodiments.

FIG. 12A is a plot of tensile stress (in mega Pascals or MPa) as a function of tensile strain (in percent or %) illustrating tensile stress-strain curves of the samples NC-12-0.41 after curing for 7 days according to various embodiments.

FIG. 12B is a plot of tensile stress (in mega Pascals or MPa) as a function of tensile strain (in percent or %) illustrating tensile stress-strain curves of the samples NC-12-0.41 after curing for 28 days according to various embodiments.

FIG. 12C is a plot of tensile stress (in mega Pascals or MPa) as a function of tensile strain (in percent or %) illustrating tensile stress-strain curves of the samples OC-12-0.41 after curing for 7 days according to various embodiments.

FIG. 12D is a plot of tensile stress (in mega Pascals or MPa) as a function of tensile strain (in percent or %) illustrating tensile stress-strain curves of the samples OC-12-0.53 after curing for 7 days according to various embodiments.

FIG. 12E is a plot of tensile stress (in mega Pascals or MPa) as a function of tensile strain (in percent or %) illustrating tensile stress-strain curves of the samples OC-8-0.53 after curing for 7 days according to various embodiments.

FIG. 13 is an image showing the typical crack distribution of a failed specimen (NC-12-0.41 with 7 days of curing) after unloading according to various embodiments.

FIG. 14A is an image showing the fracture surface of the specimen shown in FIG. 13 according to various embodiments.

FIG. 14B is a field emission scanning electron microscopy (FESEM) image of a pulled-out fiber shown in FIG. 14A according to various embodiments.

FIG. 14C is a field emission scanning electron microscopy (FESEM) image of a left-over tunnel in the matrix after the fiber shown in FIG. 14B is pulled out according to various embodiments.

FIG. 15 is a plot of mass (in percent or %) / heat flow (in milli-Watts or mW) as a function of temperature (in degree Celsius or °C) showing the thermogravimetric analysis (TGA) curve and the differential scanning calorimetry (DSC) curve of a sample of OC-12-0.53 according to various embodiments.

DETAILED DESCRIPTION

[0010] 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 practiced. These embodiments are described in sufficient detail to enable those skilled in the art to practice the invention. Other embodiments may be utilized and structural, and logical changes may be made without departing from the scope of the invention. The various embodiments are not necessarily mutually exclusive, as some embodiments can be combined with one or more other embodiments to form new embodiments.

[0011] Embodiments described in the context of one of the methods, compositions or structures are analogously valid for the other methods, compositions, or structures. Similarly, embodiments described in the context of a method are analogously valid for a composition and/or structure, and vice versa.

[0012] 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.

[0013] The word "over" used with regards to a deposited material formed "over" a side or surface, may be used herein to mean that the deposited material may be formed "directly on", e.g. in direct contact with, the implied side or surface. The word "over" used with regards to a deposited material formed "over" a side or surface, may also be used herein to mean that the deposited material may be formed "indirectly on" the implied side or surface with one or more additional layers being arranged between the implied side or surface and the deposited material. In other words, a first layer "over" a second layer may refer to the first layer directly on the second layer, or that the first layer and the second layer are separated by one or more intervening layers.

[0014] 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.

[0015] 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.

[0016] As used herein, the term “and/or” includes any and all combinations of one or more of the associated listed items.

[0017] Reactive magnesium oxide (MgO) cement, i.e. RMC, is an alternative binding material. Unlike hydraulic Portland cement where the hardening is a result of cement hydration, reactive MgO cement (RMC) hardens through carbonation of brucite ($\text{Mg}(\text{OH})_2$) with carbon dioxide (CO_2). In practice, reactive MgO cement (RMC) is first mixed and reacts with water to form brucite. The brucite is subsequently carbonated by the ambient CO_2 in air, or elevated CO_2 conditions in a controlled environment, to set into a hardened matrix including different hydrated magnesium carbonates (HMCs). The hydrated magnesium carbonates may have the formula of $x\text{Mg}(\text{CO}_3) \cdot y\text{Mg}(\text{OH})_2 \cdot z\text{H}_2\text{O}$. The hardened dense carbonate network may reduce sample porosity, and may provide binding strength within RMC based samples.

[0018] In addition to laboratory-scale samples reported in many studies, the use of RMC in the production of commercial-scale masonry units has been demonstrated in earlier studies, highlighting its feasibility to be utilized in various non-structural applications. Recent studies on the use of RMC as a binder focus on understanding the factors that affect the carbonation and the associated strength development of RMC formulations, including mix design, curing conditions and use of additives, leading to 28-day concrete strengths as high as ~60 MPa.

[0019] The advantages of reactive MgO cement over the Portland cement are two-fold. First, the mineral calcination temperature for the manufacturing of reactive MgO cement (about 750 °C) may be much lower than that of Portland cement (about 1450°C), which enables the use of alternative fuels. Second, the setting and hardening of brucite may take the advantage of carbonation to sequester CO_2 from the atmosphere. This makes reactive MgO cement a potential green cement to replace conventional Portland cement. Reactive MgO cement has been used as partial or complete replacement for Portland cement in the preparation of construction materials such as masonry blocks.

[0020] Reactive MgO cement may be a good sustainable alternative to Portland cement in the preparation of strain hardening cementitious composites (SHCC.)

[0021] On the other hand, reactive MgO based matrix is brittle and cannot be reinforced with traditional steel reinforcing bar due to the high risk of rebar corrosion. The relatively low pH (i.e. ~10) of carbonated RMC formulations may present a challenge in the use of steel reinforcement, which can face a risk of corrosion due to the loss of the passivated surface at such relatively low alkalinities, thereby potentially creating structural safety issues. The carbonation of MgO binder reduces pH of matrix, which causes depassivation of steel reinforcement and subsequent corrosion.

[0022] With exceptional mechanical properties such as high tensile ductility, high damage tolerance, and fine crack widths, the resulting strain hardening reactive MgO composites (SHMC) can be used in many applications where reinforcement is not necessary such as retrofitting of unreinforced masonry walls, pavement overlays, and surface repair of dams and earth retaining walls. Other potential applications of unreinforced SHMC may include shotcrete for underground rock cavern and tunnel linings.

[0023] Although continuous research on RMC formulations has achieved significant improvements in terms of mechanical performance, RMC-based concrete is still considered as a brittle material, which could highly benefit from the use of reinforcement in the development of structural members.

[0024] It may therefore be highly desirable to enhance the toughness of such material which can greatly widen the potential applications of reactive MgO cement.

[0025] It may be desirable to develop alternative methods that enhances the ductility of RMC-based formulations, in order to increase the application spectrum of RMC within the construction industry. The inclusion of a small amount of short polymeric fibers has been proven to be very effective in eliminating the brittleness and enhancing the tensile ductility of Portland cement (PC)-based composites.

[0026] As highlighted above, one of the successful derivatives involving the use of fibers is engineered cementitious composites (ECC), which include polymeric fibers. The fibers may occupy a fraction of volume, typically about 2%. Unlike the strain-softening conventional PC, ECC demonstrates strain-hardening behavior as their tensile stress continues to increase even in the presence of cracks. ECC samples can achieve tensile ductilities of about 1 % to about 5%, enabled by the formation of multiple fine cracks ($< 100 \mu\text{m}$) with very small spacing (about 1 mm to about 5 mm). The tensile properties of ECC may be further tailored with micromechanics to

achieve multiple attributes such as high impact resistance and fatigue resistance. Therefore, to increase the use of RMC without relying on steel reinforcements, it may be desirable to engage similar tensile strain-hardening behavior and high ductility within RMC-based formulations via the addition of short fibers, such as polymeric fibers.

[0027] Despite the fast development of SHCC and reactive MgO cement, these two technologies, respectively having superior mechanical/durability performance and good sustainability, have never been integrated together. Various embodiments may relate to a CO₂ sequestering strain hardening brittle matrix structure or composite formed using reactive magnesium oxide cement as the binder.

[0028] Various embodiments may relate to a cementitious composition. Various embodiments may relate to a cement-based structure. The cement-based structure may refer to a cement-based composite. In various embodiments, the term “cement-based structure” may be used to refer to the microstructure of the composite, i.e. the internal structure of the composite. The cementitious composition may be used to form a cement-based structure or composite. In other words, the phrase “cementitious composition” may refer to the mix composition of the composite (before hardening).

