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(54) Title: CARBONATABLE COMPOSITIONS WITH ADMIXTURES

(57) **Abstract:** The invention provides novel methods and novel additive compositions and use thereof in a wide range of concrete production for improving properties of concrete materials. The methods and compositions of the invention may be applied in a variety of cement and concrete components in the infrastructure, construction, pavement and landscaping industries.

CARBONATABLE COMPOSITIONS WITH ADMIXTURES

CROSS-REFERENCE TO RELATED APPLICATION

[0001] This application claims priority to and the benefit of U.S. Provisional Application No. 63/040,070, filed on June 17, 2020, the disclosure of which is incorporated herein by reference in its entirety.

FIELD OF THE INVENTION

[0002] The present invention generally relates to carbonatable calcium silicate-based cements and concretes. More specifically, the present invention relates to, for example, carbonatable calcium silicate-based cements and concretes that comprise admixture(s) that can improve one or more properties associated with the carbonatable calcium silicate-based cements and concretes. The present invention also relates to methods for making carbonatable calcium silicate-based cements and concretes that comprise admixture(s). The methods and compositions of the invention may be applied in a variety of cement and concrete components in the infrastructure, construction, pavement and landscaping industries.

BACKGROUND OF THE INVENTION

[0003] In this specification where a document, act or item of knowledge is referred to or discussed, this reference or discussion is not an admission that the document, act or item of knowledge or any combination thereof was at the priority date, publicly available, known to the public, part of common general knowledge, or otherwise constitutes prior art under the applicable statutory provisions; or is known to be relevant to an attempt to solve any problem with which this specification is concerned.

[0004] Concrete is the most consumed man-made material in the world. A typical concrete is made by mixing Portland cement, water and aggregates such as sand and crushed stone. Portland cement is a synthetic material made by burning a mixture of ground limestone and clay, or materials of similar composition in a rotary kiln at a sintering temperature of around 1,450 °C. Portland cement manufacturing is not only an energy-intensive process, but also one that releases considerable quantities of greenhouse gas (CO_2). The cement industry accounts for approximately 5% of global anthropogenic CO_2 emissions. More than 60% of such CO_2 comes from the chemical decomposition or calcination of limestone.

[0005] Recently, a revolutionary form of cement that is based on carbonatable calcium silicate materials has emerged as a promising substitute to traditional cements. Production of carbonatable calcium silicate-based cements involves significantly reduced CO_2 emissions and energy consumption. In addition, this new cement sequesters CO_2 when cured into concrete products because CO_2 is needed to react with the carbonatable calcium silicate materials during the curing process to form cured or densified concrete products.

[0006] However, even with these revolutionary forms of cements, a need exists for solutions to improve one or more properties associated with cement in the field of concrete production, particularly for precast concrete produced with carbonatable calcium silicate-based cements, for low cost materials and reliable and efficient processing and curing methodologies that achieve improved properties in concrete products.

SUMMARY OF THE INVENTION

[0007] The invention provides methods and compositions for improving one or more properties of carbonatable calcium silicate-based cement and concrete products. The carbonatable calcium silicate-based cement composition of the invention comprises one or more selected admixtures that improve properties. Examples of properties that can be improved include aesthetic qualities and physical properties (*e.g.*, mechanical and durability properties), and combinations thereof. In addition, one or more admixtures may be used to improve or optimize processing and/or curing of carbonatable calcium silicate-based cement and concrete products.

[0008] In one aspect, the invention generally relates to a calcium silicate-based material comprising one or more admixture.

[0009] According to a further aspect, the calcium silicate-based material of comprises any one or more of the admixtures disclosed in the present specification, in any combination.

[0010] A calcium silicate-based material formed according to certain embodiments includes: grains of carbonatable phases selected from wollastonite or pseudowollastonite ($CaSiO_3$, CS), rankinite ($Ca_3Si_2O_7$, C3S2) and larnite (Ca_2SiO_4, C2S, belite); grains of partially reactive amorphous phases; or grains or particles of uncarbonatable phases selected from melilite ($(Ca, Na, K)2[(Mg, Fe^{2+}, Fe^{3+}, Al, Si)_3O_7]$) and crystalline silica (SiO_2); or a combination of any two or more types thereof; and a combination of one or more admixtures selected from: strength enhancers, hydrophobic compounds, set retarders, pH enhancing additives, efflorescence reducers, ettringite growth inhibitors, minerals, corrosion inhibitors, air-entraining admixtures, shrinkage-reducing admixtures, evaporation controlling admixtures, plasticizers, superplasticizers, and crystallization inhibitors.

[0011] The calcium silicate-based above, wherein the calcium silicate-based material can be curable by carbonation.

[0012] The calcium silicate-based material above, wherein the calcium silicate-based material can be curable by carbonation at a temperature of about 35°C to about 105°C to form $CaCO_3$ with a mass gain of about 10% or more.

[0013] The calcium silicate-based material above, wherein elemental Ca and elemental Si can be present in the material at a molar ratio from about 0.8 to about 1.2; and metal oxides of Al, Fe and Mg can be present in the material at about 30% or less by mass.

[0014] The calcium silicate-based material above, wherein at least one hydraulic species can be present in an amount of 5% or less.

[0015] The calcium silicate-based material above, wherein the admixture may include a set-retarding admixture, is present in an amount of about 0.1 to about 10 g per kg of the calcium silicate-based material, and is selected from one or more of: monosaccharides (xylose), disaccharides (sucrose), trisaccharides (raffinose), citric acid, tartaric acid, oxalic acid, malic acid, lignosulfonates, hydroxycarboxylic acids, gluconic acid, gluconic acid salts, boric acid, boric acid salts, orthophosphates, metaphosphates, zinc salts, sugar alcohols, salicylic acid, mucic acid, galactaric acid, sorbitol, heptonic acid salts, pentose sugars, arabinose.

[0016] The calcium silicate-based material above, wherein the admixture may have a water-reducer, plasticizer, superplasticizer and dispersant admixture, is present in an amount of about 0.01 to 5 g per kg of the calcium silicate-based material, and is one or more of a polycarboxylate ether type polymer.

[0017] The calcium silicate-based material above, wherein the polycarboxylate ether type polymer can include poly(oligo(ethylene glycol) methyl ether methacrylate/methacrylic acid, having a comb-like polymer built up with ionic hydrophilic carboxylate groups and long, elastic side nonionic hydrophilic oligo(ethylene oxide) chains, where the long ethylene oxide side chains exert steric hindrance that keeps the carbonatable calcium silicate grains away from each other to prevent agglomeration.

[0018] The calcium silicate-based material above, wherein the polycarboxylate ether type polymer can be selected from one or more of: vinyl acetate, methyl acrylate, methacrylamide, 2-hydroxylethyl methacrylate, sodium 2-methyl-2-propene-1-sulphonate, sodium allyl sulfonate, 2-methacryloyloxy-ethyl-trimethyl-ammonium chloride, 3-trimethoxysilyl-propyl-methacrylate, 2-(methacryloyloxy)-ethyl phosphate, 2-acrylamido-2-methyl-1-propanesulfonic acid, β-cyclodextrin with methacrylic ester group, β-cyclodextrin with a maleic ester group, and octadecyl phosphate.

[0019] The calcium silicate-based material above, wherein the admixture may include a water-proofing and hydrophobic admixture, is present in an amount of about 0.1 to about 10 g per kg of the calcium silicate-based material, and is selected from one or more of: silanes, siloxanes, alkaline earth stearates, stearic acid dissolved in alcohols, alkali oleates, oleic acid salts, fatty acids, valeric acid, archidic acid, palmitic acid, arachidonic acid, erucic acid, lionoleic acid, lauric acid and their respective salts.

[0020] The calcium silicate-based material above, wherein the admixture may have a pH-regulating admixture, is present in an amount of about 0.1 to about 10 g per kg of the calcium silicate-based material, and is selected from one or more of: calcined alkaline earth oxides, dolomitic hydrated lime, alkali hydroxides, sodium silicate, water glass, high alkalinity recycled concrete, slag aggregate, Ordinary Portland Cement (OPC), calcium nitrite, calcium nitrate tetrahydrate, alkali carbonates and alkali bicarbonates.

[0021] The calcium silicate-based material above, wherein the admixture may include a carbonation-curing enhancer, accelerator and $CaCO_3$ crystal structure-controlling admixture, is present in an amount of about 0.1 to about10 g per kg of the carbonatable calcium silicate material, and is selected from one or more of: an aqueous solution of dilute acetic acid, an aqueous solution of alkaline earth oxides solubilized in acetic or citric acid, an aqueous suspension of alkaline earth hydroxides, water soluble salts of alkaline earth elements, triethanolamine, diethanolamine, triisopropanolamine, triehtylenepentamine, hydroxyethyldiethylenetriamine, and aminoethylethanolamine.

[0022] The calcium silicate-based material above, wherein the water-reducing admixture can be selected from plasticizers based on naphthalene (PNS, polynaphthalene sulfonates) or lignosulphonates.

[0023] The calcium silicate-based material above, wherein forming/mixing water used in production of the material can be pre-carbonated with CO_2 gas to increase the dissolved CO_2 concentration of the water from almost zero to around 1 to 6 g per liter, preferably to about 1.5 g per liter, at room temperature and pressure.

[0024] The calcium silicate-based material above, wherein the admixture may enhance the rate of water removal from the material, in attaining uniform distribution of moisture within the material, and in carbonation-curing with an improved total CO_2 uptake by the solid body.

[0025] The calcium silicate-based material above, wherein the admixture may include a combination of two or more of: a water-reducer, superplasticizer, a set retarder, a curing enhancer, an air-entrainer, an efflorescence control agent, and a liquid hydrophobe.

[0026] The calcium silicate-based material above, wherein the admixture can be a combination of two or more of: strength enhancers, hydrophobic compounds, set retarders, pH enhancing additives, efflorescence reducers, ettringite growth inhibitors, minerals, corrosion inhibitors, air-entraining admixtures, shrinkage-reducing admixtures, evaporation controlling admixtures, plasticizers, superplasticizers, and crystallization inhibitors.

[0027] The calcium silicate-based material above, wherein the combination can be premixed in water and then added and mixed with the calcium silicate-based material as a single liquid admixture.

[0028] The calcium silicate-based material above, wherein carbonation of the calcium silicate-based material may result in the formation of one or more phases of calcium carbonates, such as amorphous and hydrated calcium carbonate, dry amorphous calcium carbonate, monohydrocalcite, $CaCO_3 \cdot H_2O$, calcium carbonate hexahydrate, $CaCO_3 \cdot 6H_2O$, calcite, vaterite and aragonite.

[0029] A composite material comprising the calcium silicate-based material as described above, may further include one or more aggregate.

[0030] A calcium silicate-based material formed according to further aspects may include: grains of carbonatable phases selected from wollastonite or pseudowollastonite ($CaSiO_3$, CS), rankinite ($Ca_3Si_2O_7$, C3S2) and larnite (Ca_2SiO_4, C2S, belite); grains of partially reactive amorphous phases; or grains or particles of uncarbonatable phases selected from melilite ($(Ca, Na, K)2[(Mg, Fe^{2+}, Fe^{3+}, Al, Si)_3O_7]$) and crystalline silica (SiO_2); or a combination of any two or more types thereof; and a curing enhancing admixture selected from: sucrose, glucose, fructose, acetic acid, malic acid, tartaric acid, citric acid, gluconic acid, hydroxycarboxylic acid, magnesium, magnesium compounds, and combinations thereof.

[0031] The calcium silicate-based material above, wherein the admixture may include magnesium oxide or a magnesium salt.

[0032] The calcium silicate-based material above, wherein the calcium silicate-based material may be present at about 0.02% to about 20%,of the admixture, by weight.

[0033] According to additional aspects, a method of forming a cured calcium silicate-based material may include: forming a mixture of a carbonatable calcium silicate-based material; a curing enhancing admixture selected from sucrose, glucose, fructose, acetic acid, malic acid, tartaric acid, citric acid, gluconic acid, hydroxycarboxylic acid, magnesium, magnesium compounds, and combinations thereof; and water; drying the mixture; and curing the mixture by exposing the mixture to carbon dioxide to form the cured calcium silicate-based material; wherein the cured calcium silicate-based material has a compressive strength of at least 6,000 psi.

[0034] The method above, wherein the carbonatable calcium silicate-based material may include grains of carbonatable phases selected from wollastonite or pseudowollastonite ($CaSiO_3$, CS), rankinite ($Ca_3Si_2O_7$, C3S2) and larnite (Ca_2SiO_4, C2S, belite); grains of partially reactive amorphous phases; or grains or particles of uncarbonatable phases selected from melilite ($(Ca, Na, K)2[(Mg, Fe^{2+}, Fe^{3+}, Al, Si)_3O_7]$) and crystalline silica (SiO_2); or a combination of any two or more types thereof.

[0035] The method above, wherein the admixture may include magnesium oxide or a magnesium salt.

[0036] The method above, wherein the mixture may have about 0.02% to about 20%,of the admixture, by weight.

[0037] The method above, wherein the cured calcium silicate-based material may have a compressive strength of at least 8,000 psi.

[0038] The method above, wherein the cured calcium silicate-based material may have a compressive strength of at least 8,000 psi.

BRIEF DESCRIPTION OF THE DRAWINGS

[0039] The objects and features of the invention can be better understood with reference to the drawings described below, and the claims. The drawings are not necessarily to scale, emphasis instead generally being placed upon illustrating the principles of the invention. In the drawings, similar numerals are used to indicate similar parts throughout the various views.

[0040] **FIG. 1** is a phase diagram of the $CaO\text{-}SiO_2\text{-}CO_2$ system at a pressure of 1 kilobar.

[0041] **FIG. 2** is a graph showing flow (slump) behavior in the presence of admixtures according to Example 1.

[0042] **FIG. 3** is a graph showing compressive strength development in the presence of admixtures according to Example 1.

[0043] **FIG. 4** is a graph showing drying rates of CCSC (Carbonatable Calcium Silicate Cement) specimens according to Example 2.

[0044] **FIG. 5** is a graph showing degree of saturation (DoS) and distribution of moisture as a function of sample depth after 24 hours of drying according to Example 2.

[0045] **FIG. 6** is a graph showing CO_2 uptake rates of CCSC specimens over the course of 24 hours according to Example 3.

[0046] **FIG. 7** shows CCSC concrete pavers produced with and without a curing enhancer after curing and application of phenolphthalein dye according to Example 3.

[0047] **FIG. 8** is a graph showing the impact of curing enhancers on compressive strength of European Norm (EN) mortar cubes according to Example 4.

[0048] **FIG. 9** is a graph showing the impact of curing enhancers on compressive strength of concrete pavers according to Example 4.

[0049] **FIG. 10** is a graph showing the impact of curing enhancers on compressive strength of 4x8" concrete cylinders according to Example 4.

[0050] **FIGS. 11A - 11B** are graphs showing a distribution curve of compressive strength results for Mix A (FIG. 11A) without a curing enhancer, and Mix B (FIG. 11B) with Na-citrate (hydroxycarboxylic acid) curing enhancer, according to Example 5.

[0051] **FIG. 12** shows water absorption of mortar mixes containing fatty acids representative of short carbon chain lengths (valeric acid, 5:0), medium chain lengths (lauric acid, 12:0), and saturated (stearic acid, 18:0) or unsaturated (oleic acid, 18:1) long chain lengths, according to Example 6. All mixes produced with fatty acids reduced the rate of water absorption relative to the control mix.

[0052] **FIG. 13** is mortar specimens shown at the end of water absorption testing. Relative to the (A) control, specimens containing (B) valeric acid 0.25%, (C) lauric acid 0.25%, (D) oleic acid 0.25%, and (E) stearic acid 0.25% exhibit reduced rate and total absorption of water according to Example 6.

[0053] **FIG. 14** shows water absorption of mortar mixes containing salts of fatty acids and two proprietary silanes according to Example 6. Both the salts of fatty acids and the silanes reduced the rate and total absorption of water relative to the control mix.

[0054] **FIG. 15** is mortar specimens shown at the end of water absorption testing both with and without the addition of fatty acid salts. Relative to the (A) control, specimens containing (B) Na-oleate 1.0% and (C) Ca-stearate 1.0% exhibit reduced rate and total absorption of water according to Example 6.

[0055] **FIG. 16** is mortar specimens shown at the end of water absorption testing both with and without the addition of silanes. Relative to the (A) control, specimens containing (B) Silane A and specimens containing (C) Silane B exhibit reduced rate and total absorption of water according to Example 6.

[0056] **FIGS. 17A - 17B** are mortar specimens tested according to procedures outlined in ASTM C67 using 10% NaCl solution to simulate severe efflorescence. (FIG. 17A) Control specimens showed significant deposition of surface salts while (FIG. 17B) specimens containing 1.0% Ca-stearate showed minimal ingress of water and no apparent efflorescence, according to Example 6.

[0057] **FIG. 18** shows average water absorption of two different raw material concrete mixes produced with and without calcium stearate dosed by percent weight of cement. The use of calcium stearate at each of the tested dosages reduced total water absorption relative to the control batches, according to Example 7.

[0058] **FIG. 19** is a comparison between Concrete Mix B without Ca-stearate (top) and Concrete Mix B containing 1.0% Ca-stearate (bottom). The presence of fatty acid based salts improved water resistance, according to Example 7.

[0059] **FIG. 20** is a comparison between ground installations after rain exposure of pavers containing Concrete Mix A without Ca-stearate (left) and Concrete Mix A with 1.0% Ca-stearate (right). Pavers produced with 1.0% Ca-stearate exhibit visibly reduced penetration and permeation of water in comparison to control pavers, according to Example 7.

[0060] **FIG. 21** shows ASTM C67 efflorescence testing of CCSC pavers partially submerged in 10% NaCl solution. Pavers produced without Ca-stearate (A) show significant deposition of surface salts while pavers produced with 1.0% Ca-stearate (B) show significant reduction in water ingress and deposition of surface salts, according to Example 7.

[0061] **FIG. 22** shows water absorption of mortar mixes containing fatty acids representative of short carbon chain lengths (valeric acid, 5:0), medium chain lengths (lauric acid, 12:0), and saturated (stearic acid, 18:0) or unsaturated (oleic acid, 18:1) long chain lengths, according to Example 8. All mixes produced with fatty acids reduced the rate of water absorption relative to the control mix.

[0062] **FIG. 23** is mortar specimens shown at the end of water absorption testing. Relative to the (A) control, specimens containing (B) valeric acid 0.25%, (C) lauric acid 0.25%, (D) oleic acid 0.25%, and (E) stearic acid 0.25% exhibit reduced rate and total absorption of water, according to Example 8.