[0029] FIG. 1 shows a general illustration of a cementitious composition 100 according to various embodiments. The cementitious composition 100 may include a mixture 102 including a binder component 104 including reactive magnesium oxide cement (RMC). The mixture may further include water 106. The cementitious composition 100 may also include one or more fibers 108 dispersed in the mixture 102.

[0030] In other words, various embodiments may relate to a cement-based composition 100 including a binder component 104 and water 106, which may form a mixture 102. The composition 100 may also include fiber(s) 108 mixed into the mixture 102.

[0031] For avoidance of doubt, FIG. 1 serves purely for illustrating various possible constituents of the composition 100 according to various embodiments, and may not denote, for instance, the arrangement of the different constituents in the composition 100.

[0032] In various embodiments, the composition 100 may be referred to as a cement.

[0033] The reactive magnesium oxide cement (RMC) may include predominantly magnesium oxide (MgO). The reactive magnesium oxide cement may include a small amount of other

materials such as calcium oxide (CaO), silicon oxide (SiO₂), iron oxide (Fe₂O₃), and/or aluminum oxide (Al₂O₃). The reactive magnesium oxide cement may include more than about 50% magnesium oxide, e.g. more than about 80% magnesium oxide, e.g. more than 90% about magnesium oxide, e.g. more than about 95% magnesium oxide, e.g. more than about 96% magnesium oxide, e.g. more than about 97% magnesium oxide, e.g. more than about 98% magnesium oxide, e.g. more than about 99% magnesium oxide, e.g. about 100% magnesium oxide by mass.

[0034] SHCC is a superior construction material, but may not be environment-friendly due to the high Portland cement usage. Reactive MgO cement (RMC) may present sustainability advantages due to its lower manufacturing temperatures and ability to sequester carbon dioxide. Various embodiments may integrate reactive MgO cement into SHCC, resulting in a sustainable construction material. Compared with traditional Portland cement-based SHCC, various embodiments may reduce carbon dioxide emissions, from raw material manufacturing to SHCC field applications, by at least about 40% to about 60%.

[0035] In various embodiments, the binder component 104 may further include any one or more binders selected from a group consisting of hydraulic cement, coal fly ash, silica fume, and ground granulated blast furnace slag. The addition of such binders may greatly reduce the cost of production, and may contribute to mechanical performance through cementitious and pozzolanic reactions. Such binders may be obtained from industrial wastes.

[0036] In various embodiments, the binder component 104 may include reactive magnesium oxide cement (RMC), and coal fly ash (alternatively referred to as fly ash (FA)). FA may increase fluidity and may improve the rheological properties of the composition due to its spherical shape, which decreases inter-particle friction. In various embodiments, fly ash may occupy any value from about 0% to about 60%, e.g. from about 0% to about 30%, of the binder component 104 by mass. Fly ash may include predominantly silicon oxide (SiO₂) and aluminum oxide (Al₂O₃). Silicon oxide (SiO₂) and aluminum oxide (Al₂O₃) may occupy more than 50%, e.g. more than 60%, more than 70%, more than 80% by mass of fly ash. Fly ash may also include a small amount of other materials such as magnesium oxide (MgO), calcium oxide (CaO), iron oxide (Fe₂O₃), potassium oxide (K₂O), titanium oxide (TiO₂) etc.

[0037] In various other embodiments, the binder component 104 may consist of only reactive magnesium oxide cement.

[0038] In various embodiments, a percentage of reactive magnesium oxide cement in the binder component 104 by mass may be any one percentage value selected from a range from about 40 % to about 100%.

[0039] In various embodiments, a mass ratio of water to binder component (w/b ratio) may be any one ratio selected from a range from about 0.4 (i.e. 0.4 : 1) to about 0.8 (i.e. 0.8 : 1), e.g. from about 0.4 (i.e. 0.4 : 1) to about 0.6 (i.e. 0.6: 1). A low w/b ratio may lead to higher viscosity for better fiber dispersion. A low w/b ratio may also be associated with high compressive strength of the resultant composite. However, reduction of w/b, e.g. from 0.53 to 0.41, may enhance first cracking and ultimate tensile strength, as well as lead to better ductility.

[0040] In various embodiments, the mixture 102 may further include a water reducing agent. The water reducing agent may be sodium hexametaphosphate solution ($\text{Na}(\text{PO}_3)_6$). A percentage of the water reducing agent relative to the binder component by mass may be any one percentage value selected from about 2% to about 4%.

[0041] In various embodiments, the mixture 102 may also include a viscosity controlling agent. The viscosity controlling agent may be hydroxypropyl methylcellulose (HPMC). A percentage of the viscosity controlling agent relative to the binder component by mass may be any one percentage value selected from a range from about 0.05% to about 0.5%.

[0042] The water 106 may be present in the mixture 102 in conjunction with the water reducing and/or the viscosity control agent to achieve adequate rheological properties.

[0043] In various embodiments, the mixture 102 in the fresh stage may be a Bingham liquid.

[0044] The one or more fibers 108 may be one or more types of fibers selected from a group consisting of metallic fibers, polymeric fibers, and natural fibers.

[0045] The one or more fibers 108 or polymeric fibers may be any one type of fibers selected from a group consisting of polyvinyl alcohol (PVA) fibers, ethyl vinyl acetate (EVOH) fibers, (PE) polyethylene fibers, acrylic fibers, polypropylene (PP) fibers, and acrylamide fibers.

[0046] A percentage of the one or more fibers 108 in the cementitious composition by volume may be any one percentage value selected from a range from about 0.5% to about 10%, from about 1% to about 3%, e.g. from about 1% to about 2%.

[0047] The one or more fibers 108 may have an average tensile strain capacity of about 1% to about 10%, e.g. of about 3% to about 7%. The one or more fibers 108 may have an average diameter selected from a range from about 10 μm to about 60 μm , e.g. from about 25 μm to about 50 μm , e.g. from about 35 μm to about 45 μm . The one or more fibers 108 may have an average length selected from a range from about 5 mm to about 30 mm, e.g. from about 6 mm to about 25 mm, e.g. from about 6 mm to about 18 mm, e.g. from about 8 mm to about 12 mm. As described in more detail below, an increase in fiber aspect ratio may lead to improvements in tensile strength and/or ductility.

[0048] In various embodiments, each of the one or more fibers 108 may include a coating of an oiling agent (may alternatively be referred to as oil). The oiling agent may be poly-oxyethylene. Any other suitable oiling agents may also be used.

[0049] In various embodiments, the one or more fibers 108 may be hydrophilic fibers. The hydrophilicity of certain types of fibers 108 may introduce strong interfacial bonds between fibers and the surrounding matrix when the composition 100 is cured. The oiling agent may be applied to prevent over-enhancement of the interfacial bonds. The oiling agent may help improve tensile ductility.

[0050] In various other embodiments, each of the one or more fibers 108 may not include, i.e. may be devoid of, a coating of an oiling agent.

[0051] Various embodiments may involve using fibers 108 to reinforce brittle matrix including reactive MgO cement. The resulting strain hardening reactive MgO composites (SHMC) or structures may have a density of any value in the range from about 1,500 kg/m^3 to about 2,500 kg/m^3 , and may have a tensile ductility of at least about 1%. Various embodiments may sequester carbon dioxide (CO_2) of up to 1 ton during the curing process before it reaches its designed compressive strength.

[0052] Various embodiments may relate to a composition 100 formed by any suitable method as described herein.

[0053] Various embodiments may relate to a composition including reactive MgO cement (RMC), water, and fibers in different proportions. Other optional constituents, such as water reducing agents and viscosity controlling agents, may be needed to adjust thixotropic rheology and viscosity characteristics to achieve adequate workability and to disperse the fibers uniformly.

[0054] Reactive MgO cement may be obtained from the calcination of magnesium carbonate or magnesium hydroxide at temperatures lower than 1000°C. Other binders, like hydraulic cement, coal fly ash, silica fume, and ground granulated blastfurnace slag may be added as optional supplements. The addition of such binders from industrial wastes may greatly reduce the cost of MgO, and may contribute to mechanical performance through cementitious and pozzolanic reactions. The fraction of reactive MgO cement in the binder component may be of any percentage selected from a range from about 40% to about 100%. The binders may set in the presence of water and may gain strength under exposure to carbon dioxide.

[0055] Water may be present in the fresh mixture in conjunction with a water reducing and viscosity controlling or modifying agent to achieve adequate rheological properties. A water-to-binder ratio of any value selected from a range from about 0.4 to about 0.8 may be used to achieve the desired strength. A water reducing agent may be used to adjust the desired workability level after the water content in the composite is determined. The quantity of water reducing agent needed may vary with the water-to-binder ratio, composition of binder, and/or type of water reducing agent. An illustrative water reducing agent may be sodium hexametaphosphate (NaHMP) ($\text{Na}(\text{PO}_3)_6$) solution. The amount of $\text{Na}(\text{PO}_3)_6$ may be of any percentage selected from a range from about 2% to about 4% of the binder by mass. An illustrative viscosity controlling agent is hydroxypropyl methylcellulose (HPMC). The typical amount of HPMC may be of any percentage selected from a range from about 0.05% to about 0.5% of the binder by mass.

[0056] The fibers may be one or more of any suitable types of discontinuous fibers, and may be provided in a bundled form. Examples of suitable fibers may include, but may not be limited to polyvinyl alcohol (PVA) fibers, ethyl vinyl acetate (EVOH) fibers, polyethylene (PE) fibers, acrylic fibers, polypropylene (PP) fibers and acrylamide fibers.

[0057] The amount of fibers, the nature of the fibers, and/or the size of the fibers in the composition may vary. The amount of fibers required may be so that it is sufficiently high enough for the provision of the required ductility to the composition, but may be of a low level enough to allow self-compaction

[0058] In various embodiments, the tensile strain capacity of the composition may be of any percentage selected from a range from about 1% to about 10%, e.g. from about 3% to about 7%.

[0059] In general, with conventional fiber sizes, compaction may be difficult without vibration if the fiber content exceeds 2.5%.

[0060] Fibers included in SHMC may be of any percentage selected from a range of about 0.5% to 10% by volume, e.g. from about 1% to about 3% by volume, e.g. from about 1% to about 2% by volume. The fibers may have diameters of from about 10 μm to about 60 μm , e.g. from about 10 μm to about 20 μm , or from about 25 μm to about 50 μm , e.g. from about 35 μm to about 45 μm , and lengths from about 5 mm to about 30 mm, e.g. from about 6 mm to about 25 mm, e.g. from about 6 mm to about 18 mm, e.g. from about 8 mm to about 12 mm.

[0061] In various embodiments, the fibers may be PVA fibers. The surface of PVA fibers may be coated with oiling agent (such as poly-oxymethylene) by up to about 1.5% by the weight of the fibers, e.g. of any value selected from a range from about 0.8% to about 1.2% by weight relative to the fibers. The fibers may be coated with the oiling agent by any conventional manner, such as by dip-coating or spraying the fibers. Other oiling agents may be used as well. The hydrophilicity of PVA fibers may introduce strong interfacial bonds between fibers and surrounding matrix. The oiling agent may be applied to prevent over-enhancement of the interfacial bonds.

[0062] Various embodiments may relate to a cement-based structure. The cement-based structure may be a composite structure. The cement-based structure may be formed from the cementitious composition.

[0063] FIG. 2 shows a general illustration of cement-based structure according to various embodiments. The cement-based structure 200 may include a matrix 202 including one or more hydrated magnesium carbonates. The cement-based structure 200 may include one or more fibers 204 embedded in the matrix 202.

[0064] In other words, various embodiments may provide a structure having fibers 204 within a matrix 202 including one or more hydrated magnesium carbonates.

[0065] The structure 200 may be a composite structure, and may be referred to as a composite. The structure 200 may be formed by hardening of the cementitious composition. In various embodiments, the structure 200 may be formed by curing of the cementitious composition.

[0066] For avoidance of doubt, FIG. 2 serves purely for illustrating various possible constituents of the cement-based structure 200 according to various embodiments, and may not denote, for instance, the arrangement of the various constituents within the structure 200.

[0067] In various embodiments, the one or more hydrated magnesium carbonates may be selected from a group consisting of nesquehonite ($\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$), hydromagnesite ($4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$), dypingite ($4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$), and artinite ($\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 3\text{H}_2\text{O}$).

[0068] The one or more fibers 204 may be bonded to the matrix 202. There may be interfacial bonds between the matrix 202 and the one or more fibers 204.

[0069] The one or more fibers 204 may extend or may be uniformly dispersed throughout the structure 200.

[0070] In various embodiments, the cement-based structure 200 may be concrete. In various other embodiments, the cement-based structure 200 may be mortar.

[0071] Various embodiments may relate to a structure 200 formed by any suitable method described herein.

[0072] Various embodiments may relate to a method of forming a cementitious composition. FIG. 3 is a schematic showing a method of forming a cementitious composition according to various embodiments. The method may include, in 302, forming a mixture. The mixture may include a binder component including reactive magnesium oxide cement. The mixture may also include water. The method may include, in 304, dispersing one or more fibers in the mixture.

[0073] In other words, various embodiments may relate to forming a cement. The cement may include a binder including reactive magnesium oxide cement. The cement may also include water. The cement may also include one or more fibers.

[0074] The binder component may further include any one or more binders selected from a group consisting of hydraulic cement, coal fly ash, silica fume, and ground granulated blast furnace slag.

[0075] In various embodiments, a percentage of reactive magnesium oxide cement in the binder component by mass may be any one percentage value selected from a range from 40 % to 100%.

[0076] In various embodiments, a mass ratio of water to binder component may be any one ratio selected from a range from 0.4 to 0.8.

[0077] In various embodiments, the mixture may further include a water reducing agent, such as sodium hexametaphosphate ($\text{Na}(\text{PO}_3)_6$) solution. A percentage of the water reducing agent

relative to the binder component by mass may be any one percentage value selected from 2% to 4%.

[0078] In various embodiments, the mixture may further include a viscosity controlling agent, such as hydroxypropyl methylcellulose. A percentage of the viscosity controlling agent relative to the binder component by mass may be any one percentage value selected from a range from 0.05% to 0.5%.

[0079] In various embodiments, the one or more fibers may be any one type of fibers selected from a group consisting of polyvinyl alcohol fibers, ethyl vinyl acetate fibers, polyethylene fibers, acrylic fibers, polypropylene fibers, and acrylamide fibers. A percentage of the one or more fibers in the cementitious composition by volume may be any one percentage value selected from a range from 0.5% to 10%.

[0080] Each of the one or more fibers may include a coating of an oiling agent.

[0081] Various embodiments may relate to a cementitious composition formed from any method described herein.

[0082] The fiber-reinforced cementitious composition may be prepared in any suitable manner. A method of preparing the fiber-reinforced cementitious composition may follow the steps of 1) mixing dry powders including reactive MgO cement and supplementary binders like fly ash; 2) mixing of the above with water and $\text{Na}(\text{PO}_3)_6$ solution for several minutes; 3) adding fibers, such as PVA fibers into the fresh mixture and mixing until a homogenous mixture is achieved. A cement-based structure may be formed from the composition by curing in ambient air or elevated carbon dioxide (CO_2) conditions in a manually controlled environment until it achieves desirable mechanical strength.

[0083] Various embodiments may relate to a method of forming a cement-based structure.

[0084] FIG. 4 is a schematic showing a method of forming a cement-based structure according to various embodiments. The method may include, in 402, forming a matrix including one or more hydrated magnesium carbonates. One or more fibers may be embedded in the matrix.

[0085] In other words, various embodiments may relate to a method of forming a cement-based structure, such as concrete or mortar, including a matrix containing of hydrated magnesium carbonates, and a plurality of fibers within the matrix.

[0086] In various embodiments, the method may include embedding or dispersing the one or more fibers in the matrix.

[0087] In various embodiments, forming the matrix, wherein the one or more fibers are embedded in the matrix, may include forming a cementitious composition. The cementitious composition may include a mixture including a binder component (including reactive magnesium oxide cement), and water. Forming the matrix may further include curing the cementitious composition by exposing the cementitious composition to carbon dioxide (CO₂) so that the one or more hydrated magnesium carbonates is formed from the reactive magnesium oxide cement.