[0063] **FIG. 24** is a graph showing water absorption of mortar mixes containing salts of fatty acids and two proprietary silanes. Both the salts of fatty acids and the silanes reduced the rate and total absorption of water relative to the control mix, according to Example 8.

[0064] **FIG. 25** is mortar specimens shown at the end of water absorption testing both with and without the addition of fatty acid salts. Relative to the (A) control, specimens containing (B) Na-oleate 1.0% and (C) Ca-stearate 1.0% exhibit reduced rate and total absorption of water, according to Example 8.

[0065] **FIG. 26** is mortar specimens shown at the end of water absorption testing both with and without the addition of silanes. Relative to the (A) control, specimens containing (B) Silane A and specimens containing (C) Silane B exhibit reduced rate and total absorption of water, according to Example 8.

[0066] **FIG. 27** is a graph showing average water absorption of two different raw material concrete mixes produced with and without calcium stearate (CS) dosed by percent weight of cement, according to Example 9. The use of calcium stearate at each of the tested dosages reduced total water absorption relative to the control batches.

[0067] **FIG. 28** shows Concrete Mix B without Ca-stearate (top) and Concrete Mix B containing 1.0% Ca-stearate (bottom), according to Example 9. The presence of a fatty acid based salt improved water resistance.

[0068] **FIG. 29** shows ground installations after rain exposure of pavers containing Concrete Mix A without Ca-stearate (left) and Concrete Mix A with 1.0% Ca-stearate (right), according to Example 9. Pavers produced with 1.0% Ca-stearate exhibit visibly reduced penetration and permeation of water in comparison to control pavers.

[0069] **FIG. 30** shows mass loss per unit area of CCSC Concrete pavers produced with and without the addition of 1.0% calcium stearate during exposure to deicing salt and freeze-thaw cycling according to Example 9.

[0070] **FIG. 31** is a plot showing set-retarding properties according to Example 13.

[0071] **FIG. 32** is a plot showing set-accelerator properties according to Example 13.

[0072] **FIG. 33** is a plot showing compressive strength data according to Example 14.

[0073] **FIG. 34** is a plot showing compressive strength data for Example 15.

[0074] **FIG. 35** is an SEM image of Ca-citrate crystals according to Example 16.

[0075] **FIG. 36** is a plot showing water absorption data according to Example 16.

[0076] **FIG. 37** is a plot showing compressive strength data according to Example 16.

[0077] **FIG. 38** is a plot showing compressive strength data according to Example 17.

[0078] **FIG. 39** is a plot showing water absorption data according to Example 17.

[0079] **FIG. 40** is a plot showing compressive strength data according to Example 22.

DETAILED DESCRIPTION OF THE INVENTION

[0080] Provided herein are carbonatable calcium silicate-based cements and concrete products that contain one or more admixtures, and methods of preparing carbonatable calcium silicate-based cements and concrete products that contain one or more admixtures.

The admixture(s) can improve one or more properties of carbonatable calcium silicate-based cements and concrete products, and/or improve the processing thereof.

[0081] The carbonatable calcium silicate-based cement composition of the invention comprises coarse, fine, and ultra-fine specially selected mineral additives to improve the strength, durability and aesthetic properties of concrete products in various precast applications.

[0082] Carbonatable calcium silicate-based cements and concretes are revolutionary replacements for conventional cement and concrete products. These materials can be produced and utilized with significantly reduced energy requirement and CO_2 emissions. The carbonatable calcium silicate compositions are made from widely available, low cost raw materials by a process suitable for large-scale production with flexible equipment and production requirements. This unique approach is accompanied by a remarkable proficiency for permanent and safe sequestration of CO_2. A wide variety of applications can benefit from the invention through improved energy consumption and more desirable carbon footprint, from construction, pavements and landscaping, to infrastructure and transportation.

[0083] As used herein, the singular forms "a," "an" and "the" are intended to include the plural forms as well, unless the context clearly indicates otherwise. The use of “or” is intended to include “and/or”, unless the context clearly indicates otherwise. Additionally, the use of “and” is intended to encompass “and/or,” unless the context clear indicates otherwise.

[0084] As used herein, “about” is a term of approximation and is intended to include minor variations in the literally stated amounts, as would be understood by those skilled in the art. Such variations include, for example, standard deviations associated with techniques commonly used to measure the recited amounts.

[0085] All of the numerical values contained in this disclosure are to be construed as being characterized by the above-described modifier "about," are also intended to include the exact numerical values disclosed herein. The ranges disclosed herein should be construed to encompass all values within the upper and lower limits of the ranges, unless indicated otherwise. Moreover, all ranges include the upper and lower limits.

[0086] As used herein, “carbonatable cement” refers to cement that is principally cured by reaction with carbon dioxide, CO_2, in any of its forms, such as, gaseous CO_2 in the presence of water, CO_2 in the form of carbonic acid, H_2CO_3, or in other forms that permit the reaction of CO2 with the non-hydraulic cement material.

Carbonatable calcium silicate-based cement and concrete products

[0087] Carbonatable calcium silicate-based cement, or low calcium silicate-based cement, and concrete products for use in the compositions and methods provided herein include any known to one of skill in the art. FIG. 1 is a phase diagram of the $CaO\text{-}SiO_2\text{-}CO_2$ system at a pressure of 1 kilobar. As used herein, "based on" means a component that makes up greater than 50% by weight of the total composition, or greater than 50% by weight of a distinct constituent of the total composition. As used herein, "low calcium silicate-based cement" means cements with a Ca/Si atomic ratio less than 2. In some embodiments, the starting materials to synthesize these cement chemistries are expected to be raw materials used in cement production such as limestone and shale, clay sand, and the like.

[0088] In certain embodiments, the carbonatable calcium silicate-based cement is a carbonatable low calcium silicate based uncarbonated concrete material, such as those described herein (e.g., Solidia Cement™ and Solidia Concrete™). The carbonation of the calcium silicate phases of the Solidia Cement™ can occur in the presence of CO_2 according to the following equations 1-3.

$$CaSiO_3(s) + CO_2(g) \xrightarrow{H_2O} CaCO_3(s) + SiO_2(s) \qquad (1)$$

$$Ca_3Si_2O_7(s) + 3CO_2(g) \xrightarrow{H_2O} 3CaCO_3(s) + 2SiO_2(s) \qquad (2)$$

$$Ca_2SiO_4(s) + CO_2(g) \xrightarrow{H_2O} 2CaCO_3(s) + SiO_2(s) \qquad (3)$$

[0089] Any suitable calcium silicate composition can be used. As used herein, the term "calcium silicate composition" can refer to naturally-occurring minerals or synthetic materials that are comprised of one or more of a group of calcium silicate phases including CS (wollastonite or pseudowollastonite, and sometimes formulated $CaSiO_3$ or $CaO\cdot SiO_2$), C3S2 (rankinite, and sometimes formulated as $Ca_3Si_2O_7$ or $3CaO\cdot 2SiO_2$), C2S (belite, β-Ca_2SiO_4 or larnite, β-$Ca_7Mg(SiO_4)_4$ or bredigite, α-Ca_2SiO_4 or γ-Ca_2SiO_4, and sometimes formulated as Ca_2SiO_4 or $2CaO\cdot SiO_2$), a calcium-silicate based amorphous phase, each of which material may include one or more other metal ions and oxides (*e.g.*, aluminum, magnesium, iron or manganese oxides), or blends thereof, or may include an amount of magnesium silicate in naturally-occurring or synthetic form(s) ranging from trace amount (1%) to about 50% or more by weight.

[0090] In certain embodiments, carbonatable calcium silicate-based cement comprises calcium silicate and one or more discrete calcium silicate phases selected from CS (wollastonite or pseudowollastonite), C3S2 (rankinite), C2S (belite, larnite), and an amorphous calcium silicate phase at about 30% or more (e.g., 35% or more, about 40% or more, about 45% or more) by mass of the total phases.

[0091] Thus, in one aspect, the invention generally relates to a carbonatable composition. The carbonatable composition can include: calcium silicate; one or more discrete calcium silicate phases selected from CS (wollastonite or pseudowollastonite), C3S2 (rankinite), C2S (belite, larnite, beta-C_2S or gamma-C_2S), and an amorphous calcium silicate phase at about 10% or more by mass of the total phases; and one or more minerals comprising magnesium oxide, such that magnesium oxide therein accounts for about, about 0.02% to 20%, by weight of the carbonatable composition. The elemental Ca and elemental Si can be present in the composition at a molar ratio less than 2.0, such as from about 0.5 to about 1.5; and metal oxides of Al, Fe and Mg can be present in the composition at about 30% or less by mass. The composition can be suitable for carbonation with CO_2 at a temperature of about 10 °C to about 90 °C to form $CaCO_3$ with a mass gain of about 10% or more.

[0092] In certain embodiments, as noted above, the molar ratio of Ca to Si of the composition is less than 2.0, such as from about 0.5 to about 1.5. In certain preferred embodiments, the molar ratio of Ca to Si of the composition is from about 0.5 to about 1.2. In certain preferred embodiments, the molar ratio of Ca to Si of the composition is from about 0.5 to about 1.15. In certain preferred embodiments, the molar ratio of Ca to Si of the composition is from about 0.8 to about 1.5. In certain preferred embodiments, the molar ratio of Ca to Si of the composition is from about 0.8 to about 1.2. In certain preferred embodiments, the molar ratio of Ca to Si of the composition is from about 0.8 to about 1.15. In certain preferred embodiments, the molar ratio of Ca to Si of the composition is from about 0.85 to about 1.15. In certain preferred embodiments, the molar ratio of Ca to Si of the composition is from about 0.90 to about 1.10. In certain preferred embodiments, the molar ratio of Ca to Si of the composition is from about 0.95 to about 1.05. In certain preferred embodiments, the molar ratio of Ca to Si of the composition is from about 0.98 to about 1.02. In certain preferred embodiments, the molar ratio of Ca to Si of the composition is from about 0.99 to about 1.01.

[0093] In some embodiments, the carbonatable composition includes one or more melilite type phases having the general formula $(Ca,Na,K)_2[(Mg, Fe^{2+},Fe^{3+},Al,Si)_3O_7]$ or ferrite type phases having the general formula $Ca_2(Al,Fe^{3+})_2O_5$.

[0094] In certain embodiments, the metal oxides of Al, Fe and Mg contained within the calcium silicate composition are generally less than about 30%. In certain preferred embodiments, the composition has about 20% or less of metal oxides of Al, Fe and Mg by total oxide mass. In certain embodiments, the composition has about 15% or less of metal oxides of Al, Fe and Mg by total oxide mass. In certain embodiments, the composition has about 12% or less of metal oxides of Al, Fe and Mg by total oxide mass. In certain embodiments, the composition has about 10% or less of metal oxides of Al, Fe and Mg by total oxide mass. In certain embodiments, the composition has about 5% or less of metal oxides of Al, Fe and Mg by total oxide mass.

[0095] Illustrative compositions according to optional embodiments are provided in Example 1.

[0096] In some embodiments, the invention generally relates to a composite material produced by carbonation of calcium silicate cement with CO_2, comprising interlocking acicular polymorphs of calcium carbonate.

[0097] In yet another aspect, the invention generally relates to a composite material. The composite material includes: a plurality of bonding elements, wherein each bonding element includes a core comprising primarily calcium silicate, a silica-rich inner layer, and a calcium carbonate-rich outer layer. The composite material includes a plurality of filler particles. The plurality of bonding elements and the plurality of filler particles together form one or more interlocking acicular polymorphs.

[0098] In some embodiments, the filler particles are made from a silicon dioxide-rich material. In some embodiments, the plurality of filler particles comprise one or more of quartz, mica and feldspar.

[0099] In some embodiments, the plurality of bonding elements are chemically transformed from ground wollastonite. In some embodiments, the plurality of bonding elements are chemically transformed from a precursor calcium silicate other than wollastonite.

[00100] In some embodiments, the composite material further includes a colorant, *e.g.*, one or more of iron oxide, cobalt oxide and chromium oxide. In some embodiments, the colorant is present in an amount from 0% to about 10% by weight of the composite material.

[00101] In some embodiments, the composite material further includes a discoloration control additive, *e.g.*, one or more of magnesium, magnesium oxide, magnesium nitrate, magnesium sulphate, magnesium chloride, and magnesium acetate. In some embodiments, the discoloration control additive is present in an amount from 0.02 to about 20% by weight of the bonding elements.

[00102] In some embodiments, the concrete product comprises one or more $CaCO_3$ phase selected from calcite-aragonite, aragonite, calcite-aragonite-dolomite, calcite-dolomite, aragonite-dolomite and dolomite.

[00103] In some embodiments, the concrete product is characterized by acid rain resistant properties.

[00104] The calcium silicate compositions can also include small quantities of residual CaO (lime) and SiO_2 (silica). The calcium silicate composition can also include small quantities of C3S (alite, Ca_3SiO_5).

[00105] The C2S phase present within the calcium silicate composition can exist in any α-Ca_2SiO_4, β-Ca_2SiO_4 or γ-Ca_2SiO_4 polymorph or combination thereof.

[00106] The calcium silicate compositions can also include quantities of inert phases such as melilite type minerals (melilite or gehlenite or akermanite) with the general formula $(Ca,Na,K)_2[(Mg, Fe^{2+},Fe^{3+},Al,Si)_3O_7]$ and ferrite type minerals (ferrite or brownmillerite or C4AF) with the general formula $Ca_2(Al,Fe^{3+})_2O_5$. In certain embodiments, the calcium silicate composition is comprised only of amorphous phases. In certain embodiments, the calcium silicate comprises only of crystalline phases. In certain embodiments, some of the calcium silicate composition exists in an amorphous phase and some exists in a crystalline phase.

[00107] In certain embodiments, the carbonatable composition includes reactive phases that are present at about 50% or more (*e.g.*, about 55% or more, about 60% or more, about 65% or more, about 70% or more, about 75% or more, about 80% or more, about 85% or more, about 90% or more, about 95% or more) by mass.

[00108] It is noted that preferably the carbonatable calcium silicate compositions of the invention do not hydrate. However, minor amounts of hydratable calcium silicate phases (*e.g.*, C2S, C3S and CaO) may be present. C2S exhibits slow kinetics of hydration when exposed to water and is quickly converted to $CaCO_3$ during CO_2 curing processes. C3S and CaO hydrate quickly upon exposure to water and thus should be limited to <5% by mass.

[00109] It should be understood that, calcium silicate compositions, phases and methods disclosed herein can be adopted to use magnesium silicate phases in place of or in addition to calcium silicate phases. As used herein, the term "magnesium silicate" refers to naturally-occurring minerals or synthetic materials that are comprised of one or more of a groups of magnesium-silicon-containing compounds including, for example, Mg_2SiO_4 (also known as "forsterite"), $(Mg, Fe)_2SiO_4$ (also known as "olivine"), $Mg_3Si_4O_{10}(OH)_2$ (also known as "talc"), $CaMgSi_2O_6$ (also known as "diopside"), and $CaMgSiO_4$ (also known as "monticellite"), each of which material may include one or more other metal ions and oxides (*e.g.*, calcium, aluminum, iron or manganese oxides), or blends thereof, or may include an

amount of calcium silicate in naturally-occurring or synthetic form(s) ranging from trace amount (1%) to about 50% or more by weight.

[00110] A major utility of the carbonatable composition is that it can be carbonated to form composite materials that are useful in a variety of application. The carbonation, for example, may be carried out reacting it with CO_2 via a controlled Hydrothermal Liquid Phase Sintering (HLPS) process to create bonding elements that hold together the various components of the composite material. For example in preferred embodiments, CO_2 is used as a reactive species resulting in sequestration of CO_2 and the creation of bonding elements in the produced composite materials with in a carbon footprint unmatched by any existing production technology. The HLPS process is thermodynamically driven by the free energy of the chemical reaction(s) and reduction of surface energy (area) caused by crystal growth. The kinetics of the HLPS process proceed at a reasonable rate at low temperature because a solution (aqueous or nonaqueous) is used to transport reactive species instead of using a high melting point fluid or high temperature solid-state medium.

[00111] Discussions of various features of HLPS, carbonatable calcium silicate-based cements, carbonation and formation of bonding elements, apparatus and processes thereof, and related topics can be found in U.S. Patent No. 8,114,367, U.S. Pub. No. US 2009/0143211 (Appl. Serial No. 12/271,566), U.S. Pub. No. US 2011/0104469 (Appl. Serial No. 12/984,299), U.S. Pub. No. 2009/0142578 (Appl. Serial No. 12/271,513), U.S. Pub. No. 2013/0122267 (Appl. Serial No. 13/411,218), U.S. Pub. No. 2012/0312194 (Appl. Serial No. 13/491,098), WO 2009/102360 (PCT/US2008/083606), WO 2011/053598 (PCT/US2010/054146), WO 2011/090967 (PCT/US2011/021623), U.S. Provisional Patent Application No. 61/708,423 filed October 1, 2012, and U.S. Pub. No. 2014/0127450 (Appl. Serial No. 14/045,758), U.S. Pub. No. 2015/0266778 (Appl. Serial No. 14/045,519), U.S. Pub. No. 2014/0127458 (Appl. Serial No. 14/045,766), U.S. Pub. No. 2014/0342124 (Appl. Serial No. 14/045,540), U.S. Pub. No. 2014/0272216 (Appl. Serial No. 14/207,413), U.S. Pub. No. 2014/0263683 (Appl. Serial No. 14/207,421), U.S. Pat. Publ. No. 2014/0314990 (Appl. Serial No. 14/207,920), U.S. Pat. No. 9,221,027 (Appl. Serial No. 14/209,238), U.S. Pub. No. 2014/0363665 (Appl. Serial No. 14/295,601), U.S. Pub. No. 2014/0361471 (Appl. Serial No. 14/295,402), U.S. Pub. No. 2016/0355439 (Appl. Serial No. 14/506,079), U.S. Pub. No. 2015/0225295 (Appl. Serial No. 14/602,313), U.S. Pub. No. 2015/0056437 (Appl. Serial No. 14/463,901), U.S. Pub. No. 2016/0168720 (Appl. Serial No. 14/584,249), U.S. Pub. No. 2015/0336852 (Appl. Serial No. 14/818,629), U.S. Pub. No. 2016/0031757 (Appl. Serial No. 14/817,193), U.S. Pub. No. 2016/0272544 (Appl. Serial No. 15/074,659), U.S.

Pub. No. 2016/0096773 (Appl. Serial No. 14/874,350), U.S. Pub. No. 2016/0340261 (Appl. Serial No. 14/715,497), U.S. Pub. No. 2016/0272545 (Appl. Serial No. 15/074,692), U.S. Pub. No. 2017/0102373 (Appl. Serial No. 15/290,328), U.S. Pub. No. 2017/0121223 (Appl. Serial No. 15/335,520), U.S. Pub. No. 2017/0204010 (Appl. Serial No. 15/409,352), U.S. Pub. No. 2017/0253530 (Appl. Serial No. 15/449,736), U.S. Pub. No. 2017/0260096 (Appl. Serial No. 15/451,344), U.S. Pub. No. 2017/0320781 (Appl. Serial No. 15/587,705), U.S. Pub. No. US 2017/0341989 (Appl. Serial No. 15/609,908), U.S. Appl. Serial No. 15/716,392, filed September 26, 2017, U.S. Appl. Serial No. 15/831,135, filed December 4, 2017, each of which is expressly incorporated herein by reference in its entirety for all purposes.

[00112] In exemplary embodiments of carbonation of the composition of the invention, ground calcium silicate composition is used. The ground calcium silicate composition can have a mean particle size from about 1 μm to about 100 μm (*e.g.*, about 1 μm to about 80 μm, about 1 μm to about 60 μm, about 1 μm to about 50 μm, about 1 μm to about 40 μm, about 1 μm to about 30 μm, about 1 μm to about 20 μm, about 1 μm to about 10 μm, about 5 μm to about 90 μm, about 5 μm to about 80 μm, about 5 μm to about 70 μm, about 5 μm to about 60 μm, about 5 μm to about 50 μm, about 5 μm to about 40 μm, about 10 μm to about 80 μm, about 10 μm to about 70 μm, about 10 μm to about 60 μm, about 10 μm to about 50 μm, about 10 μm to about 40 μm, about 10 μm to about 30 μm, about 10 μm to about 20 μm, about 1 μm, 10 μm, 15 μm, 20 μm, 25 μm, 30 μm, 40 μm, 50 μm, 60 μm, 70 μm, 80 μm, 90 μm, 100 μm), a bulk density from about 0.5 g/mL to about 3.5 g/mL (loose, *e.g.*, 0.5 g/mL, 1.0 g/mL, 1.5 g/mL, 2.0 g/mL, 2.5 g/mL, 2.8 g/mL, 3.0 g/mL, 3.5 g/mL) and about 1.0 g/mL to about 1.2 g/mL (tapped), a Blaine surface area from about 150 m^2/kg to about 700 m^2/kg (*e.g.*, 150 m^2/kg, 200 m^2/kg, 250 m^2/kg, 300 m^2/kg, 350 m^2/kg, 400 m^2/kg, 450 m^2/kg, 500 m^2/kg, 550 m^2/kg, 600 m^2/kg, 650 m^2/kg, 700 m^2/kg). In exemplary embodiments of carbonation of the calcium silicate composition of the invention, ground calcium silicate particles used have a particle size having a cumulative 10% diameter greater than 1 μm in the volume distribution of the particle size distribution.

[00113] Any suitable aggregates can be used to form composite materials from the carbonatable composition of the invention, for example, calcium oxide-containing or silica-containing materials. Exemplary aggregates include inert materials such as trap rock, construction sand, pea-gravel. In certain preferred embodiments, lightweight aggregates such as perlite or vermiculite may also be used as aggregates. Materials such as industrial waste materials (*e.g.*, fly ash, slag, silica fume) may also be used as fine fillers.

[00114] The plurality of aggregates can have any suitable mean particle size and size distribution. In certain embodiments, the plurality of aggregates has a mean particle size in the range from about 0.25 mm to about 25 mm (*e.g.*, about 5 mm to about 20 mm, about 5 mm to about 18 mm, about 5 mm to about 15 mm, about 5 mm to about 12 mm, about 7 mm to about 20 mm, about 10 mm to about 20 mm, about 1/8", about ¼", about 3/8", about ½", about ¾").

[00115] The carbonatable composition disclosed herein can be employed in concrete production via drycast or via wetcast.

Admixtures

[00116] In some embodiments, a carbonatable calcium silicate-based cement composition contains one or more admixtures. According to further embodiments, the carbonatable calcium silicate based cement composition contains a combination of two or more admixtures. The combination of two or more admixtures may comprise a combination of any of the admixtures described herein. For example, the admixtures can be selected from among one or more, or a combination of two or more, of: strength enhancer, hydrophobic compounds, set retarders, pH enhancing additives, efflorescence reducers, ettringite growth inhibitors, minerals, carbon dioxide, corrosion inhibitors, air-entraining admixtures, shrinkage-reducing admixtures, evaporation controlling admixtures, plasticizers, superplasticizers, crystallization inhibitors, and any other admixtures described herein.

[00117] Admixtures can be typically dispensed in a portion of mixing water in cement or concrete mixing. Dosage ranges for the admixtures are highly variable due to different cement particle size-distributions, different admixture efficiencies, different admixture active contents (solids fraction), different applications, etc. For purposes of illustration only, a non-limiting typical dosage range is about 0 g to 6 g active admixture content per kg of cement.

[00118] Admixtures can be added in any suitable manner. In one exemplary scheme of admixture addition, one can first load the concrete mixer with all the dry and solid ingredients (sand, cement and aggregates), then water will be added while the mix is being stirred in the mixer, then one or more admixtures can be discretely added. For example, a first admixture (or combination of admixtures) is added, then an optional second admixture (or second combination of admixtures) can be added. This way of admixture addition, as it is evident, introduces multiple admixtures (or combination of admixtures) in discrete and separate steps.

[00119] In another, more advanced scheme of admixture addition, a plurality of admixtures are all pre-mixed in a certain amount of water (typically 50 to 75 wt% of all water that shall go into the concrete mixer) to obtain a single admixture solution. This solution is then added at once to the concrete mixer to ensure homogeneous, intimate and rapid mixing of all the admixtures destined for a particular mix with the solid ingredients/constituents (sand, cement plus aggregates). In concrete mixing operations at the industrial scale there is a strict limitation for the time of mixing, which is typically 90 or 100 seconds. Therefore, adding all the admixtures in the form of a single solution occurs rapidly, effectively and homogeneously.

Strength Enhancers

[00120] In some embodiments, a carbonatable calcium silicate-based cement composition contains one or more strength enhancer(s). In some examples, the strength enhancer is an organic molecule with at least one primary, secondary or tertiary amine group, or a combination thereof. In some examples, the strength enhancer is an organic molecule with at least one primary, secondary or tertiary amine group, and at least one hydroxyl group, or a combination thereof. In some examples, the strength enhancer is an organic molecule with at least one primary, secondary or tertiary amine group, and at least two hydroxyl groups, or a combination thereof. In some examples, a strength enhancer is an organic molecule with at least one primary, secondary or tertiary amine group, and at least three hydroxyl groups, or a combination thereof. In some examples, the strength enhancer is an organic acid, such as oxalic acid or a salt thereof, acetic acid or a salt thereof, or a combination thereof.

[00121] In some examples, the strength enhancer is selected from the group consisting of N,N bis-(2-hydroxyethyl)-2-propanolamine) (DIEPA), N,N bis-(2-hydroxypropyl)-N-(hydroxyethyl) amine (EDIPA), diethanolamine (DEA), triethanolamine (TEA), triisopropanolamine (TIPA), triethylenetetramine (TETA), triethylenepentamine (TEPA), hydroxyethyldiethylenetriamine (HEDETA), and aminoethylethanolamine (AEEA) or a combination thereof.

[00122] In some examples the strength enhancer is selected from the group consisting of N,N bis-(2-hydroxyethyl)-2-propanolamine) (DIEPA), triethanalomine (TEA), triisopropanolamine (TIPA), or a combination thereof.

[00123] In some embodiments, the strength enhancer is selected from the group consisting of triethanalomine (TEA), triisopropanolamine (TIPA), or a combination thereof.

[00124] In some embodiments, the strength enhancer is TEA.

[00125] In some examples, the strength enhancer can be present in an amount between 0.1 wt. % and 5.0 wt. % of the amount of cement, more preferably between 0.1 wt. % and 2.0 wt. % of the amount of cement. The strength enhancer can be present in an amount between 0.1 wt. % and 0.3 wt. % of the amount of cement; between 0.1 wt. % and 0.5 wt. % of the amount of cement; between 0.1 wt. % and 0.8 wt. % of the amount of cement; between 0.1 wt. % and 1 wt. % of the amount of cement; between 0.1 wt. % and 2 wt. % of the amount of cement; between 0.1 wt. % and 5 wt. % of the amount of cement; between 0.2 wt. % and 0.5 wt. % of the amount of cement; between 0.2 wt. % and 0.8 wt. % of the amount of cement; between 0.2 wt. % and 1.0 wt. % of the amount of cement; between 0.2 wt. % and 2.0 wt. % of the amount of cement; between 0.2 wt. % and 5.0 wt. % of the amount of cement; between 0.5 wt. % and 0.8 wt. % of the amount of cement; between 0.5 wt. % and 1.0 wt. % of the amount of cement; between 0.5 wt. % and 2.0 wt. % of the amount of cement; between 0.5 wt. % and 5.0 wt. % of the amount of cement; between 1.0 wt. % and 2.0 wt. % of the amount of cement; between 1.0 wt. % and 5.0 wt. % of the amount of cement; or between 2.0 wt. % and 5.0 wt. % of the amount of cement.

[00126] In some examples, the carbonatable calcium silicate-based cement composition contains one or more strength enhancer(s) and a source of calcium sulfate. In some examples, the source of calcium sulfate is gypsum.

[00127] In some examples, the source of calcium sulfate is present in an amount between 0.01 wt. % and 15.0 wt. % of the amount of cement. More preferably, the quantity of the source of calcium sulfate in the cement compositions of the invention is between 0.05 wt. % and 5 wt. %, between 0.05 wt. % and 10 wt. %, between 0.1 wt. % and 5 wt. %, between 0.1 wt. % and 10 wt. %, between 1 wt. % and 5 wt. %, between 1 wt. % and 10 wt. %, between 1.5 wt. % and 5 wt. %, or between 1.5 wt. % and 10 wt. %.

Hydrophobic compound

[00128] In some embodiments, a carbonatable calcium silicate-based cement composition contains one or more hydrophobic compound(s), also referred to as hydrophobe(s). In some examples, the hydrophobic compound is a hydrophobic organic acid, or a salt thereof, or a silane, or a polysiloxane.

[00129] The hydrophobic compound can be in the form of powder, emulsion or liquid. Preferably, the hydrophobic organic acid, or a salt thereof, is one or more fatty acid(s), or one or more salt(s) thereof, advantageously one or more alkali or alkali-earth metal salt(s) thereof, more advantageously a calcium or sodium salt(s) thereof.

[00130] A fatty acid according to this invention can be a carboxylic acid with a long aliphatic chain, which is either saturated or unsaturated, preferably is saturated. Preferably, the long aliphatic chain has carbon atoms from 4 to 35, even more preferably from 5 to 28 carbon atoms.

[00131] Advantageously, the long aliphatic chain has carbon atoms from 10 to 35, more advantageously from 10 to 28 carbon atoms, even more advantageously from 10 to 20 carbon atoms and can be either saturated or unsaturated, preferably is saturated.

[00132] Advantageously, the long aliphatic chain can have 10, 11, 12, 13, 14, 15, 16, 17, 18, 19 or 20 carbon atoms and can be either saturated or unsaturated, preferably is saturated.

[00133] Preferably, the fatty acid, or a salt thereof, is selected from the group consisting of a stearic acid, or a salt thereof; an oleic acid, or a salt thereof; an arachidic acid, or a salt thereof; a palmitic acid, or a salt thereof; an arachidonic acid, or a salt thereof; an erucic acid, or a salt thereof; a linoleic acid, or a salt thereof; a linolenic acid, or a salt thereof; a lauric acid, or a salt thereof; a valeric acid, or a salt thereof; or a combination thereof.

[00134] More advantageously, the fatty acid, or a salt thereof, is selected from the group consisting of lauric acid, or a salt thereof; stearic acid, or a salt thereof; oleic acid, or a salt thereof; or a combination thereof.

[00135] Preferably, the fatty acid is stearic acid or a salt thereof. More preferably, a salt of the fatty acid is calcium stearate.

[00136] In some examples, the fatty acid is oleic acid or a salt thereof. For example, a salt of the fatty acid can be sodium oleate.

[00137] In some examples, stearic acid is first dissolved in ethyl alcohol (e.g., 0.2 to 4 g of stearic acid powder dissolved in a liter of ethyl alcohol) and then the resultant solution is applied (spraying onto or dipping into) to the external surfaces of the cured concrete samples, upon the rapid evaporation of the ethyl alcohol component, the surfaces of the concrete samples exhibit superior hydrophobic properties.

[00138] The hydrophobic compound can be present in an of about 0.02 to about 10 g per kg of cement.

[00139] In some examples, the carbonatable calcium silicate-based cement composition contains one or more hydrophobic compound(s) and an organic amine molecule. In some examples, the organic amine molecule contains at least one primary, secondary, or tertiary amine group. In some examples the organic amine is one or a combination of one or more hydroxyalkylamine(s) that has a maximum molar weight of 1000 g/mol. In some examples, the organic amine is selected from the group consisting of N,N bis-(2-hydroxyethyl)-2-propanolamine) (DIEPA), N,N bis-(2-hydroxypropyl)-N-(hydroxyethyl) amine (EDIPA), diethanolamine (DEA), triethanolamine (TEA), triisopropanolamine (TIPA), triethylenetetramine (TETA), triethylenepentamine (TEPA), hydroxyethyldiethylenetriamine (HEDETA), and aminoethylethanolamine (AEEA) or a combination thereof.

[00140] In some examples the organic amine is selected from the group consisting of N,N bis-(2-hydroxyethyl)-2-propanolamine) (DIEPA), triethanalomine (TEA), triisopropanolamine (TIPA), or a combination thereof.

[00141] In some embodiments, the organic amine is selected from the group consisting of triethanalomine (TEA), triisopropanolamine (TIPA), or a combination thereof.

[00142] In some embodiments, the organic amine is TEA.

[00143] The organic amine can be present in an amount of about 0.02 to 10 g per kg of cement.

Set retarders

[00144] In some embodiments, a carbonatable calcium silicate-based cement composition contains one or more set retarders described herein.

[00145] Carbonatable calcium silicate cements are not designed to set and harden by reacting with water. This special cement does not hydrate to any appreciable degree during the mixing or forming processes. However, the presence of hydraulic species, either formed during the synthesis of the cement or introduced by process contamination during the production of this cement in an OPC plant, can react with mix water, resulting in partial setting and hardening. This negates the production advantages of the carbonatable calcium silicate cement such as easy cleaning of the mixer and forming equipment as well as the recycling of unused concrete.

[00146] When mortar and concrete elements made with carbonatable calcium silicate cements are cured in the presence of CO_2 at elevated temperatures, the carbonation process is preceded by removal of water and the introduction of CO_2 gas into the pores of the concrete products. The subsequent reaction between the CO_2 and the carbonatable calcium silicate

cement leads to hardening. The removal of water from pores during this curing process is an important step to achieve uniform and high rates of CO_2 diffusion throughout the body of the concrete. This ensures uniform reaction and strength development within the body of the concrete product.

[00147] Contamination of carbonatable calcium silicate cements by hydraulic phases can be detrimental to water removal from the formed concrete elements. Water transport from the interior of the concrete element can be slowed significantly due to pore blockage caused by the hydration products. Water transport can also be slowed by the adsorption of water molecules onto hydraulic contaminants or hydration products.

[00148] Set-retarding or hydration-controlling admixtures can be used to treat contaminated cement to maintain mix workability. For example, organic and/or inorganic set-retarding admixtures can be utilized. Exemplary organic set-retarding admixtures can include lignosulfonates and salts thereof (e.g. Na-lignosulfonates, Ca-lignosulfonates), hydroxycarboxylic acids and salts thereof (e.g., malic acid, tartaric acid, citric acid, gluconic acid and salts thereof), phosphonates (e.g., aminotris (methylene phosphonic acid)), sugars (saccharides), hexose sugars (e.g., sucrose, glucose, fructose), pentose sugars (e.g., arabinose, ribose, xylose) sugar alcohols (e.g., sorbitol, xylitol, erythritol, maltitol, mannitol, isomalt, and lactitol), mucic acid (galactaric acid) and salts thereof, salicylic acid and salts thereof, heptanoic acid and salts thereof, oxalic acid and salts thereof, and combinations thereof.

[00149] Exemplary inorganic set-retarding admixtures include borates (e.g., boric acid and salts thereof), phosphates (e.g., sodium hexametaphosphate, tri-sodium orthophosphate), zinc salts (e.g., ZnO), and combinations thereof.

[00150] In certain preferred embodiments, the set-retarding admixture can include a sugar-based compound. In certain preferred embodiments, the set-retarding admixture can include a gluconate-based compound. In certain preferred embodiments, the set-retarding admixture can include a sugar-based compound and a gluconate-based compound.

[00151] The set-retarding admixture can be present in an amount of about 0.02 to about 10 g per kg of cement.

[00152] Not wishing to be bound by the theory, it is believed that molecules of these chemicals can adsorb onto the cement particle surface. The adsorption bond links the molecule onto the cement surface, thereby blocking and slowing down the rate of initial hydration of the cement. These molecules can also chelate calcium ions in solution, thereby slowing the crystallization of $Ca(OH)_2$ and $Ca_6Al_2(SO_4)_3(OH)_{12}{\bullet}26H_2O$ as well as suppressing the nucleation of CSH gel. Set-retardation is mainly controlled by the hydration

of $Ca_4Al_2Fe_2O_{10}$ in the presence of above chemicals forming complexes. Hydration control primarily affects the hydration of Ca_3SiO_5 and Ca_2SiO_4. Many of these chemicals listed above affect both set retarding and hydration control, which take place simultaneously.

[00153] Thus, set-retarding or hydration-controlling admixtures can allow deactivation of hydraulic contaminants present in carbonatable calcium silicate cements and/or suppress the rate at which the hydraulic contaminants react with water. Either of these effects can increase drying rates and improve the CO_2 curing process. This deactivation can also prevent, reduce or delay the setting of contaminated carbonatable calcium silicate cement.

[00154] In certain embodiments, the carbonateable calcium silicate composition includes a hydrating phase of CaO or a contamination from Ordinary Portland Cement.

pH enhancing additives and moisture resistance additives

[00155] In some embodiments, a carbonatable calcium silicate-based cement composition contains one or more pH enhancing additives and/or moisture resistance additives described herein. In some examples, the carbonatable calcium silicate-based cement composition is a carbonatable low calcium silicate based cement composition.