[0088] In various embodiments, curing may be carried out for any suitable duration. In various embodiments, curing may be carried out for any suitable duration from 7 days to 28 days. An increased curing duration may lead to an improvement in ultimate tensile strength, and reduction in strain hardening.

[0089] Curing may be carried out in a carbonation chamber or in air under ambient conditions. Curing may take place at any suitable temperature, e.g. any temperature selected from a range from 25 °C to 40 °C, e.g. from 30 °C to 35 °C. Curing may be carried out at any suitable CO₂ concentration, e.g. any concentration selected from 5% to about 20%, by volume, e.g. about 10% by volume. Curing may be carried out at any suitable relative humidity, e.g. a relative humidity of above 50%, e.g. above 60%, above 70%, above 80% e.g. about 90%.

[0090] Forming the one or more hydrated magnesium carbonates may include forming brucite (Mg(OH)₂) from the reactive magnesium oxide cement, and forming the one or more hydrated magnesium carbonates from brucite. The magnesium oxide from the reactive magnesium oxide cement may react with water to form brucite. Brucite may react with carbon dioxide to form hydrated magnesium carbonates, such as such as nesquehonite (MgCO₃·3H₂O), hydromagnesite (4MgCO₃·Mg(OH)₂·4H₂O), dypingite (4MgCO₃·Mg(OH)₂·5H₂O), and/or artinite (MgCO₃·Mg(OH)₂·3H₂O).

[0091] Various embodiments may involve sequestration of carbon dioxide from the atmosphere or surroundings.

[0092] In various embodiments, the one or more fibers may be bonded to the matrix.

[0093] In various embodiments, the cement-based structure may be concrete or mortar. The cement-based structure may achieve tensile ductility or tensile strain capacity of above 1%.

Various embodiments may have an average crack width of less than 150 μm , e.g. less than 100 μm .

[0094] Experimental Details

[0095] Experiment 1

[0096] Two exemplary mixes are presented for preparing strain hardening reactive MgO composites (SHMC). These mixes may include reactive MgO cement, coal fly ash, water, $\text{Na}(\text{PO}_3)_6$, and fibers. The mix proportions are tabulated in Table 1. Reactive MgO cement provided by International Scientific Ltd. of Singapore, coal fly ash provided by Bisley Asia Pte Ltd. of Singapore, and $\text{Na}(\text{PO}_3)_6$ provided by VMR Pte Ltd. of Singapore, were used in both mixes. Reactive MgO and fly ash were used as the main binders, while the $\text{Na}(\text{PO}_3)_6$ was used as a water reducer to achieve the required workability for good fiber dispersion. The polyvinyl alcohol (PVA) fibers were manufactured by Kuraray Co. Ltd., Japan. The fiber length was 12 mm and the fiber diameter was 39 μm . Two different fiber surface oil-coating contents at 0.0% and 1.2% relative to mass of the fibers were used respectively for the two example mixes (Mix 1 and Mix 2).

Mix	PVA fiber type	MgO cement (kg/m^3)	Fly ash (kg/m^3)	Water (kg/m^3)	$\text{Na}(\text{PO}_3)_6$ (kg/m^3)	PVA fiber	
						(kg/m^3)	(vol.%)
1	0.0% oil-coating	799	343	598	59	27	2.1
2	1.2% oil-coating	799	343	598	59	27	2.1

Table 1 Exemplary mix proportions

[0097] The compositions (Mix 1 and Mix 2) were prepared in a mixer with a planetary rotating blade. The mixing process followed the following steps: 1) $\text{Na}(\text{PO}_3)_6$ was dissolved into the water, forming a $\text{Na}(\text{PO}_3)_6$ solution; 2) all the solid raw materials in powder form, i.e. MgO cement and fly ash, were dry-mixed for more than five minutes; 3) the $\text{Na}(\text{PO}_3)_6$ solution was slowly added into the dry powder mixture; 4) this blend was mixed for over three minutes until the liquid and solid were uniformly mixed; 5) PVA fibers were added into the mixture; 6) the mixing process continued for another three minutes. In Mix 1, the PVA fibers were not coated with oiling agent, while in Mix 2, the PVA fibers were coated oiling agent.

[0098] The prepared fresh compositions (Mix 1 and Mix 2) were each casted into dog bone-shaped molds for uniaxial tensile tests. The specimens were removed from the molds after 1 day

of preparation. They were then cured in a carbon dioxide (CO₂) chamber (CO₂ concentration = 10%, temperature = 35 °C, relative humidity = 40%) for seven days.

[0099] Once curing was completed, powders were scratched off from the specimens. Two methods were used to quantify the amount of CO₂ sequestered during curing. Firstly, the scratched-off powders underwent thermogravimetric analysis (TGA, 40-900 °C, 10 °C/min), and differential thermal analysis (DTA, 40-900 °C, 10 °C/min). Secondly, 3N hydrochloric (HCl) solution was used to decarbonate the scratched-off powders, and the weight change due to CO₂ release was measured. Uniaxial tensile tests were conducted with the dog-bone specimens after seven days of CO₂ curing. The loading rate was set as 0.2 mm/min.

[00100] FIG. 5A is a plot of weight percentage (in percent or %) /heat flow (in milli-Watts or mW) as a function of temperature (in degrees Celsius or °C) showing the thermogravimetric analysis (TGA) and differential thermal analysis (DTA) results of samples formed from Mix 1 and Mix 2 according to various embodiments.

[00101] For both mix designs, a weight loss (lines (i) and (ii)), corresponding to the decomposition of hydrated magnesium carbonates (HMC), may be observed between 388 °C to 900 °C. Heat absorption may also be observed in the same temperature range (lines (iii) and (iv)). The amount of carbon dioxide (CO₂) sequestered during curing may be determined quantitatively with the weight loss. Table 2 shows the CO₂ sequestration measured by the TGA/ DTA methods, as well as the hydrochloric acid (HCl) decarbonation method.

Mix.	Density (kg/m ³)	CO ₂ sequestration (g/g)	
		TGA/DTA	HCl decarbonation
1	1806	0.219	0.286
2	1806	0.195	0.155

Table 2 Density and CO₂ sequestration of reactive MgO-based SHMC

[00102] FIG. 5B is a plot of tensile stress (in mega-Pascals or MPa) as a function of tensile strain (in percent or %) showing the uniaxial tensile stress-strain curves of samples formed from Mix 1 according to various embodiments. FIG. 5C is a plot of tensile stress (in mega-Pascals or MPa) as a function of tensile strain (in percent or %) showing the uniaxial tensile stress-strain curves of samples formed from Mix 2 according to various embodiments. It can be seen that both Mix.1 and Mix.2 may achieve ultra-high tensile ductility of at least 1%.

[00103] Commercial applications of the compositions as well as structures/composites may include the manufacturing of unreinforced structural and building components, which include bricks, blocks and pavers, the market size of which is estimated to reach 8.9 billion USD in 2018.

[00104] Experiment 2

[00105] One of the key factors to be considered in increasing the ductility of RMC-based strain-hardening composites (SHC) is the provision of a desirable fiber dispersion. Previous studies that looked into the rheology of fresh ECC mixtures have reported that high plastic viscosity and flowability, which could be achieved via the adjustment of the water/binder (w/b) ratio and mix design (e.g. fly ash (FA) content), may effectively prevent the entangling of fibers, thereby leading to high ductility. While increasing the w/b ratio reduces viscosity and leads to a low yield stress, the use of FA increases fluidity and improves the rheological properties of cement mixes due to its spherical shape, which decreases inter-particle friction. The relationship between the rheology of cement pastes and tensile ductility, assessed via the measurements of the uniformity of fiber dispersions, has revealed that an increase in viscosity due to good fiber dispersion can enable a higher ductility.

[00106] While a desirable fiber dispersion is critical, it does not necessarily guarantee strain-hardening behavior or high ductility. FIG. 6 is a plot of fiber-bridging stress (σ) as a function of crack opening displacement (δ) showing the tensile stress-crack opening displacement curve and strain-hardening criteria, illustrating the fiber-bridging constitutive law. As shown in FIG. 6, the hardened composites may need to satisfy the two strain-hardening criteria. Specifically, the complementary energy of the fiber-bridging curve, J_b (i.e. the hatched area) may be required to be greater than the crack tip toughness of the matrix, J_{tip} , as shown in Equation (1).

$$[00107] \quad J_{tip} \leq \sigma_0 \delta_0 - \int_0^{\delta_0} \sigma(\delta) d\delta \equiv J_b' \quad (1)$$

[00108] σ_0 is the maximum fiber-bridging strength, and δ_0 is the crack opening corresponding to the maximum fiber-bridging strength, σ_0 . Also, σ_{ss} is the steady-state cracking strength, while δ_{ss} is the crack opening corresponding to the steady-state cracking strength, σ_{ss} .