[00156] Hydration of ordinary portland cement (OPC) in the presence of water produces a solution within the porous material that consists mainly of alkali hydroxides, such as, $Ca(OH)_2$, NaOH and KOH. Depending on the composition of the cement and the aggregates, the pH of the pore solution is typically between 12.5 and 13.5. However, OPC can also undergo a carbonation reaction upon exposure to CO_2 under certain conditions. For example, $Ca(OH)_2$ can react with CO_2 to form $CaCO_3$ and H_2O. When conventional concrete undergoes carbonation, the pH of a solution of water and ions dissolved from cement (e.g., calcium, sodium and/or potassium ions) resident within pores of the material ("pore solution") drops to values approaching pH of 9 as a consequence of drastic reduction in the concentration of hydroxyl ions. Penetration of salts from the environment can also lead to a remarkable change in the composition of the pore solution.

[00157] Corrosion of metal, such as iron or steel components (*e.g.*, plain carbon steel, epoxy coated steel, galvanized steel, and/or stainless steel, reinforcement bars or meshes) in conventional concrete can be initiated when a passive film on the surface of the metal is removed either by lowering of the pore solution pH or by combination of low pore solution pH and presence of chlorides. OPC typically provides an initial pore solution pH value higher than 12, helping the rebar avoid or slow the corrosion process. However, during the service lifetime, OPC can be affected by chloride penetration from salts during winter season

and/or a carbonation reaction with atmospheric carbon dioxide (CO_2) that reduces the pore solution pH of conventional concrete. Corrosion products formed due to the corrosion are volumetrically expansive in nature. These corrosion products from the corrosion of the rebar can produce severe internal stresses on the surrounding OPC, leading to cracking, spalling, and ultimately, structural failure.

[00158] Similar to OPC based conventional concrete, carbonatable calcium silicate-based uncarbonated cement composition, such as carbonatable low calcium silicate based uncarbonated concrete materials, such as those described herein (*i.e.*, Solidia Cement™ and Solidia Concrete™,) can have a pore solution which has a pH value of greater than 12 when it is freshly mixed. However, upon carbonation, the pH value of the pore solution can decrease during curing. Hardening of the material can be facilitated through a curing process in which calcium silicates carbonate to form calcium carbonate. The pH value of the pore solution in a fully reacted low calcium silicate based carbonated concrete with compressive strength of 10,000 psi, or more, can be about 9.5. With the pore solution having such a low pH value, a passive film on the surface of reinforcing or embedded metal can be susceptible to corrosion as soon as fresh water or chloride ions reaches the surface of the reinforcement material.

[00159] pH enhancing admixtures can maintain a beneficial pH environment that prevents, mitigates or delays corrosion and affords adequate compressive strength required for service conditions, increased water resistance, without affecting the material's freeze-thaw durability and suitability for cold weather applications. This feature can allow significant improvement in the service life and utility of calcium silicate-based cement composite materials, such as manufactured low calcium silicate cement-based composite materials, and objects formed therefrom.

[00160] Carbonated low calcium silicate cement-based material, according to certain aspects of the present invention, can have a plurality of pores with modified pore solution located in one or more of the pores having a pH of greater than about 9.5, preferably greater than about 10, preferably greater than about 11, preferably greater than about 11.5, preferably greater than about 12.0, preferably greater than about 12.5, preferably greater than about 13.0, and preferably about 13.5. The modified pore solution can have a pH from about 9.5 to about 13.5, inclusive of these upper and lower limits, and all integers encompassed within the range.

[00161] Carbonated low calcium silicate cement-based composite material having at least one, or a plurality of pores, with the modified pore solution having a pH value as

described above can also have a suitable compressive strength of, for example, 3,500 psi or greater, greater than about 4,000 psi, greater than about 5,000 psi, greater than about 6,000 psi, greater than about 7,000 psi, greater than about 8,000 psi, greater than about 9,000 psi, or equal to or greater than about 10,000 psi. The compressive strength may be from about 3,500 psi to about 10,000 psi, inclusive of these upper and lower limits, and all integers encompassed within the range. Such compressive strengths can be obtained from a total curing time of less than 7 days from the date of the beginning of carbonation, and about 8 hours or more. In certain embodiments, such compressive strengths can be obtained from a total curing time of less than about 14 days from the date of beginning carbonation, and about 8 hours or more. In other embodiments, such compressive strengths can be obtained from a total curing time of less than about 28 days from the date of beginning carbonation, and about 8 hours or more. Thus, the total curing times can range from about 8 hours to about 28 days. The total curing times include the upper and lower limits mentioned above, as well as all time values falling within the specified range. The total curing times can include any optional pre-curing times, as further described herein.

[00162] In certain embodiments, concrete composite materials and objects made from low calcium silicate cement can contain a porous body. The porous body can further include one or more pH enhancing additives. Exemplary pH enhancing additives include calcium nitrate tetrahydrate, calcium nitrite, NaOH, sodium bicarbonate, OPC, sodium silicate, dead-burnt CaO, dead-burnt MgO, dolomitic hydrated lime (e.g., a 55:45 wt% mixture of $Ca(OH)_2$ and $Mg(OH)_2$ also known as type-S masonry cement), high alkalinity concrete recycled material (CRM), slag aggregate, and combinations thereof. As used herein "dead-burnt" CaO and MgO are oxides of calcium and magnesium having little or no reactivity as a result of being calcined at high temperatures. The pH enhancing additive(s) can be present to the formulation at dosage of about 1% to about 20%, by mass, relative to the total amount of cementitious materials. These additives can be added to the dry mix in a mixer along with low calcium silicate cement. As used herein "dead-burnt" CaO and MgO are oxides of calcium and magnesium having little or no reactivity as a result of being calcined at high temperatures.

[00163] In certain embodiments, the porous body can further include one or more additives to improve water resistance. Exemplary additives to improve water resistance can be selected from the group consisting of Class C fly ash, Class F fly ash, ground granulated blast furnace slag (GGBFS), fine glass powder, vitreous calcium aluminosilicate (VCAS), silica fume, limestone powder, and combinations thereof. The water resistance additives can

be present at dosage of about 1% to about 20%, by mass, relative to the total amount of cementitious materials. These additives can be added to the dry mix in a mixer along with low calcium silicate cement.

[00164] Other examples of moisture resistance admixtures include soaps and fatty acids, silanes and siloxanes, wax emulsions, oils, and combinations thereof. For example, moisture resistance admixtures include Ca or NH_4 salts of fatty acids; stearic acid and salts thereof; oleic acid and salts thereof; arachidic acid and salts thereof; palmitic acid and salts thereof; arachidonic acid and salts thereof; erucic acid and salts thereof; linoleic acid and salts thereof; linolenic acid and salts thereof; lauric acid and salts thereof; caprylic acid and salts thereof; capric acid and salts thereof; calcium stearate; sodium or potassium oleate; silanes and siloxanes; ammonium stearate; butyl stearate; vegetable/animal fats; emulsions based on white grease, tallow, or soy bean oil; derivations of petroleum residues, heavy mineral oil paraffin waxes, bitumen emulsions; finely divided wax emulsions with emulsifying agents, and combinations thereof.

[00165] In some embodiments, moisture resistance admixtures include finely divided solids which are inert pore filling materials (e.g., fullers earth, talc, bentonite, siliceous powders, and combinations thereof), chemically reactive finely divided solids (e.g., silicates, ground blast furnace slag, pozzolans such as fly ash and diatomaceous earth, and combinations thereof), conventional water-reducing, air-entraining, and accelerating admixtures, sodium methyl siliconates, lithium silicates, and combinations thereof, such as aliphatic fatty acids combined with aqueous emulsions of polymers or such as stearate soaps blended with talc or fine silica sand.

Efflorescence reducers

[00166] In some examples, a carbonatable calcium silicate-based cement composition contains an admixture that mitigates or reduces efflorescence. Efflorescence is a surface phenomenon of ordinary portland cement (OPC) concrete that contributes to poor aesthetic and long-term durability of concrete. Typically, efflorescence in an OPC system is a family of crystalline products that are comprised of salts of carbonates, sulfates and chlorides. These crystalline products can appear as white deposits that form and grow on the surface of concrete products over time. Efflorescence in OPC systems can arise from carbonates of calcium, sodium and potassium originating from the cement or concrete components. These deposits can form as soluble calcium hydroxide migrates from the interior of the sample to the outer surface and subsequently react with atmospheric CO_2 to form calcium carbonate.

White deposits can also be formed in the OPC system from the transport and redisposition of soluble salts such as alkali sulfates or chlorides. These white deposits of soluble salts can cause hazing.

[00167] Carbonatable calcium silicate-based cements generally do not contain or produce $Ca(OH)_2$ under ordinary circumstances. Any easily carbonatable materials within the cement can react and thereby be passivated during the CO_2 curing process. However, other soluble salts, such as alkali sulfates or chlorides, present in the carbonatable calcium silicate cement or contributed from the concrete mixture components can cause hazing.

[00168] When curing carbonatable calcium silicate-based cements to make concrete products, the transport and evaporation of water can be an integral part of the process. A significant quantity of water present in the concrete can travel from the interior of the sample to its surface and evaporate during the curing process. If the water contains dissolved salts, such as dissolved salts from the cement or concrete components, various degrees of hazing can occur due to transport and precipitation of the salts onto the surface of the product. Examples of contributors to haze include potassium and sodium sulfates (K_2SO_4 and Na_2SO_4). Potassium and sodium sulfates are highly soluble salts and thus can easily be transported in an aqueous environment through a porous concrete structure. These salts can precipitate on the surface of concrete.

[00169] Water ingress can be a major contributor to the visible deposition of salts on concrete surfaces often referred to as efflorescence. Fatty acids, salts of fatty acids, and silanes can be used in carbonatable calcium silicate-based cement (CCSC) concrete to limit the ingress of water and subsequently mitigate the occurrence of efflorescence or other aesthetic defects. Examples of efflorescence reducers include valeric acid and salts thereof, lauric acid and salts thereof, oleic acid and salts thereof, stearic acid and salts thereof, Na-oleate, Ca-stearate, and silanes.

[00170] Efflorescence reducing admixtures can be present in a carbonatable calcium silicate-based cement composition. In some examples, an efflorescence reducing admixture can react with one or more of soluble alkali, alkaline earth, sulfate or chloride ions to form a low solubility material. In some examples, efflorescence reducing admixtures include calcium and aluminum-containing compounds. Exemplary efflorescence reducing admixtures include solid calcium aluminates such as crystalline tricalcium aluminate, monocalcium aluminate or similar amorphous materials, which can mitigate or reduce hazing related to soluble sulfate species through the reaction of the solid component and the sulfate. Without wishing to be bound by the theory, calcium and aluminum-containing compounds can react

with dissolved SO_4^{2-} to form ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12}$•$26H_2O$). This reaction can sequester sulfate ions because ettringite has a significantly lower solubility than unadulterated Na_2SO_4 or K_2SO_4. The soluble salts can be immobilized, and haze formation can be prevented or reduced.

[00171] Examples of admixtures that can mitigate or reduce efflorescence include ground granulated blast furnace slag (GGBFS), fly ash (e.g., class C fly ash), gypsum, and combinations thereof.

[00172] Examples of admixtures that can mitigate or reduce efflorescence include liquid admixtures, such as soluble calcium ion sources, including calcium nitrate $Ca(NO_3)_{2\,(aq)}$, calcium nitrate tetrahydrate, calcium nitrite $Ca(NO_2)_{2\,(aq)}$, calcium chloride $CaCl_{2(aq)}$, and combinations thereof. Calcium ion sources can create sparing soluble precipitates such as $CaSO_4$•$2H_2O$ and thereby immobilize haze-producing sulfates. In some cases, liquid admixtures can also complex ions and prevent their precipitation. Examples of admixtures that can mitigate or reduce efflorescence include soluble aluminum salts, such as aluminum nitrate or aluminum chloride, alone or in combination with tartaric acid.

[00173] Examples of admixtures that can mitigate or reduce efflorescence include solid admixtures, such as calcium aluminate, calcium sulfoaluminate, or a combination thereof. In some examples, an admixture is calcium aluminate, calcium sulfoaluminate, or a combination thereof, with a small amount (*e.g.,* from 0.1% to about 2%, from 0.5% to about 1.5%, from 0.8% to about 1.2% by weight of the cement mixture) of calcium hydroxide.

[00174] In certain embodiments, the solid admixture includes one or more selected from GGBFS and class C fly ash. In certain embodiments, the admixture of GGBFS and/or Fly Ash accounts for from about 1% to about 25% by weight of the cement mixture (e.g., from about 1% to about 20%, from about 1% to about 20%, from about 1% to about 15%, from about 1% to about 10%, from about 1% to about 5%, from about 5% to about 25%, from about 10% to about 25%, from about 15% to about 25%, from about 5% to about 20%).

[00175] In certain embodiments of the method, the solid admixture includes one or more selected from GGBFS and Class C Fly Ash with the addition of a small amount (e.g., from 0.1% to about 2%, from 0.5% to about 1.5%, from 0.8% to about 1.2% by weight of the cement mixture) of gypsum ($CaSO_4$•$2H_2O$). In certain embodiments, the admixture of GGBFS and/or Fly Ash accounts with a small amount (*e.g.,* from 0.1% to about 2%, from 0.5% to about 1.5%, from 0.8% to about 1.2% by weight of the cement mixture) of gypsum for from about 1% to about 25% by weight of the cement mixture (e.g., from about 1% to about 20%, from about 1% to about 20%, from about 1% to about 15%, from about 1% to

about 10%, from about 1% to about 5%, from about 5% to about 25%, from about 10% to about 25%, from about 15% to about 25%, from about 5% to about 20%).

[00176] In certain embodiments of the method, the solid admixture includes calcium aluminate and is added to the cement mix in an amount such that calcium aluminate accounts for about 0.1% to about 10% (e.g., from about 0.5% to about 10%, from about 1% to about 10%, from about 2% to about 10%, from about 3% to about 10%, from about 5% to about 10%, from about 0.1% to about 5%, from about 0.1% to about 3%, from about 0.1% to about 2%, from about 0.1% to about 1.0%, from about 1% to about 8%, from about 2% to about 5%) by weight of the cement mixture.

[00177] In certain embodiments, the solid admixture includes calcium aluminate, which accounts for about 0.1% to about 1.0% by weight of the cement mixture. In certain embodiments, calcium aluminate accounts for about 1.0% to about 10% by weight of the cement mixture.

[00178] In certain embodiments, the solid admixture includes calcium sulfoaluminate, which accounts for about 0.1% to about 1.0% by weight of the cement mixture. In certain embodiments, calcium sulfoaluminate accounts for about 0.1% to about 1.0% by weight of the cement mixture.

[00179] In certain embodiments, the liquid admixture is an aqueous solution including one or more highly soluble calcium salts. In certain embodiments of the method, the highly soluble calcium is selected from calcium nitrate, calcium nitrite, calcium chloride, and combinations thereof.

[00180] In certain embodiments of the method, the liquid admixture is an aqueous solution including calcium nitrite, calcium chloride, or a combination thereof.

[00181] In certain embodiments of the method, the liquid admixture is an aqueous solution including one or more highly soluble aluminum salts. In certain embodiments of the method, the highly soluble aluminum salt is selected from aluminum nitrate, aluminum nitrate nonahydrate, and a combination thereof. In certain embodiments of the method, the highly soluble aluminum salt is present in combination with tartaric acid ($C_4H_6O_{6(aq)}$). In certain embodiments of the method, the liquid admixture is an aqueous solution of aluminum nitrate and tartaric acid. In certain embodiments of the method, the liquid admixture is an aqueous solution of aluminum nitrate nonahydrate and tartaric acid.

[00182] In certain embodiments of the method, the liquid admixture comprises calcium nitrate, calcium nitrite and/or calcium chloride and is added to the cement at about 0.5 g to about 30 g (e.g., from about 0.5 g to about 20 g, from about 0.5 g to about 15 g, from about

0.5 g to about 10 g, from about 0.5 g to about 5 g, about 1 g to about 30 g, about 5 g to about 30 g, about 10 g to about 30 g, about 15 g to about 30 g, about 1 g to about 20 g, about 3 g to about 15 g, about 5 g to about 10 g) calcium nitrate, calcium nitrite and/or calcium chloride per kg of cement.

[00183] In certain embodiments of the method, the liquid admixture comprises aluminum nitrate and/or aluminum nitrate nonahydrate and is added to the cement at about 0.5 g to about 30 g (e.g., from about 0.5 g to about 20 g, from about 0.5 g to about 15 g, from about 0.5 g to about 10 g, from about 0.5 g to about 5 g, about 1 g to about 30 g, about 5 g to about 30 g, about 10 g to about 30 g, about 15 g to about 30 g, about 1 g to about 20 g, about 3 g to about 15 g, about 5 g to about 10 g) aluminum nitrate and/or aluminum nitrate nonahydrate per kg of cement.

[00184] In certain embodiments of the method, the aqueous solution including calcium nitrate, calcium nitrite and/or calcium chloride at about 5% to about 50% (e.g., from about 5% to about 40%, from about 5 % to about 30%, from about 5% to about 20%, from about 5% to about 10%, from about 10% to about 50%, from about 20% to about 50%, from about 30% to about 50%, from about 10% to about 40%, from about 15% to about 30%) by weight.

[00185] In certain embodiments of the method, the aqueous solution including aluminum nitrate and/or aluminum nitrate nonahydrate at about 5% to about 50% (e.g., from about 5% to about 40%, from about 5 % to about 30%, from about 5% to about 20%, from about 5% to about 10%, from about 10% to about 50%, from about 20% to about 50%, from about 30% to about 50%, from about 10% to about 40%, from about 15% to about 30%) by weight.

[00186] In certain embodiments of the method, the liquid admixture is an aqueous solution including aluminum nitrate at about 0.1% to about 3.0% by weight of cement in the concrete mixture and tartaric acid at about 0.1% to about 3.0% by weight of cement. In certain embodiments of the method, the liquid admixture is an aqueous solution including aluminum nitrate at about 0.5% to about 2.0% by weight of cement in the concrete mixture and tartaric acid at about 0.5% to about 2.0% by weight of cement. In certain embodiments of the method, the liquid admixture is an aqueous solution including aluminum nitrate at about 0.5% to about 1.5% by weight of cement in the concrete mixture and tartaric acid at about 1.0% to about 2.0% by weight of cement. In certain embodiments of the method, the liquid admixture is an aqueous solution including aluminum nitrate at about 0.8% to about 1.2% by weight of cement in the concrete mixture and tartaric acid at about 1.3% to about 1.7% by

weight of cement. In certain embodiments, the alkali, alkaline earth, sulfate or chloride ions are selected from Ca^{2+}, Na^{+}, K^{+} , Mg^{2+}, Cl^{-}, and SO_3^{2-} ions, and combinations thereof.

[00187] Further, generally speaking the previously disclosed hydrophobic compounds admixtures can inhibit efflorescence, and can be so used according to further embodiments.

Ettringite growth inhibitor

[00188] In some embodiments, a carbonatable calcium silicate-based cement composition contains one or more admixture(s) that are ettringite growth inhibitors. In some examples, the ettringite growth inhibitors are selected from among sorbitol, sugar alcohols, mucic acid (galactaric acid) and salts thereof, salicylic acid and salts thereof, heptanoic acid and salts thereof, pentose sugars (e.g., arabinose, ribose, xylose), and combinations thereof.

[00189] Ettringite tends to form high surface area acicular needles which can potentially block pores and hinder the drying process. Ettringite growth inhibitors may modify the morphology of ettringite or induce the formation of different sulfate-based salts which are less prone to "pore-blocking."

Mineral admixtures

[00190] In some embodiments, a carbonatable calcium silicate-based cement composition contains one or more admixture(s) that is a mineral admixture. In some examples, the mineral contains magnesium or magnesium compounds, such as magnesium salts, or a mixture thereof.

[00191] Addition of certain mineral compositions (*e.g.*, minerals containing magnesium, magnesium compounds, magnesium salts, or a mixture thereof) to a concrete mix can mitigate or reduce aesthetic defects and surface depositions resulting from a porous matrix that can allow the ingress of water.

[00192] Without wishing to be bound by the theory, the formation of needles or whisker-like crystals of hydrated or anhydrous magnesium carbonates, calcium magnesium carbonates and/or magnesium hydroxycarbonates, if and when they form inside the open-ended capillaries or orifices of the bonding element-rich areas of compositions, can alter the nature and extent of water transport there. Water can readily penetrate and transport through, at the ambient pressure and temperature, capillaries, orifices and interconnected pore channels having sizes greater than 1.4 μm, but the formation of such submicron-sized crystals within such waterways will drastically alter the water flow pattern and will render the situation more similar to the case of ordinary Portland cement (OPC)-based pavers.

[00193] Addition of certain mineral compositions containing magnesium (*e.g.*, magnesium oxide) to a concrete mix can significantly improve the mechanical properties and durability of a product.

[00194] Without wishing to be bound by the theory, strength generation during carbonation of calcium silicate powders, which do not have the hydraulic mineral hatrurite (C3S) and which possess a Ca/Si molar ratio much lower than that of ordinary Portland cement, proceeds in two steps: (i) the formation of an X-ray-amorphous layer of silicate-rich (or Ca-deficient) gel, through which the Ca^{2+} must diffuse out to the external surface that is in contact with the $CO_2(g)$, on the calcium silicate particles, and (ii) the formation of individual $CaCO_3$ crystals on that X-ray-amorphous gel layer and the further evolution of such individual $CaCO_3$ crystals into a 3D interconnected, intermingling network of $CaCO_3$.

[00195] The intentional addition of an alkali earth cation with an ionic radius smaller than that of Ca^{2+} (114 pm), such as Mg^{2+} (86 pm), can decrease the amount of unreacted calcium silicate remaining at the end of carbonation, which can increase strength.

[00196] Again without wishing to be bound by the theory, magnesium compounds, such as magnesium oxide can provide *in situ* internal de-humidification of the construction material and block undergoing CO_2 carbonation owing to the high affinity of magnesium oxide to the dynamic water films or water molecules that would be present through the pores and pore channels of the body.

[00197] Magnesium hydroxide (brucite, $Mg(OH)_2$) initially can form during the preparation of the concrete mix, upon the addition of magnesium, magnesium oxide or magnesium salt to the liquid admixture portion of the concrete mix, can *in situ* carbonate itself, during CO_2 curing, to one or more of magnesite ($MgCO_3$), dolomite ($CaMg(CO_3)_2$), Mg-calcite (magnesian), hydromagnesite ($Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$), nesquehonite ($Mg(HCO_3)(OH) \cdot 2H_2O$ or $MgCO_3 \cdot 3H_2O$), dypingite ($Mg_5(CO_3)_4(OH)_2 \cdot 5H_2O$), artinite ($Mg_2CO_3(OH)_2 \cdot 3H_2O$), barringtonite ($MgCO_3 \cdot 2H_2O$), or lansfordite ($MgCO_3 \cdot 5H_2O$). These phases can be present in the MgO-CO_2-H_2O ternary system. The formation of such phases can require the *in situ* and in realtime, dynamic water removal from their immediate surroundings. These basic (*i.e.*, with intrinsic pH values above neutral) phases can crystallize in acicular or needle forms and the interlocking/intermingling of these needles with one another can increase the strength in the products (*e.g.*, composite construction materials such as wall panels, blocks, pavers, and stonecast). The formation of such needles or whisker-like crystals of the magnesium carbonates, calcium magnesium carbonates and/or magnesium

hydroxycarbonates, can alter the nature and extent of water transport there, since such phases can instantly increase the surface roughness of waterways intrinsic to the concrete products cured by using CO_2.

[00198] In some examples, the carbonatable calcium silicate-based cement composition can further contain acetate ions and/or acetic acid in the forming waters of concrete and mortar batches, which can increase the mean strength in the calcium silicate-based samples upon carbonation.

[00199] In some examples, the magnesium compound, such as magnesium oxide, is a powder. The powder can have a particle size distributions of, for example, about 100 nm, about 10 μm or about 50 μm average particle sizes, and reactivity.

[00200] In some examples, the magnesium compound is magnesium acetate, or a water soluble salt of magnesium acetate ($Mg(CH_3COO)_2 \cdot 4H_2O$) or a solution of controlled pH value formed by dissolving a prescribed quantity of MgO powder in a prescribed volume of dilute acetic acid into the forming water of paste, mortar or concrete samples resulted in a noticeable strength increase upon carbonation.

[00201] Magnesium, when present even in low concentrations (<1%), can be a strong aragonite promoter when present in aqueous systems prone to nucleate $CaCO_3$, regardless of the processing temperature.

[00202] In certain embodiments, the admixture can include an ultra-fine (*e.g.*, about 100 nm mean particle size) magnesium oxide powder, from about 0.02% to about 20% (*e.g.*, from about 0.1% to about 20%, from about 0.5% to about 20%, from about 1% to about 20%, from about 5% to about 20%, from about 0.02% to about 10%, from about 0.02% to about 5%, from about 0.02% to about 1%, from about 0.02% to about 0.1%), to the liquid admixtures, which are typically acidic solutions due to the superplasticizers/dispersants used with pH values less than 5, in order to help raise the pH of these solutions, for example, to a pH of about 9 (*e.g.*, from about 8.5 to about 9.5, from about 8.7 to about 9.3, from about 8.8 to about 9.2). This can facilitate the *in situ* formation of magnesium hydroxide, or brucite, and can enhance the availability of magnesium to various beneficial ternary phases.

[00203] In certain embodiments of the invention, magnesium oxide can regulate the viscosity of pastes or slurries through the formation of hydroxylated magnesium molecules in aqueous solutions.

[00204] In certain embodiments of the invention, the admixture can contain magnesium ions in solution, which can improve the reactivity of calcium-bearing silicate

phases through crystallographic distortion or modification of ortho- or pyro-silicate networks containing calcium.

[00205] In certain embodiments of the invention, magnesium oxide can be added to mixtures of carbonatable calcium silicate-based cement mixtures to reduce or eliminate the occurrence of metastable polymorphs of calcium carbonate and to reduce or prevent the formation of aesthetic surface defects arising from precipitation of metastable phases such as vaterite.

[00206] In certain embodiments of the invention, magnesium oxide at small percentages, from about 0.02% to 20% (*e.g.*, from about 0.1% to about 20%, from about 0.5% to about 20%, from about 1% to about 20%, from about 5% to about 20%, from about 0.02% to about 10%, from about 0.02% to about 5%, from about 0.02% to about 1%, from about 0.02% to about 0.1%), is added to carbonatable calcium silicate-based cement mixtures to promote the formation of Mg-calcite phases such as magnesian.

[00207] In certain embodiments of the invention, magnesium oxide is added, from about 0.02% to 20% (*e.g.*, from about 0.1% to about 20%, from about 0.5% to about 20%, from about 1% to about 20%, from about 5% to about 20%, from about 0.02% to about 10%, from about 0.02% to about 5%, from about 0.02% to about 1%, from about 0.02% to about 0.1%), to carbonatable calcium silicate-based cement mixtures to promote the formation of acicular calcium carbonate phases such as aragonite.

[00208] In certain embodiments of the invention, magnesium oxide is added, from about 0.02% to 20% (*e.g.*, from about 0.1% to about 20%, from about 0.5% to about 20%, from about 1% to about 20%, from about 5% to about 20%, from about 0.02% to about 10%, from about 0.02% to about 5%, from about 0.02% to about 1%, from about 0.02% to about 0.1%), to carbonatable calcium silicate-based cement mixtures to promote the formation of dolomite.

[00209] In certain embodiments of the invention, magnesium oxide is added, from about 0.02% to 20% (*e.g.*, from about 0.1% to about 20%, from about 0.5% to about 20%, from about 1% to about 20%, from about 5% to about 20%, from about 0.02% to about 10%, from about 0.02% to about 5%, from about 0.02% to about 1%, from about 0.02% to about 0.1%), to carbonatable calcium silicate-based cement mixtures to stabilize Mg-calcite and/or aragonite and to minimize formation of vaterite.

[00210] In certain embodiments of the invention, magnesium oxide is added from about 0.02% to 10% (*e.g.*, from about 0.1% to about 10%, from about 0.5% to about 10%, from about 1% to about 10%, from about 5% to about 10%, from about 0.02% to about 5%,

from about 0.02% to about 2%, from about 0.02% to about 1%, from about 0.02% to about 0.1%), to carbonatable calcium silicate-based cement mixtures to enrich the microstructural diversity of the binder matrix and reduce the occurrence of structural and aesthetic degradation through water ingress.

[00211] In certain embodiments of the invention, magnesium oxide is added, from about 0.02% to 20% (*e.g.*, from about 0.1% to about 20%, from about 0.5% to about 20%, from about 1% to about 20%, from about 5% to about 20%, from about 0.02% to about 10%, from about 0.02% to about 5%, from about 0.02% to about 1%, from about 0.02% to about 0.1%), to carbonatable calcium silicate-based cement mixtures to promote the formation of ternary phases resistant to potential structural and aesthetic degradation in concrete applications involving exposure to acidic chemicals (*e.g.*, from acidic rain).

[00212] In certain embodiments of the invention, magnesium oxide is added, from about 0.02% to 20% (*e.g.*, from about 0.1% to about 20%, from about 0.5% to about 20%, from about 1% to about 20%, from about 5% to about 20%, from about 0.02% to about 10%, from about 0.02% to about 5%, from about 0.02% to about 1%, from about 0.02% to about 0.1%), to carbonatable calcium silicate-based cement mixtures to modify carbonated calcium silicate-based cement pore structures through formation of fine needle-like or acicular calcium carbonate polymorphs. This pore structure modification can inhibit the transport of aqueous phases containing salts, organic residues, minerals, and other contaminants that may degrade the aesthetic qualities and durability of carbonatable calcium silicate-based concrete.

[00213] In certain embodiments of the invention, magnesium oxide is added, from about 0.02% to 20% (*e.g.*, from about 0.1% to about 20%, from about 0.5% to about 20%, from about 1% to about 20%, from about 5% to about 20%, from about 0.02% to about 10%, from about 0.02% to about 5%, from about 0.02% to about 1%, from about 0.02% to about 0.1%), to carbonatable calcium silicate-based cement mixtures to reduce the drying-shrinkage resulting from rapid drying regimes or high water/solid mixtures.

[00214] In certain embodiments of the invention, magnesium oxide is added, from about 0.02% to 20% (*e.g.*, from about 0.1% to about 20%, from about 0.5% to about 20%, from about 1% to about 20%, from about 5% to about 20%, from about 0.02% to about 10%, from about 0.02% to about 5%, from about 0.02% to about 1%, from about 0.02% to about 0.1%), to carbonatable calcium silicate-based cement mixtures to increase the degree of carbonation and sequestration of carbon dioxide.

[00215] In certain embodiments of the invention, ground limestone or dolomitic limestone is added, from about 0.02% to 10% (*e.g.*, from about 0.1% to about 10%, from

about 0.5% to about 10%, from about 1% to about 10%, from about 5% to about 10%, from about 0.02% to about 5%, from about 0.02% to about 2%, from about 0.02% to about 1%, from about 0.02% to about 0.1%), to carbonatable calcium silicate-based cement mixtures to refine the pore structure of carbonated calcium silicate-based binders and inhibit the transport of aqueous phases containing salts, organic residues, minerals, and other contaminants that may degrade the aesthetic qualities and durability of carbonatable calcium silicate-based concrete.

[00216] In certain embodiments of the invention, ground dolomite is added, from about 0.02% to 20% (*e.g.*, from about 0.1% to about 20%, from about 0.5% to about 20%, from about 1% to about 20%, from about 5% to about 20%, from about 0.02% to about 10%, from about 0.02% to about 5%, from about 0.02% to about 1%, from about 0.02% to about 0.1%), to carbonatable calcium silicate-based cement mixtures to refine the pore structure of carbonated calcium silicate-based binders and inhibit the transport of aqueous phases containing salts, organic residues, minerals, and other contaminants that may degrade the aesthetic qualities and durability of carbonatable calcium silicate-based concrete.

[00217] In certain embodiments of the invention, suspensions of magnesium hydroxide, or milk of magnesia, is added, from about 0.02% to 20% (*e.g.*, from about 0.1% to about 20%, from about 0.5% to about 20%, from about 1% to about 20%, from about 5% to about 20%, from about 0.02% to about 10%, from about 0.02% to about 5%, from about 0.02% to about 1%, from about 0.02% to about 0.1%), to carbonatable calcium silicate-based cement mixtures to modify the pore structure of carbonated calcium silicate-based binders and inhibit the transport of aqueous phases containing salts, organic residues, minerals, and other contaminants that may degrade the aesthetic qualities and durability of carbonatable calcium silicate-based concrete.

[00218] In certain embodiments of the invention, combinations of coarse and fine ground limestone with different particle size distributions can be added, from about 0.02% to 20% (*e.g.*, from about 0.1% to about 20%, from about 0.5% to about 20%, from about 1% to about 20%, from about 5% to about 20%, from about 0.02% to about 10%, from about 0.02% to about 5%, from about 0.02% to about 1%, from about 0.02% to about 0.1%), to carbonatable calcium silicate-based cement mixtures to improve the particle packing of carbonatable calcium silicate-based cements and to reduce the paste permeability thereby inhibiting the ingress of water. This approach can be used to limit the transport of salts, organic residues, minerals, and other contaminants that may degrade the aesthetic qualities and durability of carbonatable calcium silicate-based concrete.

[00219] In some embodiments, the one or more minerals can further comprise one or more of magnesium, magnesium nitrate, magnesium sulphate, magnesium chloride, and magnesium acetate.

[00220] In some embodiments, a precipitate-free solution of magnesium nitrate is produced by dissolving magnesium oxide powders of any particle size, over the typical mean particle size interval of about 0.05 to about 100 μm, in technical grade concentrated nitric acid diluted with water to prepare stock solutions of Mg^{2+} ions over the concentration range of about 0.001 to about 1 M (*e.g.*, about 0.01 to about 1 M, about 0.1 to about 1 M, about 0.001 to about 0.1 M, about 0.001 to about 0.01 M) to replace the addition of powdery magnesium nitrate salt.

[00221] In some embodiments, a precipitate-free solution of magnesium chloride is produced by dissolving magnesium oxide powders of any particle size, over the typical mean particle size interval of about 0.05 to about 100 μm, in technical grade concentrated hydrochloric acid diluted with water to prepare stock solutions of Mg^{2+} ions over the concentration range of about 0.001 to about 1 M (*e.g.*, about 0.01 to about 1 M, about 0.1 to about 1 M, about 0.001 to about 0.1 M, about 0.001 to about 0.01 M) to replace the addition of powdery magnesium chloride salt.

[00222] In some embodiments, a precipitate-free solution of magnesium sulphate is produced by dissolving magnesium oxide powders of any particle size, over the typical mean particle size interval of about 0.05 to about 100 μm, in technical grade concentrated sulfuric acid diluted with water to prepare stock solutions of Mg^{2+} ions over the concentration range of about 0.001 to about 1 M (*e.g.*, about 0.01 to about 1 M, about 0.1 to about 1 M, about 0.001 to about 0.1 M, about 0.001 to about 0.01 M) to replace the addition of powdery magnesium sulphate salt.

[00223] Carbonate minerals of divalent cations (such as Ca^{2+}, Mg^{2+}, Sr^{2+}, Zn^{2+}, *etc.*) are usually divided into two classes; (1) rhombohedral (term related to crystallographic structure) carbonates and (2) orthorhombic carbonates. Calcite is a rhombohedral carbonate and the Ca^{2+}in calcite, like all other divalent cation-based rhombohedral carbonates exhibit, is nested among six O^{2-} anions (*i.e.*, six-fold coordination). Aragonite, on the other hand, is an orthorhombic carbonate and Ca^{2+} in aragonite is nested in a larger cation site among nine oxygens (*i.e.*, nine-fold coordination). To compare, Ca^{2+} cation has an ionic radius of 114 pm, whereas the smaller Mg^{2+} has the ionic radius of 86 pm. The presence of magnesium, cobalt, zinc, iron, manganese, cadmium, strontium, barium or lead ions, even in small concentrations, in one or more of the sand or aggregates of the concrete mix, such ions being

solubilized by the forming water and other liquid admixtures of the concrete mix, may result in the formation of small amounts of the below carbonates of varying thermodynamic stability and carbon-capturing capacity (CCC).

[00224] Some examples of "rhombohedral" carbonate minerals of divalent cations less soluble than calcite (which can capture CO_2 up to 43.97wt%, ΔG_f from ions at 25°C: -48 kJ/mol – more negative, more stable):

(a) magnesite ($MgCO_3$, CO_2-capturing capacity (*CCC*) is 52.2 wt%, ΔG_f from ions at 25°C: -48 kJ/mol),

(b) dolomite ($CaMg(CO_3)_2$, CCC: 47.73 wt%, , ΔG_f from ions at 25°C: -57 kJ/mol),

(c) sphaerocobaltite ($CoCO_3$, CCC: 37 wt%, Co^{2+} radius: 88 pm, ΔG_f from ions at 25°C: -56 kJ/mol),

(d) smithsonite ($ZnCO_3$, CCC: 35.1 wt%, Zn^{2+} radius: 88 pm, ΔG_f from ions at 25°C: -57 kJ/mol),

(e) siderite ($FeCO_3$, CCC: 37.99 wt%, Fe^{2+} radius: 75 pm, ΔG_f from ions at 25°C: -60 kJ/mol),

(f) rhodochrosite ($MnCO_3$, CCC: 38.3 wt%, Mn^{2+} radius: 81 pm, ΔG_f from ions at 25°C: -60 kJ/mol)

(g) otavite ($CdCO_3$, CCC: 25.5 wt%, Cd^{2+} radius: 109 pm, ΔG_f from ions at 25°C: -70 kJ/mol).