[00109] Furthermore, the maximum fiber-bridging strength, σ_0 (i.e. the curve peak), may be required to be higher than the tensile cracking strength of the matrix, σ_c , as shown in Equation (2).

$$[00110] \quad \sigma_c < \sigma_0 \quad (2)$$

[00111] As the fiber-bridging and matrix crack tip toughness are influenced by factors such as the w/b ratio, fiber aspect ratio, and the bond between the fibers and cement matrix (which may be influenced by the fiber surface treatment), it may be important to study the effect of these factors on the tensile performance of RMC-based strain-hardening composites (SHC).

[00112] Various embodiments may relate to RMC-based strain-hardening composites (SHC) or structures. Various embodiments relating to various composites or structures may be influenced by key parameters during the process of forming the composites or structures.

[00113] The first part of Experiment 2 focuses on the effect of water/binder (w/b) ratio and fly ash (FA) content on the rheological properties of RMC compositions or pastes, with the goal of determining a suitable mix design that leads to a desired viscosity and sufficient flowability for good fiber dispersion. The second part of Experiment 2 focuses on the inclusion of fibers within the mix design determined in the first stage and investigates the effect of certain factors such as the w/b ratio, fiber aspect ratio, fiber surface treatment and curing age on the performance of the developed formulations.

[00114] Materials

[00115] Reactive magnesium oxide cement (RMC), obtained from International Scientific Ltd. (Singapore), was the main binder used in this study. Class F fly ash (FA), obtained from Bisley Asia Ltd. (Malaysia), was used to adjust the rheology of the fresh mixtures and function as a binder via its pozzolanic reaction with brucite.

[00116] Table 3 shows the chemical compositions of reactive magnesium oxide cement (RMC) and fly ash (FA).

Material	MgO	CaO	SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	K ₂ O	TiO ₂	Others
RMC	97%	1.3%	1.3%	0.2%	0.2%	-	-	-
FA	0.8%	1.2%	58.6%	4.7%	30.4%	1.5%	2.0%	0.8%

Table 3 Chemical composition of RMC and FA

[00117] FIG. 7 is a plot of cumulative fraction (in percent or %) as a function of particle diameter (in micrometers or μm) showing particle size distribution of reactive magnesium oxide cement (RMC) and fly ash (FA) used in compositions according to various embodiments.

[00118] Sodium hexametaphosphate ($\text{Na}(\text{PO}_3)_6$), acquired from VWR International Ltd. (Singapore), was added to the prepared formulations as a water reducer at 10% of the water content. Polyvinyl alcohol (PVA) fibers, one of the most common types of fibers used in ECC, were obtained from Kuraray Ltd. (Japan) and included in selected RMC-SHC samples in three different forms, with varying aspect ratios (i.e. lengths of 8 mm and 12 mm) and surface treatments (i.e. oil coating (OC) and no oil-coating (NC)). The properties of the PVA fibers used in this study are listed in Table 4.

Fiber type	Length (mm)	Diameter (μm)	Fiber aspect ratio, i.e. length/diameter	Density (kg/m^3)	Nominal tensile strength (MPa)	Surface oil- content (%)
12mm (NC)	12	39	307	1300	1600	0
12mm (OC)	12	39	307	1300	1600	1.2
8mm (OC)	8	39	205	1300	1600	1.2

Table 4 Properties of the PVA fibers used in this study.

[00119] Methodology

[00120] As highlighted above, the first part of Experiment 2 studied the effect of water/binder (w/b) and fly ash/binder (FA/b) ratios on the rheology of fresh mixtures before the inclusion of fibers. The goal of this part was to determine a suitable mix design (i.e. w/b ratio and FA content) that led to a desired plastic viscosity and flowability for good fiber dispersion. The second part, during which PVA fibers were introduced into the mix design determined in the first part, studied the effect of the w/b ratio, fiber aspect ratio, fiber surface treatment (i.e. oil content) and curing age on the mechanical properties of the RMC-based strain-hardening composite (SHC).

[00121] The details of the seven different mix proportions prepared in the first part of the study are provided in Table 5.

Sample	RMC (kg/m^3)	FA (kg/m^3)	Water (kg/m^3)	$\text{Na}(\text{PO}_3)_6$ (kg/m^3)	FA (%)	w/b	Solid (RMC+FA) volume fraction
--------	----------------------------	---------------------------	------------------------------	---	-----------	-----	---

FA0-0.58	1102	0	639	64	0	0.58	0.35
FA30-0.47	840	360	570	57	30	0.47	0.42
FA30-0.53	789	338	595	59	30	0.53	0.39
FA30-0.58	744	319	617	62	30	0.58	0.37
FA60-0.47	462	693	548	55	60	0.47	0.44
FA60-0.53	435	653	573	57	60	0.53	0.42
FA60-0.58	411	616	596	60	60	0.58	0.39

Table 5 Mix proportions of fiber-free RMC mixtures prepared for rheology measurements.

[00122] The notation for sample names followed a format of FA(X)-(Y), where X represented the FA content (i.e. as a percentage of the total binder) and Y represented the w/b ratio. A range of w/b (0.47-0.58) and FA/b (0-0.6) ratios were determined from preliminary samples prepared for each formulation.

[00123] The sample preparation process started with the dissolving of $\text{Na}(\text{PO}_3)_6$ in the pre-determined amount of water. This solution was then added to the dry mix of RMC and FA during the mixing process. A stopwatch was set to notify two minutes from the moment the solution was added to the dry RMC-FA mix. After two minutes of mixing, one spoon of the fresh mixture was placed onto a 39 mm proliferated base plate on the rheometer, equipped with a 39 mm P35 TiL top plate pressed against the mixture at 0.5 N.

[00124] The rheology measurements were performed via a HAAKE MARS III 379-0400 rheometer, which was used to measure the shear resistance of the fresh mixtures at a designated rotation speed. FIG. 8A shows the rheometer used to measure the samples according to various embodiments. FIG. 8B shows the test setup used to measure the samples according to various embodiments.

[00125] Three rheology measurements were taken at 6 minutes, 12 minutes, and 18 minutes. For each measurement, the top plate was first rotated at a relatively high speed (about 50 /s) for 30 seconds to prevent any agglomeration, followed by an increase in the shear rate from 1 to 100 /s within 180 seconds. The shear resistance, τ , was recorded throughout the total 210 seconds. The sample was kept in-situ between measurements. Both the sample preparation and subsequent measurements were conducted under an ambient temperature (25 °C).

[00126] A certain level of plastic viscosity is crucial for good fiber dispersion and tensile ductility. Results from the first part of the study were used in the selection of w/b and FA/b ratios to be incorporated in the mix designs in the second part. Previous literature has shown that while the fiber dispersion coefficient increased with plastic viscosity, tensile ductility stabilized after a threshold fiber dispersion coefficient. This value corresponded to a plasticity of about 3.5 Pa·s, which was also adopted in this study for the preparation of samples used in the testing of tensile properties. Referring to the results obtained in the first part of the study to identify samples that demonstrated good fiber dispersion (e.g. FA30-0.53), the four mix proportions listed in Table 6 were prepared to assess the effect of w/b ratio, fiber aspect ratio, fiber surface treatment (i.e. oil content), and curing age on the tensile performance of the RMC-based strain-hardening composite (SHC).