[00225] Some examples of "orthorhombic" carbonate minerals of divalent cations less soluble than aragonite (which can capture CO_2 up to 43.97wt%, ΔG_f from ions at 25°C: -47 kJ/mol) are

(a) strontionite ($SrCO_3$, CCC: 29.81 wt%, Sr^{2+} radius: 132 pm, ΔG_f from ions at 25°C: -51 kJ/mol),

(b) alstonite ($BaCa(CO_3)_2$, CCC: 29.59 wt%, Ba^{2+} radius: 149 pm, ΔG_f from ions at 25°C: -50 kJ/mol), and

(c) cerussite ($PbCO_3$, CCC: 16.47 wt%, Pb^{2+} radius: 133 pm, ΔG_f from ions at 25°C: -73 kJ/mol).

Carbonated Water

[00226] In some examples, water used in preparing concrete mixes can be carbonated. Carbonated water can be prepared, for example, by bubbling CO_2 into a forming water tank at the ambient temperature and pressure. When the pressure is increased to the range of 3 to 5 atmospheres (atm), the following dissolved CO_2 amounts in that water will increase. In some

embodiments, the amount of CO_2 can be from about 0.1 to about 1.5 g/L, from about 0.3 to about 1.5 g/L, from about 0.5 to about 1.5 g/L, from about 0.7 to about 1.5 g/L, from about 1.0 to about 1.5 g/L, from about 1.2 to about 1.5 g/L, or from about 1.4 to about 1.5 g/L dissolved CO_2.

[00227] Carbonated water can also contain small amounts (up to 2000 ppm) of dilute (5%) acetic acid, which is a curing aid. Any calcium acetate formed (small amounts) then acts as a curing enhancer, in accord with the below reactions: Reaction 1 -- $CaSiO_3$ (s) + $2CH_3COOH$ (aq) (acetic acid) $\rightarrow$ Ca^{2+} (aq) + $2CH_3COO-$ (aq) + H_2O (l) + amorphous SiO_2 (s); and Reaction 2 -- Ca^{2+} (aq) + $2CH_3COO-$ (aq) (acetate ions) + CO_2 (aq) + H_2O (l) $\rightarrow$ $CaCO_3$(s) + $2CH_3COOH$ (aq) (acetic acid). These two reactions continue to take place until the consumption of free acetic acid in the system.). During the later stages of the carbonation-curing processes, some of the pore solution could still be available, although in a lesser amount with respect to that in the earlier stages. The solid surfaces through which the pore solution moves around start to decrease in pH towards 9, and right under those conditions, the concentration of the (carbonate) CO_3^{2-} ions, which are only stable and available at quite high pH values, start to decrease while the concentration of the (bicarbonate) HCO_3^- ions start to increase (which are stable at pH 8 to 9). This is the point where the aqueous $Ca(HCO_3)_2$ ions (calcium bicarbonate ions) start to form. Once these ions form, it is very difficult to dissociate them in the pore solution. The product will be recovered from the carbonation-curing chamber, and if the concentration of those $Ca(HCO_3)_2$ ions are rather significant, then they may further generate calcium carbonate crystals when the concrete starts attaining lower and lower residual moisture contents.

Corrosion inhibitors

[00228] In some embodiments, an admixture is a corrosion inhibiting admixture. A corrosion inhibitor can prevent, mitigate, or delay corrosion by forming a passive film on metal, such as iron or steel components (*e.g.*, plain carbon steel, epoxy coated steel, galvanized steel, and/or stainless steel, reinforcement bars or meshes) used with or at least partially embedded in concrete composite materials. Examples of corrosion inhibitors include inorganic corrosion inhibitors (e.g., calcium nitrite, lithium nitrate, sodium nitrite, potassium chromate, sodium phosphate, and Na_2PO_3F), organic corrosion inhibitors (e.g., amines, alkanolmines, carboxylate, and amino acids), “green inhibitors” (bauxite residue, flavonoids, alkaloids and other natural products obtained from natural sources like plants),

pharmaceutical compounds (e.g., Carbamazepine, Paracetamol) and combinations thereof. Other examples of corrosion inhibitors are set forth in Table 1.

Table 1: Corrosion inhibitors

Manufacturer	Product	Chemical basis	Method of usage
Sika	CNI	Calcium nitrite	Mixed into concrete
	FerroGard 901	Amino alcohols	Mixed into concrete
	FerroGard 903	Amino alcohols	Applied on concrete
BASF	MasterLife 222	Amines and esters	Mixed into concrete
	MasterLife CI30	Calcium nitrite	Mixed into concrete
W. R. Grace	DCI	Calcium nitrite	Mixed into concrete
Cortec Co.	MCI 2000	Amino alcohols	Mixed into concrete
	MCI 2005	Amine carboxylate	Mixed into concrete
	MCI 2007	Superplasticizer + amine carboxylate	Mixed into concrete
	MCI 2020	Amino alcohols + carboxylic acid salt	Applied on concrete
Euclid chemical	EUCON BCN	Calcium nitrite	Mixed into concrete
	EUCON CIA	Calcium nitrite	Mixed into concrete

Air-entraining admixtures

[00229] In some embodiments, an admixture is an air-entraining admixture. Air-entraining admixtures facilitate the development of a stable air-void system within concrete that can increase the durability of the concrete. Concrete durability is greatly affected by freeze-thaw cycles. In OPC concrete the hydration process involves the reaction of water and cement and leaves capillary cavities that become filled with water when concrete is exposed to the environment. As the water freezes it expands approximately 9%, which exerts pressure on the concrete that exceeds its tensile strength, causing cracking and eventual disintegration. Air-entraining admixtures can prevent or mitigate damage from freeze-thaw forces. Entrained air can provide a relief system for pressure, by providing avenues for the expansion caused when the water freezes.

[00230] Examples of air entraining admixtures for use in the compositions and methods provided herein include liquids produced from wood resins, synthetic detergents, sulfonated lignins, petroleum acids, proteinaceous materials, sulfonated hydrocabons, protein hydrolysate, cereal storage protein, modified rosin, cellulose acetate, soy bean protein hydrolysate, polylactic acid, polyvinyl alcohol, polyglycolic acid, poly(3-hydroxybutyrate), admixtures shown in Table 2, and combinations thereof. Air entraining admixtures can improve freeze thaw durability of a carbonatable calcium silicate-based cement composition.

Table 2: Air entraining admixtures

Manufacturer	Product	Chemical basis
BASF	MasterAir AE 200	Not known
	MasterAir AE 400	Not known

	MasterAir AE 90	Not known
	Master VR 10	neutralized vinsol resin admixture
Sika	Sika® AIR, Sika AEA -14	aqueous solution of organic materials
	Sika® Air-260	

Shrinkage-reducing admixtures

[00231] In some embodiments, an admixture is a shrinkage-reducing admixture. Shrinkage and volume change during the curing and hardening process of concrete can lead to reduced performance and durability from the formation of microstructural stresses, deformation, and cracking. Minimizing shrinkage cracks can mitigate or prevent migration of one or more of oxygen, moisture, chlorides, and other deleterious chemicals into the concrete matrix.

[00232] Shrinkage-reducing admixtures can limit the volume change of concrete and mortar and the potential for subsequent cracking from resulting stresses by reducing capillary tension of the pore water. The energy made available from drying can be used in either the generation of interfacial area or in deformation. Shrinkage-reducing admixtures can increase the fraction of energy used in the creation of interfacial area by reducing surface tension at the liquid-air interfaces (menisci and water films) thereby limiting energy available for deformation and shrinkage.

[00233] Shrinkage-reducing admixtures include single-type non-ionic surfactants or mixtures of non-ionic surfactants, cosolvents, and hydrotropes. Non-ionic admixtures can favor adsorption at liquid-vapor interfaces rather than liquid-solid interfaces. Examples of shrinkage-reducing admixtures include monoalcohols (e.g., R—OH where R is a linear, branched, or cyclic alkyl radical, such as tert-butyl alcohol), glycols (including diols, or alcohols that possess two hydroxyl functional groups attached to two adjacent carbon atoms, e.g., alkane diols, dimethyl propanediols, polyoxyalkylene glycols, propylene glycol derivatives, hexylene glycols, and mixtures thereof), polyoxylalkylene glycol alkyl ethers (hydrophobic functional groups of linear, branched, or cyclic alkyl radicals and hydrophilic heads consisting of hydrated oxy-alkylene chains, e.g., polyethers, propyleneglycol ethers, and combinations thereof), polymeric surfactants (e.g., single or multi-headed polymeric non-ionic surfactants), hydroxyl compounds, alkylamine compounds, oxyalkylamine compounds, and combinations of the above with or without cosolvents.

Evaporation Controlling Admixtures

[00234] In some embodiments, an admixture is an evaporation controlling admixture. Evaporation controlling admixtures limit drying-induced shrinkage and can also be used to

control the drying and curing behavior of CCSC-based concretes. Evaporation controlling admixtures can form monomolecular films at the evaporative surfaces of concrete which can control drying and curing rates.

[00235] Evaporation controlling admixtures include emulsified fatty alcohols, such as cetyl alcohol, stearyl alcohol, liquid paraffins, and combinations thereof.

Plasticizers and superplasticizers

[00236] In some embodiments, an admixture is a water-reducing admixture (plasticizer), a high-range water-reducing admixture (superplasticizer, also referred to as liquefying admixture) or a combination thereof.

[00237] Efficiency of plasticizer and supersplasticizer admixtures can evaluated by the possible reduction of the water content (in wt%) to be present in the concrete mix, while keeping the same consistency. This reduction (as compared to the control mix) can be ≥ 5 wt% for the plasticizers and ≥ 12 wt% for superplasticizers.

[00238] The effectiveness of superplasticizers can depend on various technological factors, such as for example, concrete constituent characteristics (e.g., mainly cement, superplasticizers and mineral additives characteristics), mixture proportions (e.g., water to binder mass ratio, superplasticizer, cement and mineral additives content, presence of other chemical admixtures in mixture), methods and conditions of concrete production (e.g., order of addition, temperature of the mixture), and combinations thereof.

[00239] Polycarboxylate admixtures, based mainly on the polymers with carboxylate and oligo(ethylene oxide) side groups, can be effective superplasticizers. The methacrylate copolymers of methacrylic acid and methacrylic ester with the oligo(ethylene oxide) group is an example of such admixture, commonly called the polycarboxylate (PCE) superplasticizer. PCE superplasticizers can be chemically described as polymers of poly(oligo(ethylene glycol) methyl ether methacrylate/methacrylic acid. This is a comb-like polymer built up with ionic hydrophilic carboxylate groups (COO^-) and long, elastic side nonionic hydrophilic oligo(ethylene oxide) chains. The main function of the ethylene oxide side chains is to exert steric hindrance that keeps the cement grains away from each other and hence prevents cement agglomeration. Common superplasticizers (dispersants) for cementitious materials such as concrete include carboxylated comb polymers which strongly chelate Ca^{2+} ions. Thus, a substrate holding Ca^{2+} as docking site on its surface and of a narrow particle size distribution was expected to produce reliable values for the adsorbed layer thickness (ALT) of polycarboxylate comb polymers, as measured *via* dynamic light scattering. ALT presents a

key parameter which controls the dispersion power of such polymers and provides the steric hindrance effect between cement particles.

[00240] Superplasticizers can be used in methods of obtaining a dispersion of the cement grains/particles in water. For example, carboxylate groups (COO-) can interact with the surface of the cement grain/particle, which leads to polymer adsorption and electrostatic repulsion between grains (COO- groups create a negative charge around the grain/particle). The "steric repulsion" is commonly considered as a potential mechanism of cement particle dispersion. Simultaneously, the wettability of cement particles can be improved, fostering the full cement hydration (setting). When and if cement hydration happens, a set retarder can be included. Overall, the viscosity of the concrete mix can decrease leading to a consistency improvement.

[00241] An exemplary side chain used for polycarboxylate superplasticizers is oligo(ethylene oxide). Polymers (usually denoted as PCEs) with carboxylate and oligo(ethylene oxide) groups can be synthesized by radical copolymerization of monomer introducing the carboxylic group into polymer (*e.g.*, acrylic acid) with macromonomer introducing the oligo(ethylene oxide) chain into polymer (*e.g.*, oligo(ethylene oxide) acrylate). Some types of superplasticizers can cause excessive air content and exhibit undesired foaming action.

[00242] Methods of preparing PCEs include, for example: a) obtaining polycarboxylate superplasticizers by terpolymerization of macromonomer – monoester of maleic acid, oligo(ethylene oxide) acrylate and acrylic acid; b) using poly(acrylic acid) and poly(ethylene oxide) terminated with amino and methoxy groups as reactants for synthesis of amide-PCE; c) obtaining a structurally modified PCE superplasticizer which was synthesized from methacrylic acid and 2-hydroxyethyl methacrylate, 3-hydroxypropyl methacrylate or 4-hydroxybutyl methacrylate esters, which then result in PCEs possessing hydroxyalkyl side chains; and d) synthesis of terpolymers from maleic anhydride, monoalkyl maleate esters, and 4-hydroxybutyl vinyl ether.

[00243] Methods of PCE synthesis can be categorized to the following groups: a) EsMa – type PCEs, when Esters and Monoprotic acids are used as substrates; b) EsPa – type PCEs, when Esters and Polyprotic acids or anhydrides are used as substrates; c) AlMa – type PCEs, when Allyl or ether compounds and Monoprotic acids are used as substrates; d) AlPa – type PCEs, when Allyl or ether compounds and Polyprotic acids or anhydrides are used as substrates; and e) Amide – type PCEs, when amide bonds are formed.

[00244] Polycarboxylate superplasticizers can modified by insertion of other monomers to afford terpolymers. For example, polycarboxylates modified with methoxysilanes, contrary to the traditional superplasticizers, can be very effective when added to cements with high sulfates content. The side chain of the polycarboyxlates, i.e., polyethylene oxide, can be modified by changing its length and kind of terminal group. For example, side chains of polycarboxylate superplasticizers can contain 17, 24 or 45 repeating units of ethylene oxide, terminated with either the hydroxyl (–OH) or methoxy (–OCH_3) group.

[00245] Examples of modifier monomers that can be used to prepare polycarboxylate superplasticizers include, for example, vinyl acetate, methyl acrylate, methacrylamide, 2-hydroxylethyl methacrylate, sodium 2-methyl-2-propene-1-sulphonate, sodium allyl sulfonate, 2-methacryloyloxy-ethyl-trimethyl-ammonium chloride, 3-trimethoxysilyl-propyl-methacrylate, 2-(methacry¬loyloxy)-ethyl phosphate, 2-acrylamido-2-methyl-1-propanesul¬fonic acid, β-cyclodextrin with methacrylic ester group, β-cyclodextrin with maleic ester group, and octadecyl phosphate groups.

[00246] Plasticizer and superplasticizer admixtures can include acidic groups other than carboxylic groups, such as sulfonic acid and phosphonic acid groups. Also, the chain of poly(ethylene oxide) can be modified by introduction of other hydrophilic units, especially those characterized by branched structure, providing reduced viscosity of the polymer solution.

[00247] A competitive adsorption can exist between polycarboxylate superplasticizers and sulfate ions solubilized in the interstitial (pore) solution of cement paste, which may cause a drastic loss of dispersing properties depending on the cement composition. This can result from “competitive” weak ionic interaction between the functional acrylate groups of the polycarboxylate-based superplasticizer (SP, water-reducer) and the solubilized sulfate ions residing in the near vicinity of cement particles. Superplasticizers including trialkoxysilane functional groups synthesized via radical copolymerization of methacrylic acid, poly(ethylene glycol) methyl ether methacrylate and trimethoxysilyl propyl methacrylate, i.e., partial substitution of the acrylate groups by trialkoxysilane in the polymer composition can enhances compatibility with sulfate ions. The high adsorption capacity of silane-modified superplasticizers can result from the formation of strong bonds between the hydroxysilane groups and calcium silicate and/or calcium silicate hydrate phases present at the surfaces of the cement particles.

[00248] Foaming of a superplasticizer can contribute to porosity buildup. Foaming can be mitigated or decreased by decreasing the surface tension of liquid admixtures. When a superplasticizer has a certain surface tension by itself in its pure form, the surface tension value will decrease when it is pre-dissolved in some of the water to be used in the concrete mixer.

Crystallization inhibitors

[00249] In some embodiments, an admixture is a crystallization inhibitor. In some examples, the crystallization inhibitors inhibit crystallization of alkali sulphate. In further examples, the crystallization inhibitors inhibit crystallization of alkali sulphate throughout the bulk of the cured concrete.

[00250] Examples of admixtures that inhibit alkaline earth (*i.e.*, Ca-sulphate dihydrate, gypsum, or Ca-sulphate hemihydrate) and alkali (Na and K) sulphate crystallization out of cured concrete include dilute phosphoric acid (H_3PO_4), $(NH_4)H_2PO_4$ (ammonium dihydrogen phosphate), hexametaphosphate (HMP), NaH_2PO_4 (sodium dihydrogen phosphate), KH_2PO_4 (potassium dihydrogen phosphate), Na_2HPO_4 (disodium hydrogen phosphate), K_2HPO_4 (dipotassium hydrogen phosphate), K_3PO_4 (tripotassium phosphate, which is also used to bind H_2S (g) to KHS compound), triethyl phosphate, trimethyl phosphate, fatty acids, and combinations thereof.

[00251] In some embodiments, the crystallization inhibitor admixture is phosphoric acid. In further examples, the crystallization inhibitor admixture is phosphoric acid and inhibits Ca-sulphate (gypsum) crystallization in solutions.

[00252] In some examples, the crystallization inhibitor is present at a concentration of about 0.01 mM to about 0.2 mM, about 0.01 mM to about 0.1 mM, about 0.02 to about 0.08 mM, about 0.04 mM to about 0.06 mM, or about 0.05 mM.