Sample	RMC (kg/m ³)	FA (kg/m ³)	Water (kg/m ³)	Na(PO ₃) ₆ (kg/m ³)	PVA fiber (kg/m ³)	w/b	Fiber aspect ratio	Fiber surface oil content (%)
NC-12-0.41	864	370	510	51	26	0.41	307	0.0
OC-12-0.41	864	370	510	51	26	0.41	307	1.2
OC-12-0.53	799	342	601	59	26	0.53	307	1.2
OC-8-0.53	799	342	601	59	26	0.53	205	1.2

Table 6 Mix proportions prepared for testing hardened tensile properties

[00127] The notation for sample names followed a format of (X)-(Y)-(Z), where X, Y and Z represented the fiber surface treatment, fiber length and w/b ratio, respectively. The term 'OC' for (X) refers to oil coating, while the term 'NC' refers to no oil coating. The unit for (Y) is in millimeters (mm). For all the mix designs, the FA/b was fixed at 0.3, whereas the w/b ratio was kept at ≤ 0.53 according to the outcomes of the rheology measurements. A constant fiber fraction corresponding to 2% of the binder content was utilized, in line with previous literature on ECC.

[00128] To initiate sample preparation, RMC and FA were dry mixed in a planetary mixer for over 3 minutes, after which the prepared $\text{Na}(\text{PO}_3)_6$ solution was slowly added to form the fresh mixture. The mixing process continued for an additional 2 minutes to 3 minutes until a uniformly mixed homogenous mixture was achieved, after which the PVA fibers were slowly added within 2 minutes. During the entire mixing process, the blade rotation speed was kept constant at 6.4 rad/s.

[00129] The prepared mixture was cast into cubic (50 x 50 x 50 mm) and dog-bone shaped molds, whose dimensions are shown in FIG. 9A. FIG. 9A shows the top view and side view of a dog-bone shaped mold according to various embodiments.

[00130] The cast samples were stored in a sealed container, where silica gel was used for dehumidification. After 3 days, samples were removed from their molds and cured in a carbonation chamber set at a CO_2 concentration of 10%, temperature of 30 °C and relative humidity (RH) of 90% for 7 days. The effect of curing duration was studied by exposing one of the prepared samples (NC-12-0.41) to carbonation curing for a total of 28 days under the same conditions.

[00131] Once curing was completed, the compressive strength of the cubic samples was measured. Three specimens of each cubic sample were measured in accordance with the specifications of ASTM C109/C109M-13. The equipment used for compression testing was Landmark 370.25, operated at a loading rate of 0.25 mm/min. The uniaxial tensile tests were conducted on at least three specimens for each mix design by using an Instron 5569, as shown in FIG. 9B. FIG. 9B shows the test setup for conducting the uniaxial tensile test for the samples according to various embodiments.

[00132] During this test, the loading rate was set at 0.02 mm/min and two linear variable differential transformers (LVDTs) were used to determine the extension of the gauged length (about 60 mm to about 70 mm). After the uniaxial tensile test, the crack width and spacing on each specimen were determined with a Nikon DS-Fi2 high resolution camera at a magnification of about 420x. For each mix design, three to six specimens were analyzed to evaluate their crack patterns.

[00133] In addition to their compressive and tensile strengths, the CO_2 uptake of selected samples during carbonation curing were assessed by obtaining representative powders from each sample. These powders were ground to pass through a 75 μm sieve and vacuum dried before analysis. The quantitative measurements were performed via thermogravimetric

analysis/differential scanning calorimetry (TGA/DSC) conducted on a Perkin Elmer TGA 4000 equipment. During TGA/DSC, the samples were heated from about 40 °C to about 900 °C at a heating rate of about 10 °C/min under nitrogen flow.

[00134] Discussion

[00135] Rheological Properties

[00136] FIG. 10A is a plot of torque τ (in Pascals or Pa) as a function of shear rate N (per second or 1/s) showing the torque-shear rate ($\tau - N$) of sample FA60-0.53 at 6 minutes (mins), 12 minutes (mins), and 18 minutes (mins) according to various embodiments. FIG. 10B is a plot of torque τ (in Pascals or Pa) as a function of shear rate N (per second or 1/s) showing the magnified plot of the box outlined in FIG. 10A according to various embodiments.

[00137] FIGS. 10A-B may illustrate the relationship between the shear resistance τ (Pa) and shear rate N (/s) of a fresh RMC mixture at different elapsed times. The curves show that the fresh mixtures (i.e. without the fibers) were Bingham liquids, in which the shear force exceeded the initial mixture resistance to initiate rotation, after which the shear resistance increased linearly with the rotation speed N (/s), showing no shear thinning or thickening effect. The fresh mixtures do not contain fibers. The relationship between τ and N of Bingham liquids is quantitatively described by Equation 3, where g (Pa), the intercept on the y-axis, is the yield stress needed to break the network of interactions between particles and initiate rotation; and h (Pa·s), the slope of the curve, is the plastic viscosity.

$$[00138] \quad \tau = g + Nh \quad (3)$$

For any given fresh mixture at a designated time, g and h are constants that represent the rheological properties of that mixture.

[00139] In regular cement-based fresh mixes, shear resistance, which varies with shear rate (N) and solid volume fraction (V_s), depends on several types of particle interactions (i.e. Van der Waals forces, direct contact forces between particles and hydrodynamic forces, for which the friction between fluid layers increases with velocity). At relatively low shear rates, the yield stress (g) may be mainly determined by Van der Waals or direct contact forces. Previous studies on the yield stress of C_3S pastes, which have similar particle sizes as RMC, showed that a critical V_s existed at 0.38, beyond which the solid particles became so compacted that the dominant particle interaction shifted from Van der Waals to direct contact forces. Most of the mix designs presented in this

study, except for FA0-0.58 ($V_s = 0.35$) and FA30-0.58 ($V_s = 0.37$), had V_s values that were larger than 0.38, indicating the dominance of direct contact forces. At relatively high shear rates, the yield stress is majorly determined by hydrodynamic forces, while the effects of Van der Waals and direct contact forces still exist.

[00140] The measured values of the yield stress (g) and plastic viscosity (h) of all samples at different elapsed times are provided in Table 7.

Sample	Elapsed time = 6 min		Elapsed time = 12 min		Elapsed time = 18 min	
	g (Pa)	h (Pa·s)	g (Pa)	h (Pa·s)	g (Pa)	h (Pa·s)
FA0-0.58	60.6	1.15	-	-	-	-
FA30-0.47	153.1	5.55	-	-	-	-
FA30-0.53	172.8	3.66	183.3	4.79	-	-
FA30-0.58	48.0	2.59	76.0	3.29	94.8	4.66
FA60-0.47	26.2	2.24	40.3	2.66	54.8	3.14
FA60-0.53	6.1	1.13	11.0	1.93	31.0	3.41
FA60-0.58	2.1	0.43	1.6	0.44	5.5	1.17

Table 7 Rheological test results

[00141] For some mixes, the values of g and h at 12 and 18 minutes were not listed due to the loss of contact between the top plate and the fresh mixture, resulting in the underestimation of shear resistance. ‘-’ in Table 7 indicates g and h were not listed due to the loss of contact between the top plate and the fresh mixture. The notation for sample names followed a format of FA(X)-(Y), where X represented the FA content (i.e. as a percentage of the total binder) and Y represented the w/b ratio.

[00142] A generally increasing trend in g and h may be observed with elapsed time. This may be possibly associated with the precipitation of brucite ($Mg(OH)_2$) on the surface of RMC particles, which increased the direct contact between particles by enlarging the solid particle sizes, leading to additional drag between fluid layers.

[00143] The effects of water and FA contents on the rheological properties of RMC samples are shown in FIGS. 11A-B, where declining trends in both yield stress (g) and plastic viscosity (h) were observed with increasing water content. FIG. 11A shows a plot of plastic viscosity (in Pascals

second or Pa s) as a function of fly ash / binder ratio (FA/b) (in percent or %) illustrating the effects of the water and fly ash contents on the plastic viscosity of the mixture according to various embodiments. FIG. 11B shows a plot of yield stress (in Pascals or Pa) as a function of fly ash / binder ratio (FA/b) (in percent or %) illustrating the effects of the water and fly ash contents on the yield stress of the mixture according to various embodiments.

[00144] The reduction in plastic viscosity and yield stress with increasing w/b ratios may be attributed to the higher liquid content that decreased direct contact amongst the particles. While an increase in the FA content from 0% to 30% led to an increase in plastic viscosity, it may not have a profound effect on the yield stress since the effect of particle shape was not apparent at $V_s < 0.38$ and its influence on the direct contact force may be limited.