[00253] Inhibition of gypsum crystallization in cured concrete can become important if the Na- and K-sulfates then start their crystallization on the already-crystallized nano or sub-micron (*i.e.*, small crystal sizes at the initial stages of gypsum crystallization) Ca-sulphate crystals. If and when the gypsum is the first phase to crystallize and if it has a certain crystal size and an attractively high BET surface area, this gypsum crystal will then act as a scaffold for the templated-growth of sodium and/or potassium sulphate crystals.

Curing Enhancers

[00254] Select combinations and amounts of set-retarding or hydration-controlling admixtures used in OPC can be used to improve the workability and strength of the concrete.

These admixtures, however, can be sensitive to the dosage applied. Testing can be performed to determine the dosage of the admixtures required for improving workability and strength.

[00255] Use of these admixtures can provide advantages in improving the drying rate (rate of water removal from the concrete body) and uniform distribution of moisture within the concrete body.

[00256] Presence of these admixtures can result in one or more of the following: increased rate of carbonation of the concrete during CO_2 curing and total CO_2 uptake, improved curing uniformity of the products, improved strength gain, such as strength gain in wet-cast concrete products or dry-cast concrete products, improved compaction of products, such as vibro-cast dry products, improved green densities of products, such as vibro-cast dry products, improved reacted densities of products, such as vibro-cast dry products, more uniformity cured products with less standard deviation in strength, improved strength or product quality or both of concrete.

[00257] Exemplary chemicals that may be utilized include Saccharides (sugars), such as sucrose, glucose, or fructose; hydroxycarboxylic acids and salts thereof, such as acetic acid, malic acid, tartaric acid, citric acid, solution of citric acid and sugar in a 3 to 1 ratio, gluconic acid and salts thereof; and combinations thereof, such as sucrose and Na-gluconate and other combinations thereof. For instance, the presence of small dosages (about 0.2 to about 8 g per kg of cement) of acetic acid (in the form of dilute solutions, such as 5 wt% solution of acetic acid in water, *aka* vinegar) in the concrete mixes would lead to the early chemical reaction with the basic cement particles then resulting in the formation and concentration of calcium (Ca^{2+}) and acetate (CH_3COO^-) ions at the surfaces of cement particles. Calcium acetate, which shall start forming during the high temperature water-removal stages of the carbonation-curing process, will then act as a curing enhancer/accelerator for CCSC (e.g., Solidia Cement^{TM}).

[00258] Curing of CCSC based materials can aided by controlling the removal of forming water. Curing enhancers can improve drying rate and total moisture removal by extending the duration of capillary-driven drying. In some examples, curing enhancers can improve the homogeneity and moisture distribution of CCSC materials during the curing process.

[00259] Curing enhancers can improve the curing of CCSC based materials by assisting in the removal of forming moisture, maintaining sample homogeneity throughout

the curing process, and controlling the rate of reaction. The impact of curing enhancers on curing properties of CCSC based specimens can be evaluated, for example, using phenolphthalein dye to detect extent and uniformity of carbonation.

[00260] Curing enhancers can improve the strength development of CCSC based materials by assisting in the removal of forming moisture, maintaining sample homogeneity throughout the curing process, and controlling the rate of reaction.

[00261] Curing enhancers can reduce the variance in CCSC based material properties by improving curing consistency and minimizing the impact of variable forming properties and chamber non-uniformity.

Other admixtures

[00262] Other chemical admixtures can also be included. For example, accelerators, dispersants and other rheology-modifying agents, and combinations thereof, can be included. Certain commercially available chemical admixtures such as Glenium™ 7500 by BASF® Chemicals and Acumer™ by Dow Chemical Company can also be included. In certain embodiments, one or more pigments can be evenly dispersed or substantially unevenly dispersed in the bonding matrices, depending on the desired composite material. The pigment can be any suitable pigment including, for example, oxides of various metals (*e.g.*, black iron oxide, cobalt oxide and chromium oxide). The pigment can be of any color or colors, for example, selected from black, white, blue, gray, pink, green, red, yellow and brown. The pigment can be present in any suitable amount depending on the desired composite material, for example in an amount ranging from about 0.0% to about 10% by weight. In some embodiments, the carbonatable composition further includes a colorant (*e.g.*, one or more of iron oxide, cobalt oxide and chromium oxide).

Methods

[00263] Provided herein are methods to improve one or more properties of a carbonatable calcium silicate-based cement composition by adding an admixture described herein to a carbonateable calcium silicate composition or a precursor composition thereof. In certain embodiments of the method, adding to cement an admixture comprises adding a solid admixture. In certain embodiments of the method, adding to cement an admixture comprises adding a liquid admixture. In certain embodiments of the method, adding to cement an admixture comprises adding a solid admixture and a liquid admixture. The methods provided herein can include a step of curing the cement to form a concrete product.

[00264] In some embodiments in which more than one admixture is added, the admixtures can be added in any order. In some embodiments, two or more admixtures can be simultaneously added. In some examples, admixtures can be added to the dry mix.

[00265] For example, provided herein are methods to improve one or more strength properties of a carbonatable calcium silicate-based cement composition by adding an admixture described herein. In some examples, a strength enhancer described herein is added. Examples of strength properties that can be improved include compressive strength, flexural strength (3-point bending), torsional strength, split tensile strength, and combinations thereof.

[00266] Provided herein are methods to improve durability of a carbonatable calcium silicate-based cement composition by adding an admixture described herein. In some examples, a hydrophobic compound described herein is added.

[00267] Provided herein are methods for suppressing premature setting of a carbonatable calcium silicate composition by adding an admixture described herein. In some examples, the provided methods are for suppressing premature setting of a carbonatable calcium silicate composition comprising one or more hydraulic contaminants. Also provided herein are methods for accelerating the drying rate or the curing rate of a carbonatable calcium silicate cement. In some examples, the carbonatable calcium silicate cement comprises one or more hydraulic contaminants. The methods can include adding one or more set-retarding or hydration-controlling admixtures described herein.

[00268] Provided herein are methods to prevent, mitigate, or delay corrosion of iron or steel components (*e.g.*, plain carbon steel, epoxy coated steel, galvanized steel, and/or stainless steel, reinforcement bars or meshes) used with or at least partially embedded in concrete composite materials, and objects made from carbonatable calcium silicate-based cement composition, by adding an admixture described herein. In some examples, the carbonatable calcium silicate-based cement composition is a carbonatable low calcium silicate based cement composition. The methods can include adding one or more pH enhancing admixtures and/or moisture resistant admixtures described herein. One or more pH enhancing additive(s) and/or moisture resistance admixture(s) can be added at dosage of about 1% to about 20%, by mass, relative to the total amount of cementitious materials. In some examples, admixtures can be added to the dry mix in a mixer along with low calcium silicate cement.

[00269] Provided herein are methods to prevent or reduce haze formation in a carbonatable calcium silicate-based cement composition, by adding an admixture described

herein. In some examples, the admixture is a admixture that mitigates or reduces efflorescence. The method can include, prior to curing cement to form a concrete product, adding to the concrete mixture an admixture that mitigates or reduces efflorescence.

[00270] Provided herein are methods to control sulphate crystallization phenomena in a carbonatable calcium silicate-based cement composition, by adding an admixture described herein. In some examples, the admixture is an ettringite growth inhibitor.

[00271] Provided herein are methods to prepare a carbonatable calcium silicate-based cement composition with carbonated water. Using carbonated water has the function of bringing the needed dissolved CO_2 molecules (i.e., CO_2(aq)) directly to the mesopores of the concrete mix even during the concrete consolidation (i.e., various forming methods adopted by the concrete industry), and while the shaped green concrete samples (before carbonation-curing) wait their turn to enter into the concrete carbonation-curing chamber, the CO_2(aq) will have the opportunity to first turn into H_2CO_3(aq) and secondly into HCO_3^-(aq) at the same above-mentioned mesopores. This chain of events taking place at the mesopores will then facilitate the start of the carbonation (i.e., crystallization of $CaCO_3$) process upon the samples staring their carbonation-curing process in the curing chamber more homogeneously and from within the bulk of the bodies to be cured.

[00272] Provided herein are methods to prevent or mitigate corrosion, by adding an admixture described herein to a carbonatable calcium silicate-based cement composition. In some examples, the admixture is a corrosion inhibitor. In some examples, corrosion of a metal, such as steel reinforcement, is prevented or mitigated.

[00273] Provided herein are methods to prevent or mitigate damage from freeze-thaw cycles in a carbonatable calcium silicate-based cement composition, by adding an admixture described herein. In some examples, the admixture is an air-entraining admixture.

[00274] Provided herein are methods to improve workability and cohesiveness of calcium silicate-based cement or concrete by adding an admixture described herein. In some examples, the admixture is an air-entraining admixture.

[00275] Provided herein are methods to reduce segregation and bleeding in a carbonatable calcium silicate-based cement composition, by adding an admixture described herein. In some examples, the admixture is an air-entraining admixture.

[00276] Provided herein are methods to improve an air-void structure or network in a carbonatable calcium silicate-based cement composition, by adding an admixture described herein. In some examples, the admixture is an air-entraining admixture.

[00277] Provided herein are methods to increased resistance to scaling in a carbonatable calcium silicate-based cement composition, by adding an admixture described herein. In some examples, the admixture is an air-entraining admixture. In some examples, the scaling is from deicing salts.

[00278] Provided herein are methods to increase resistance to deterioration from cyclic freezing and thawing in a carbonatable calcium silicate-based cement composition, by adding an admixture described herein. In some examples, the admixture is an air-entraining admixture.

[00279] Provided herein are methods to improve the degree or extent of carbonation in a carbonatable calcium silicate-based cement composition, by adding an admixture described herein. In some examples, the admixture is an air-entraining admixture.

[00280] Provided herein are methods to improve one or more strength properties of a carbonatable calcium silicate-based cement composition by adding an admixture described herein. In some examples, the admixture is an air-entraining admixture. Examples of strength properties that can be improved include compressive strength, flexural strength, split tensile strength, torsional strength, and combinations thereof.

[00281] Provided herein are methods to improve control of material properties during drying processes in a carbonatable calcium silicate-based cement composition, by adding an admixture described herein. In some examples, the admixture is a shrinkage-reducing admixture, an evaporation controlling admixture, or a combination thereof.

[00282] Provided herein are methods to improve control of material properties during CO_2 curing in a carbonatable calcium silicate-based cement composition, by adding an admixture described herein. In some examples, the admixture is a shrinkage-reducing admixture, an evaporation controlling admixture, or a combination thereof.

[00283] Provided herein are methods to improve control of material properties relevant to providing strength during high-temperature curing in a carbonatable calcium silicate-based cement composition, by adding an admixture described herein. In some examples, the admixture is a shrinkage-reducing admixture, an evaporation controlling admixture, or a combination thereof.

[00284] Provided herein are methods to improve process carbonation curing efficiency in a carbonatable calcium silicate-based cement composition, by adding an admixture described herein. In some examples, the admixture is a shrinkage-reducing admixture, an evaporation controlling admixture, or a combination thereof. In some examples, improved process efficiency is due to better control over material drying and/or curing properties.

[00285] Provided herein are methods to improve concrete strength in a carbonatable calcium silicate-based cement composition, by adding an admixture described herein. In some examples, the admixture is a plasticizer, a superplasticizer, or a combination thereof. In some examples, improved strength occurs in wet-cast concrete, dry-cast concrete, or wet-cast concrete and dry-cast concrete.

[00286] Provided herein are methods to improve concrete mix consistency in a carbonatable calcium silicate-based cement composition, by adding an admixture described herein. In some examples, the admixture is a plasticizer, a superplasticizer, or a combination thereof.

[00287] Provided herein are methods to decrease an amount of cement utilized in a carbonatable calcium silicate-based cement or concrete formulation by adding an admixture described herein. In some examples, the admixture is a plasticizer, a superplasticizer, or a combination thereof. In some embodiments, cement consumption is decreased without affecting the strength of the concrete and consistency of the concrete mix.

[00288] Provided herein are methods to improve the drying rate in a carbonatable calcium silicate-based cement composition, by adding an admixture described herein. In some examples, the admixture is a plasticizer, a superplasticizer, or a combination thereof.

[00289] Provided herein are methods to improve uniform distribution of moisture in a carbonatable calcium silicate-based cement composition, by adding an admixture described herein. In some examples, the admixture is a plasticizer, a superplasticizer, or a combination thereof.

[00290] Provided herein are methods to increase the rate of carbonation of a carbonatable calcium silicate-based cement composition, by adding an admixture described herein. In some examples, the admixture is a plasticizer, a superplasticizer, or a combination thereof. In some examples, the rate of carbonation is increased during CO_2 curing or total CO_2 uptake or a combination thereof.

[00291] Provided herein are methods to improve curing uniformity of a carbonatable calcium silicate-based cement composition, by adding an admixture described herein. In some examples, the admixture is a plasticizer, a superplasticizer, or a combination thereof.

[00292] Provided herein are methods to improve compaction of vibro-cast dry products of a carbonatable calcium silicate-based cement composition, by adding an admixture described herein. In some examples, the admixture is a plasticizer, a superplasticizer, or a combination thereof.

[00293] Provided herein are methods to improve green density (i.e., the experimentally-measured densities samples just after the consolidation/shaping and before the carbonation-curing) of a carbonatable calcium silicate-based cement composition by adding an admixture described herein. In some examples, the admixture is a plasticizer, a superplasticizer, or a combination thereof.

[00294] Provided herein are methods to improve reacted density in a carbonatable calcium silicate-based cement composition, by adding an admixture described herein. In some examples, the admixture is a plasticizer, a superplasticizer, or a combination thereof.

[00295] Provided herein are methods to inhibit crystallization of a carbonatable calcium silicate-based cement composition by adding an admixture described herein. In some examples, the admixture is a crystallization inhibitor. In some examples, crystallization of alkali sulphate is inhibited. In some examples, crystallization of alkali sulphate is inhibited throughout the bulk of cured concrete.

[00296] Also provided herein are methods for forming a concrete product. The method can include: prior to curing cement to form a concrete product, adding to the concrete mixture an admixture comprising one or more minerals comprising magnesium oxide; and curing the cement to form a concrete product. The cement is a carbonatable calcium silicate-based cement. The magnesium oxide present in the one or more minerals can account for about 0.02% to about 20% (*e.g.*, about 0.02% to about 10%, about 0.05% to about 7%, about 0.05% to about 6%, about 0.05% to about 5%, about 0.05% to about 4%, about 0.05% to about 3%, about 0.05% to about 2%, about 0.05% to about 1%, about 0.05% to about 0.5%, about 0.05% to about 0.25%, about 0.1% to about 8%, about 0.5% to about 8%, about 1% to about 8%, about 2% to about 8%, about 3% to about 8%, about 4% to about 8%, about 5% to about 8%, about 6% to about 8%, about 0.25% to about 1%, about 0.5% to about 2%) by weight of the carbonatable calcium silicate-based cement.

[00297] In some embodiments, the method further includes adjusting the pH of the concrete mixture prior to curing the cement to form a concrete product.

[00298] In yet another aspect, provided herein are concrete products manufactured by a method described herein.

[00299] In some examples, one or more admixture(s) is added prior, during, or after the grinding of a calcium silicate-based cement. In some examples, one or more admixture(s) is added during, or after the grinding of a calcium silicate-based cement. In some examples, one or more admixture(s) is added during the mixing of cement with a plurality of aggregate particles to form a concrete composition.

[00300] Assays to measure one or more properties of a carbonatable calcium silicate-based cement composition are known to one of skill in the art, and include, for example, assays to measure Freeze-thaw scaling, and/or water ingress.

[00301] Freeze-thaw scaling can be tested by a suitable method known to one of skill in the art, such as according to standard ASTM C1645/C1645M with a temperature cycle according to NF EN 1338. Freeze-thaw testing can be evaluated, for example, in 3% saline solution following procedures as specified in CSA A231.2.

[00302] Water sorptivity can be assessed, for example, as specified in ASTM C1585. Water absorption can be assessed, for example, following procedures as specified in ASTM C140 Standard Test Methods for Sampling and Testing Concrete Masonry Units and Related Units.

EXAMPLES

Example 1: Compositions

[00303] Illustrative compositions according to optional embodiments are provided in the following tables. Illustrative average oxide compositions of the cement are provided in Table 3. Phase compositions of the cement are provided in Tables 4 and 5. According to further optional illustrative embodiments, mix designs of mortar samples prepared using cement-16 are provided in Table 6. The flow behavior of the mortar of mortar samples in the presence of various admixtures are provided in Figure 2. Figure 3 shows the compressive strength development in the presence of various admixtures. According to further optional illustrative embodiments, concrete (paver) and concrete (slab) formulation examples are provided in Tables 7 and 8, respectively. All percentages are percent by weight unless indicated otherwise.

Table 3. Illustrative average oxide compositions of cement.