[00145] This increase in the plastic viscosity with FA content may be due to the enhanced Van der Waals forces, due to the reduction of the distance between particles as V_s increased. The relatively constant yield stress of samples FA0-0.58 and FA30-0.58 may be due to the loose compaction of particles within these two mixes, thereby limiting the effect of particle shape on Van der Waals forces. A further increase in the FA content from 30% to 60% resulted in the decline of both g and h at all w/b ratios.

[00146] Although an increase in the solid volume fraction with an increase in the FA content could be expected due to the lower density of FA compared to RMC (2400 kg/m^3 vs. 3230 kg/m^3), the reduction of the yield stress and plastic viscosity with increasing FA content may be attributed to the spherical geometry of FA particles, which reduced the contact force between particles.

[00147] Mechanical Performance

[00148] Based on the rheological results mentioned above, samples containing 30% FA (i.e. FA/b = 0.3) with a w/b ratio of ≤ 0.53 were prepared for further analysis. The w/b ratio was reduced to achieve a higher viscosity for good fiber dispersion. Fibers were introduced into these mixes at a fixed amount of 2% by the volume of the RMC-SHC paste, in line with the previous literature on ECC.

[00149] The effects of key factors such as the fiber surface treatment (oil coated (OC) vs. non-coated (NC)), fiber aspect ratio (length of mm 8 vs. 12 mm), w/b ratio (0.41 vs. 0.53) and curing duration (7 days vs. 28 days) on the compressive and tensile strength of carbonated RMC-based samples were investigated.

[00150] The mechanical performance of the samples may be presented in Table 8. As highlighted above, the notation for sample names followed a format of (X)-(Y)-(Z), where X, Y and Z represented the fiber surface treatment, fiber length and w/b ratio, respectively. The term ‘OC’ for (X) refers to oil coating, while the term ‘NC’ refers to no oil coating. The unit for (Y) is in millimeters (mm).

Sample	Curing age (days)	Compressive strength (MPa)	Results of uniaxial tensile test				
			First cracking strength (MPa)	Ultimate tensile strength (MPa)	Tensile strain capacity (%)	Crack spacing (mm)	Average crack width (μm)
NC-12-0.41	7	18.97 ±0.48	2.19 ±0.48	2.61 ±0.48	2.64 ±1.22	1.45 ±0.14	47.21 ±15.08
	28	-	2.38 ±0.24	3.67 ±0.35	2.70 ±0.96	1.74 ±0.27	63.77 ±10.38
OC-12-0.41	7	19.09 ±3.57	2.61 ±0.42	3.73 ±0.32	3.26 ±1.33	3.08 ±1.80	84.17 ±8.74
	7	4.51 ±0.07	1.44 ±0.15	1.75 ±0.05	2.20 ±0.29	6.0 ±1.6	118.0 ±10.6
OC-8-0.53	7	5.81 ±0.63	1.31 ±0.08	1.70 ±0.20	0.36 ±0.15	27.9 ±5.8	32.25 ±21.9

Table 8 Mechanical test results.

[00151] The crack spacing may be computed by:

$$\text{Crack spacing(mm)} = \text{Gauge length} / \text{crack number} \quad (4)$$

[00152] The tensile stress recorded at the occurrence of the first crack is referred to as the “first cracking strength”, whereas the tensile stress and tensile strain approaching specimen failure are referred to as the “ultimate tensile strength” and “tensile strain capacity”, respectively. In addition to the first cracking strength, ultimate tensile strength and tensile strain capacity, crack spacing and average crack width of each sample are also provided in Table 8. The high tensile strain capacity of more than 1% in general, coupled with the limitation in the crack width of less than

100 μm for most samples, may indicate that the RMC-based composites possess strain-hardening behavior and tensile ductility.

[00153] FIGS. 12A-E show the relationship between the tensile stress and strain of composites formed from each mix. As highlighted above, the notation for sample names followed a format of (X)-(Y)-(Z), where X, Y and Z represented the fiber surface treatment, fiber length and w/b ratio, respectively. The term 'OC' for (X) refers to oil coating, while the term 'NC' refers to no oil coating. The unit for (Y) is in millimeters (mm).

[00154] FIG. 12A is a plot of tensile stress (in mega Pascals or MPa) as a function of tensile strain (in percent or %) illustrating tensile stress-strain curves of the samples NC-12-0.41 after curing for 7 days according to various embodiments. FIG. 12B is a plot of tensile stress (in mega Pascals or MPa) as a function of tensile strain (in percent or %) illustrating tensile stress-strain curves of the samples NC-12-0.41 after curing for 28 days according to various embodiments. FIG. 12C is a plot of tensile stress (in mega Pascals or MPa) as a function of tensile strain (in percent or %) illustrating tensile stress-strain curves of the samples OC-12-0.41 after curing for 7 days according to various embodiments. FIG. 12D is a plot of tensile stress (in mega Pascals or MPa) as a function of tensile strain (in percent or %) illustrating tensile stress-strain curves of the samples OC-12-0.53 after curing for 7 days according to various embodiments. FIG. 12E is a plot of tensile stress (in mega Pascals or MPa) as a function of tensile strain (in percent or %) illustrating tensile stress-strain curves of the samples OC-8-0.53 after curing for 7 days according to various embodiments.

[00155] Distinct elastic and strain-hardening stages were observed within each sample. In the elastic stage, the tensile stress may develop linearly with the strain. The continuous increase in the load led to the introduction of the first crack, which may mark the beginning of the strain-hardening stage. During the strain-hardening stage, tensile stress increased slowly with the strain, accompanied with the progressive generation of multiple fine cracks that may indicate ductility. Towards the end of strain-hardening, tensile stress may start to drop dramatically due to the deterioration of fiber bridging followed by damage localization with increasing load. At this point, the load was released immediately after specimen failure, leading to the shrinking of a majority of the cracks due to the spring effect of fiber-bridging.

[00156] FIG. 13 is an image showing the typical crack distribution of a failed specimen (NC-12-0.41 with 7 days of curing) after unloading according to various embodiments. FIG. 13 illustrates the occurrence of multiple cracks in RMC-based samples. The typical fracture surface may be seen in FIG. 14A, where the layout of fibers at the location of the crack at failure is revealed. FIG. 14A is an image showing the fracture surface of the specimen shown in FIG. 13 according to various embodiments. The fracture surface has several pulled fibers.

[00157] The pulled-out fiber and the leftover fiber tunnel at a fracture point are shown in FIGS. 14B and 14C respectively. FIG. 14B is a field emission scanning electron microscopy (FESEM) image of a pulled-out fiber shown in FIG. 14A according to various embodiments. FIG. 14C is a field emission scanning electron microscopy (FESEM) image of a left-over tunnel in the matrix after the fiber shown in FIG. 14B is pulled out according to various embodiments.

[00158] As can be seen from these images, the fiber surface was smooth with a very small amount of matrix debris attached on it, showing that a majority of the fibers were pulled out instead of ruptured. This suggests the fiber strength may not be fully utilized in the developed formulations, and the limiting factor may be the fiber-matrix interface, which may be further strengthened.

[00159] Effect of fiber surface treatment (samples OC-12-0.41 vs. NC-12-0.41)

[00160] The effect of fiber surface treatment in terms of the presence of the oil coating on sample performance may be assessed via a comparison of a sample having fibers with an oil coating (OC-12-0.41) and a sample having fibers without an oil coating (NC-12-0.41). Both samples may be cured for 7 days before being tested.

[00161] While there was not a significant difference in the compressive strength of both samples, the presence of oil coating greatly enhanced tensile ductility from 2.64% to 3.26% due to the larger crack width observed with the use of oil coated fibers (about 47 μm for NC-12-0.41 vs. about 84 μm for OC-12-0.41).

[00162] The presence of oil coating on the fibers may reduce the fiber-matrix interface bond and subsequently form wider crack spacings with larger crack widths. Therefore, adjustment of the oil content applied on the fiber surface may present an effective means in enhancing the ductility of RMC-SHC, albeit at the cost of enlarged crack widths, which can lead to increased water penetration and reduced long-term durability.

[00163] Effect of fiber aspect ratio (samples OC-8-0.53 vs. OC-12-0.53)

[00164] The effect of fiber aspect ratio caused by the differences in fiber lengths can be evaluated via a comparison of sample OC-8-0.53 containing fibers with lengths of 8 mm, and sample OC-12-0.53 containing fibers with lengths 12 mm. An increase in the fiber aspect ratio may lead to a significant improvement in tensile strength and ductility.

[00165] From the study on the failure mechanism of the samples, it may be seen from FIG. 14A that most of the fibers within the matrix were pulled instead of ruptured. This revealed the weak bonds may be present between the fiber-matrix within the composite, showing that the fiber strength was not fully utilized during pullout for the sample in FIG. 14A. An increase in the fiber embedment length may present a stronger resistance to the pullout force, leading to better fiber-bridging and stronger strain-hardening effect.

[00166] Effect of w/b ratio (samples OC-12-0.41 vs. OC-12-0.53)

[00167] The effect of w/b on the compressive and tensile strength of RMC-SHC formulations may be determined via a comparison of sample OC-12-0.41 and sample OC-12-0.53. A reduction in the compressive strength was observed with an increase in the w/b ratio from 0.41 to 0.53. This may be associated with a decrease in the diffusion rate of carbon dioxide (CO₂) within the saturated pore system at higher water contents, which would reduce the extent of carbonation and the associated formation of strength providing carbonate phases; as well as the increased porosity through the presence of additional free water. In addition to the weakening of the matrix, the fiber-matrix interface may also be weakened, causing a reduction in the strength of the bonding between the fiber and the matrix. On the other hand, reduction of the w/b ratio from 0.53 to 0.41 not only enhanced the first cracking and the ultimate tensile strength, but also provided a better tensile ductility. Improvements in the strain-hardening effect and fiber-bridging were further revealed by the reduced crack spacing and average crack width.

[00168] Effect of curing duration (sample NC-12-0.41 at 7 days vs. 28 days)

[00169] The effect of curing duration on sample performance may be determined via an investigation of a sample of NC-12-0.41 that has been cured for 7 days and another sample of NC-12-0.41 that has been cured for 28 days. The strength results indicated that there may be an improvement in the ultimate tensile strength with increased curing duration, while the tensile ductility may remain almost unchanged. The enhanced ultimate strength may be associated with

the improvements in fiber-bridging, which may be attributed to the continued formation of carbonate phases that strengthened the fiber-matrix interface over the 28-day curing period. An increase in the crack spacing and average crack width was observed with an increase in curing duration from 7 days to 28 days, indicating a reduction in strain-hardening, which was influenced by the enhanced matrix toughness at longer curing durations.

[00170] Carbon dioxide (CO₂) sequestration

[00171] The amount of CO₂ sequestered during the curing process was quantified via thermogravimetric analysis (TGA)/ differential scanning calorimetry (DSC). FIG. 15 is a plot of mass (in percent or %) / heat flow (in milli-Watts or mW) as a function of temperature (in degree Celsius or °C) showing the thermogravimetric analysis (TGA) curve and the differential scanning calorimetry (DSC) curve of a sample of OC-12-0.53 according to various embodiments.

[00172] The mass loss < 100 °C due to the loss of hygroscopic water was followed by two distinct endothermic peaks. The first peak at around 320 °C may correspond to the removal of water of crystallization in Mg-carbonates that formed during carbonation curing, and the decomposition of uncarbonated hydrates (Mg(OH)₂) into MgO. The second peak at around 460 °C may correspond to the decarbonation of carbonate phases, leaving MgO at the end of the analysis. The quantification of the mass loss at > 460 °C, which was associated with the loss of CO₂ from the carbonated RMC system, revealed an average carbonation degree of around 10%. These results indicate that the sequestration of CO₂ in the form of stable carbonates within the prepared formulations may not only provide a safe storage for atmospheric CO₂, but may also contribute to the development of a type of strain-hardening composite that does not necessitate the use of any Portland cement (PC).

[00173] While the invention has been particularly shown and described with reference to specific embodiments, it should be understood by those skilled in the art 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 cementitious composition comprising:
 - a mixture comprising:
 - a binder component comprising reactive magnesium oxide cement;
 - a water reducing agent;
 - a viscosity agent; and
 - water; and
 - one or more fibers dispersed in the mixture;
 - wherein a percentage of reactive magnesium oxide cement in the binder component by mass is any one percentage value selected from range from 40% to 100%;
 - wherein a percentage of the water reducing agent relative to the binder component by mass is any one percentage value selected from 2% to 4%;
 - wherein a percentage of the viscosity agent relative to the binder component by mass is any one percentage value selected from a range from 0.05% to 5%; and
 - wherein the cementitious composition is configured to sequester atmospheric carbon dioxide during curing.
2. The cementitious composition according to claim 1,
 - wherein the binder component further comprises any one or more binders selected from a group consisting of hydraulic cement, coal fly ash, silica fume, and ground granulated blast furnace slag.
3. The cementitious composition according to claim 1 or claim 2,
 - wherein a mass ratio of water to binder component is any one ratio selected from a range from 0.4 to 0.8.

4. The cementitious composition according to any one of claims 1 to 3,
wherein the water reducing agent is sodium hexametaphosphate solution.
5. The cementitious composition according to any one of claims 1 to 4,
wherein the viscosity controlling agent is hydroxypropyl methylcellulose.
6. The cementitious composition according to any one of claims 1 to 5,
wherein the one or more fibers are any one type of fibers selected from a group
consisting of metallic fibers, polymeric fibers, and natural fibers.
7. The cementitious composition according to any one of claims 1 to 6,
wherein a percentage of the one or more fibers in the cementitious composition by
volume is any one percentage value selected from a range from 0.5% to 10%.
8. The cementitious composition according to any one of claims 1 to 7,
wherein each of the one or more fibers comprises a coating of an oiling agent.
9. A cement-based structure comprising:
a matrix comprising one or more hydrated magnesium carbonates; and
one or more fibers embedded in the matrix;
wherein the matrix is formed by curing a cementitious composition, the
cementitious composition comprising:
a mixture comprising:
a binder component comprising reactive magnesium oxide cement;
a water reducing agent;
a viscosity agent; and
water; and
one or more fibers dispersed in the mixture;

wherein a percentage of reactive magnesium oxide cement in the binder component by mass is any one percentage value selected from range from 40% to 100%;

wherein a percentage of the water reducing agent relative to the binder component by mass is any one percentage value selected from 2% to 4%;

wherein a percentage of the viscosity agent relative to the binder component by mass is any one percentage value selected from a range from 0.05% to 5%; and

wherein the cementitious composition is configured to sequester atmospheric carbon dioxide during curing.

10. A method of forming a cementitious composition, the method comprising:

forming a mixture comprising:

a binder component comprising reactive magnesium oxide cement;

a water reducing agent;

a viscosity agent; and

water; and

dispersing one or more fibers in the mixture;

wherein a percentage of reactive magnesium oxide cement in the binder component by mass is any one percentage value selected from range from 40% to 100%;

wherein a percentage of the water reducing agent relative to the binder component by mass is any one percentage value selected from 2% to 4%;

wherein a percentage of the viscosity agent relative to the binder component by mass is any one percentage value selected from a range from 0.05% to 5%; and

wherein the cementitious composition is configured to sequester atmospheric carbon dioxide during curing.

11. The method according to claim 10,

wherein the binder component further comprises any one or more binders selected from a group consisting of hydraulic cement, coal fly ash, silica fume, and ground granulated blast furnace slag.

12. The method according to claim 10 or claim 11,

wherein each of the one or more fibers comprises a coating of an oiling agent.

13. A method of forming a cement-based structure, the method comprising:

forming a matrix comprising one or more hydrated magnesium carbonates;

wherein one or more fibers is embedded in the matrix;

wherein the matrix is formed by curing a cementitious composition, the cementitious composition comprising:

a mixture comprising:

a binder component comprising reactive magnesium oxide cement;

a water reducing agent;

a viscosity agent; and

water; and

one or more fibers dispersed in the mixture;

wherein a percentage of reactive magnesium oxide cement in the binder component by mass is any one percentage value selected from range from 40% to 100%;

wherein a percentage of the water reducing agent relative to the binder component by mass is any one percentage value selected from 2% to 4%;

wherein a percentage of the viscosity agent relative to the binder component by mass is any one percentage value selected from a range from 0.05% to 5%; and

wherein the cementitious composition is configured to sequester atmospheric carbon dioxide during curing.