Cement	**Oxides**	**SiO_2**	**CaO**	**Al_2O_3**	**Fe_2O_3**	**MgO**	**SO_3**	**K_2O**	**Na_2O**	**TiO_2**	**P_2O_5**
Cement-16	%	43.9	44.5	3.9	1.8	1.4	0.9	0.72	0.3	0.3	0.2
Cement-P	%	47.1	46.6	2.6	0.8	0.8	0.2	0.7	0.4	0.0	0.0

Table 4. Phase composition of Solidia cement–16 (by XRD, X-ray diffraction)

Phase	**%**

Pseudowollastonite	$CaSiO_3$	16.4
Rankinite	$Ca_3Si_2O_7$	24.6
Larnite (=Belite)	β - Ca_2SiO_4	3.5
Melilite (=akermanite, gehlenite)	$(Ca,Na)_2(Al,Mg,Fe^{2+})[(Al,Si)SiO_7]$	17.8
Quartz	SiO_2	1.9
Cristobalite	SiO_2	1.4
Calcite	$CaCO_3$	0.9
Amorphous		33.5

Table 5. Phase composition of Solidia cement–P (by XRD, X-ray diffraction)

Phase		**%**
Pseudowollastonite	$CaSiO_3$	36.1
Rankinite	$Ca_3Si_2O_7$	12.8
Larnite (=Belite)	β - Ca_2SiO_4	5.7
Melilite (=akermanite, gehlenite)	$(Ca,Na)_2(Al,Mg,Fe^{2+})[(Al,Si)SiO_7]$	6.8
Quartz	SiO_2	6.9
Cristobalite	SiO_2	0.5
Amorphous		31.2

Table 6. Mortar mix design

Batch ID	**Description**	**Cement**	**EN Sand**	**Water**		**Admixture**		
		g	*g*	*w/c*	*g*	*Type*	*Dosage, % solids*	*wt. solids, g*
MC-1	None	450	1350	*0.33*	*149*	None	--	--
MC-2	Superplasticizer 1	450	1350	*0.33*	*149*	Glenium 7500	0.20%	0.90
MC-3	Superplasticizer 2	450	1350	*0.33*	*149*	ACM ProCast 150	0.20%	0.90
MC-4	Superplasticizer 3	450	1350	*0.33*	*149*	ConXL DM	0.20%	0.90
MC-5	Set-retarder 1	450	1350	*0.33*	*149*	Plastiment	0.20%	0.90
MC-6	Set-retarder 2	450	1350	*0.33*	*149*	ACM ProCast 710	0.20%	0.90
MC-7	Hydrophobic 1	450	1350	*0.33*	*149*	ACM ColorScape 340	0.20%	0.90

Table 7. Concrete (paver) formulation examples

Batch #	wt% cement	wt% sand	wt% aggregate-1, Koss, ¼"	wt% aggregate-2, Hanson, ¼"	wt% aggregate-3, (slag aggreg)	wt% aggregate-4, CRM (recycled concrete)	Water-reducer, mL/kg of cement	Set retarder, mL/kg of cement	Hydrophobe, mL/kg of cement	Curing aid, g/kg of cement	Carbonation-curing time, hours	Compr. strength, mean (psi)

SP-1843	14.5	42.40	12.9	14.5	12.40	3.1	3, ConXL	5, BASF-Masterset	10, EChem-205	N/A	22	9,430
SP-1877	14.7	46.85	N/A	38.30	N/A	N/A	6, SIKA-HC300	5, BASF-Masterset	N/A	20, MgO	22	10,033
SP-1938	14.7	46.85	N/A	38.30	N/A	N/A	6, SIKA-HC300	5, BASF-Masterset	N/A	20, MgO	21	10,700
BR-174	15.45	49.85	N/A	34.40	N/A	N/A	5, Glenium	5, BASF-Masterset	N/A	7, MgO	22	11,104
ST-212	14.64	45.22	N/A	4.97 (3/8” aggreg)	31.75	3.22	N/A	N/A	N/A	7, MgO	23	7,000
ST-419	14.64	45.22	N/A	4.97 (3/8” aggreg)	31.75	3.22	7, SIKA-HC300	7.3, sugar soln	N/A	N/A	23	11,652
ST-995	14.4	44.75	N/A	5 (3/8” aggreg)	32.25	3.25	2.6, ConXL	6, sugar soln	5, Darapel	N/A	24	6.5 MPa tensile
ST-939	14.64	45.22	N/A	4.97 (3/8” aggreg)	31.75	3.22	2, ConXL	5, sugar soln	5, Darapel	2, MagCet	24	7.6 MPa tensile
ST-1495	14.64	45.22	N/A	4.97 (3/8” aggreg)	31.75	3.22	2, ConXL	5, sugar soln	5, Darapel	2, MagCet	23	10,500
ST-1742	14.5	46.55	N/A	5 (3/8” aggreg)	33.8	N/A	N/A	2.22, sugar soln, 6.84, citric acid soln	5, Darapel	N/A	21.5	11,356
ST-1840	14.5	46.55	N/A	5 (3/8” aggreg)	33.8	N/A	N/A	2.22, sugar soln, 6.84, citric acid soln	5, silane-based	N/A	21.5	11,102

Notes:

1.) All formulations of Table 7 had a water-to-cement (W/C) ratio of 0.32.

2.) ST-995 and ST-939 were 12x16” concrete samples (with 60 mm thickness), their 3-point bending (i.e., tensile) strengths were measured; all other concrete samples were of 4x8 dimensions, with 80 mm thickness. 4x8 samples made out of OPC has the strength requirement of 8000 psi and most OPC paver manufacturers suffer to meet this 8000 psi strength spec.

3.) ST-212 formulation did not use any water-reducer (=superplasticizer), set retarder or hydrophobe.

4.) ST-1495 formulation had the liquid ConXL (water-reducer), crystalline sugar, MagCet solution (i.e., a small amount of MgO pre-dissolved in vinegar or dilute acetic acid) and some (65%) of the forming water pre-mixed into a single admixture before its addition into the concrete mixer. The single admixture preparation also applies to the ST-419 formulation.

5.) ST-1742 formulation used a pre-mixed single admixture of “some (variable between 20 to 75% of the total required water for the green concrete mix) forming water + crystalline sugar + crystalline citric acid anhydrous.”

6.) ST-1840 formulation used a pre-mixed single admixture of “some (variable between 20 to 75% of the total required water for the green concrete mix) forming water + crystalline sugar + crystalline citric acid anhydrous + silane-based hydrophobe.”

7.) All of the formulations in Table 7 used Solidia Cement-16 with the exception of SP-1938 (which used the Solidia Cement-P), see Tables 4 and 5 for the XRD-based phase percentages of the Solidia cements.

Table 8. Concrete (slab) formulation examples

Mix number	wt% cement	wt% sand	wt% aggregate-¼"	wt% aggregate-3/8"	wt% aggregate-3/4"	Water/ cement ratio	Water-reducer, mL/kg of cement	Set retarder, mL/kg of cement	Hydrophobe, mL/kg of cement	Curing aid, g/kg of cement	Carbonation-curing time, hours	Compr. strength, mean (psi)
1	13.0	42.0	N/A	24.7	20.3	0.38	7, SIKA HC-300	5, SIKA Plastiment	N/A	N/A	120	7,412
2	14.5	40.0	12.0	12.7	20.3	0.38	5, BASF Glenium-7500	5, SIKA Plastiment	N/A	N/A	85	6,995

Example 2. Effect of admixtures on drying properties

[00304] In order to evaluate the impact of curing enhancers on drying behavior, carbonatable calcium silicate-based cement (CCSC) mortar specimens were prepared according to raw material proportions as specified in Table 9 and mixed for 4 minutes using a Hobart mixer. Each mortar mix was cast into a standard 15x15x5 cm mold and placed into a lab-scale chamber with environmental control. Drying rates were determined by measuring mass change over time of CCSC specimens with and without curing enhancers.

[00305] In addition to mass curves, CCSC based specimens were evaluated using neutron radiography to examine moisture distribution and degree of saturation during the drying process.

Table 9: CCSC Mortar Mix Proportions

Mix Components	Mix A	Mix B	Mix C
CCSC Binder	500 g	500 g	500 g
ASTM graded sand	1375 g	1375 g	1375 g
w/c ratio	0.35	0.35	0.35
Sucrose (saccharide)		0.23% bwoc	
Na-citrate (hydroxycarboxylic acid)			0.23% bwoc

[00306] The drying rates of CCSC specimens over the course of 24 hours are shown in Figure 4. Relative to the control mix (Mix A), Mix B produced with sucrose and Mix C produced with Na-citrate exhibit a higher degree and rate of moisture loss.

[00307] The degree of saturation and distribution of moisture as a function of sample depth after 24 hours of drying is shown in Figure 5. At both 50°C and 90°C, WHL-50C-Ret and WHL-90C-Ret, both produced with a saccharide based set-retarder (MasterSet R100) exhibit greater sample homogeneity and a lower degree of saturation than the respective control samples, WHL-50C and WHL-90C.

Example 3. Effect of admixtures on curing properties

[00308] In order to evaluate the impact of curing enhancers on curing properties, CCSC specimens were prepared according to raw material proportions as specified in Table 10 and mixed for 4 minutes using a Hobart mixer. Each mortar mix was cast into a standard 15x15x5 cm mold and placed into a lab-scale reactor. CO_2 uptake rates were determined by measuring accumulated CO_2 consumption over time by CCSC specimens with and without curing enhancers.

[00309] The impact of curing enhancers on curing properties of CCSC based specimens can also be evaluated using phenolphthalein dye to detect extent and uniformity of carbonation. Concrete pavers were produced according to raw material proportions as specified in Table 11. After curing, samples from each batch were cut and evaluated using phenolphthalein dye.

Table 10: CCSC Mortar Mix Proportions

Mix Component	Mix A	Mix B	Mix C
CCSC Binder	500 g	500 g	500 g
ASTM graded sand	1375 g	1375 g	1375 g
w/c ratio	0.35	0.35	0.35
Sucrose (saccharide)		0.23% bwoc	
Na-gluconate (hydroxycarboxylic acid)			0.23% bwoc

Table 11: CCSC Concrete Mix Proportions

Mix Component	Concrete Mix A	Concrete Mix B
Cement	14.5%	14.5%
Sand	42.4%	42.4%
Coarse aggregate I	12.9%	12.9%
Coarse aggregate II	14.5%	14.5%
Coarse aggregate III	3.15%	3.15%
Coarse aggregate IV	12.4%	12.4%

Pigment	0.15%	0.15%
MasterSet R100 (saccharide)		0.23% bwoc

[00310] The CO_2 uptake rates of CCSC specimens over the course of 24 hours are shown in Figure 6. Relative to the control mix (Mix A), Mix B produced with sucrose and Mix C produced with Na-gluconate both exhibit a higher degree and rate of CO_2 uptake.

[00311] CCSCS concrete pavers produced with and without a curing enhancer are shown after curing and application of phennolphthalein dye in Figure 7. Relative to samples from Concrete Mix A, the degree and uniformity of carbonation in samples from Concrete Mix B produced with MasterSet R100 (saccharide) is significantly improved.

Example 4. Effect of admixtures on strength development

[00312] In order to evaluate the impact of curing enhancers on strength development, mortar and concrete CCSC specimens were prepared according to raw material proportions as specified in Tables 12 (Figure 8), 13 (Figure 9) and 14 (Figure 10). After curing in a CO_2 chamber, specimens were tested for compressive strength following procedures outlined in ASTM C109, ASTM C936, and ASTM C39. Results are shown in Figures 8-10. In all specimen type (Mix A being a control - without admixture), compressive strength is significantly improved with use of curing enhancers relative to the control mixes without curing enhancers.

[00313]

Table 12: CCSC Mortar Cube Mix Proportions

Mix Component	Mix A	Mix B	Mix C	Mix D
CCS Cement	450 g	450 g	450 g	450 g
EN standard sand	1350 g	1350 g	1350 g	1350 g
w/c ratio	0.33	0.33	0.33	0.33
Sucrose (saccharide)		0.23% bwoc		
Na-gluconate (hydroxycarboxylic acid)			0.23% bwoc	
Na-citrate (hydroxycarboxylic acid)				0.23% bwoc

Table 13: CCSC Concrete Paver Mix Proportions

Mix Component	Concrete Mix A	Concrete Mix B

CCS Cement	15.45%	15.45%
Sand	50.15%	50.15%
Coarse aggregate I	34.40%	34.40%
Plastiment (hydroxycarboxylic acid)		0.23% bwoc

Table 14: CCSC Concrete Cylinder Mix Proportions

Mix Component	Concrete Mix A	Concrete Mix B
CCS Cement	17.3%	17.3%
Sand	38.1%	38.1%
Coarse aggregate I	24.3%	24.3%
Coarse aggregate II	20.3%	20.3%
Sucrose + Na-gluconate blend		0.23% bwoc

Example 5. Effect of curing enhancers on variance in strength properties

[00314] In order to evaluate the impact of curing enhancers on curing consistency, mortar CCSC specimens were prepared according to raw material proportions as specified in Table 15. After curing in a CO_2 chamber, specimens were tested for variance by measure of compressive strength following procedures outlined in ASTM C109.

Table 15: CCSC Mortar Cube Mix Proportions

Mix Component	Mix A	Mix B
CCS Cement	500 g	500 g
ASTM graded sand	1375 g	1375 g
w/c ratio	0.35	0.35
Na-citrate (hydroxycarboxylic acid)		0.23% bwoc

[00315] Distribution curves of compressive strength results for Mix A (FIG. 11A) without a curing enhancer and Mix B (FIG. 11B) with Na-citrate (hydroxycarboxylic acid) curing enhancer are shown in Figures 11A - 11B (the value of the probability density function plotted on the y axis against different values of x (i.e. normal distribution curve)).

Example 6. Effect of admixtures on aesthetic performance and efflorescence mitigation

[00316] In order to evaluate the impact of fatty acids, salts of fatty acids, and silanes on aesthetic performance and efflorescence mitigation, CCSC mortar specimens were prepared according to raw material proportions specified in Tables 16 and 17 and evaluated for water sorptivity (ASTM C1585) and efflorescence potential (ASTM C67). For water sorptivity, samples were submerged in 2±1 mm of water, and the mass of water uptake was measured over the course of 96 hours. Samples tested for efflorescence potential were partially submerged in 10% NaCl solution for 7 days in order to simulate severe efflorescence.

[00317] Each mortar was mixed for 4 min using a Hobart mixer and compacted into 100 x 60 mm cylinders using a 2 kg press head. Fatty acids, salts of fatty acids, or silanes were added at the time of mixing following the addition of water and dosed by percent weight of cement (%bwoc).

Table 16: CCSC Mortar Mix Proportions

Mix Components	Type	Material Proportions
Cement	CCSC	362 g
Sand	ASTM graded sand	1500 g
w/c ratio		0.35

Table 17: Description of Additives

Additive	Type (C:D)	Dosage, %bwoc
Valeric acid	Short-chain fatty acid (5:0)	0.25%
Lauric acid	Medium-chain fatty acid (12:0)	0.25%
Oleic acid	Long-chain fatty acid (18:1)	0.25%
Stearic acid	Long-chain fatty acid (18:0)	0.25%
Na-oleate	Sodium salt of oleic acid	1.00%
Ca-stearate	Calcium salt of stearic acid	1.00%
Silane A	Proprietary	0.25%
Silane B	Proprietary	0.25%

[00318] Water sorptivity measurements for CCSC specimens containing short, medium, and long-chain fatty acids are shown in Figure 12. Example specimens of each mix are shown in Figure 13 after sorptivity testing. Relative to the control mix (A), each of the representative fatty acids ((B) valeric acid 0.25%, (C) lauric acid 0.25%, (D) oleic acid 0.25%, and (E) stearic acid 0.25%) exhibit reduced rate and total absorption of water)

reduced the rate of water absorption and total quantity of water absorbed throughout the course of testing.

[00319] Water sorptivity measurements for CCSC specimens containing representative salts of fatty acids and silanes are shown in Figure 14. Example specimens of each mix are shown in Figures 15 and 16 after sorptivity testing. Relative to the control mix, each of the mixes containing salts of fatty acids or silanes reduced the rate of water absorption and total quantity of water absorbed throughout the course of testing.

[00320] Samples tested for efflorescence potential by partial submersion in NaCl solution are shown in Figures 17A - 17B. Control samples (Fig. 17A) exhibited significant deposition of surface salts while samples produced with 1.0% Ca-stearate (Fig. 17B) exhibited limited ingress of water and no apparent deposition of surface salts.

Example 7. Effect of admixtures on aesthetic performance and efflorescence mitigation in CCSC concrete products

[00321] Concrete pavers were produced using CCSC and raw materials supplied by two industrial concrete producers. Mix proportions are specified in Table 18 below. Ca-stearate was added to the experimental batches during mixing with dosages ranging from 0.3 to 1.5 percent by weight of cement.

[00322] Pavers were tested for water absorption following procedures as specified in ASTM C140. In this test method, samples are immersed for 24 hours with no less than 6 in. (152 mm) of water above the surface of the specimen. Following immersion in water, samples are oven-dried at 100 to 115°C until two successive weightings at intervals of 2 hours show an increment of loss no greater than 0.2% of the last previously determined weight.

[00323] In addition to testing for water absorption, concrete pavers produced with and without Ca-stearate were installed according to industry specifications and evaluated for performance during service through wetting and drying cycles.

[00324] The efflorescence mitigation potential of pavers produced with the addition of Ca-stearate was evaluated in comparison to reference pavers following procedures as outlined in ASTM C67. In order to simulate severe efflorescence, pavers were partially submerged in 10% NaCl solution.

Table 18: CCSC Concrete Mix Designs

Mix Component	Concrete Mix A	Concrete Mix B
Cement	14.5%	17.0%
Sand	42.4%	72.0%
Coarse aggregate I	12.9%	10.6%
Coarse aggregate II	14.5%	-
Coarse aggregate III	3.15%	-
Coarse aggregate IV	12.4%	-
Pigment	0.15%	0.37%

[00325] Average water absorption percentages of CCSC Concrete pavers produced without Ca-stearate (Control) and with Ca-stearate (CS) are shown in Figure 18. At each of the tested dosages ranging from 0.3 to 1.5 percent by weight of cement, water absorption was significantly reduced in comparison to the control batches. As shown in Figure 19 and Figure 20, pavers produced with Ca-stearate exhibit reduced ingress and permeation of water in comparison to control pavers.

[00326] The mitigation of efflorescence resulting from the use of Ca-stearate is demonstrated in Figure 21. After partial submersion in NaCl solution for 7 days, pavers produced without Ca-stearate (Fig. 21A) show significant ingress of water and deposition of surface salts while pavers produced with 1.0% Ca-stearate (Fig. 21B) show reduced water ingress and reduced deposition of surface salts.

Example 8. Effect of admixtures on water sorptivity in CCSC mortar

[00327] Test specimens were prepared using proportions as specified in Table 19 and 20 below. Each batch was mixed for a total of 4 min using a Hobart mixer and subsequently compacted into 100 x 60 mm cylinders using a 2 kg press head. Fatty acids, salts of fatty acids, or silanes were added at the time of mixing following the addition of water and dosed by percent weight of cement (%bwoc).

[00328] After curing, water sorptivity was measured following general procedures as specified in ASTM C1585. In this test method, the sides of each specimen are sealed, and the mass of water uptake over time is measured during partial submersion in 2±1 mm of water.

Table 19: CCSC Mortar Mix Proportions

Mix Components	Type	Material Proportions
Cement	CCSC	362 g

Sand	ASTM graded sand	1500 g
w/c ratio		0.35

Table 20: Description of Additives

Additive	Type (C:D)	Dosage, %bwoc
Valeric acid	Short-chain fatty acid (5:0)	0.25%
Lauric acid	Medium-chain fatty acid (12:0)	0.25%
Oleic acid	Long-chain fatty acid (18:1)	0.25%
Stearic acid	Long-chain fatty acid (18:0)	0.25%
Na-oleate	Sodium salt of oleic acid	1.00%
Ca-stearate	Calcium salt of stearic acid	1.00%
Silane A	Proprietary	0.25%
Silane B	Proprietary	0.25%

[00329] Water sorptivity measurements for CCSC specimens containing short, medium, and long-chain fatty acids are shown in Figure 22. Example specimens of each mix are shown in Figure 23 after sorptivity testing. Relative to the control mix, each of the representative fatty acids reduced the rate of water absorption and total quantity of water absorbed throughout the course of testing.

[00330] Water sorptivity measurements for CCSC specimens containing representative salts of fatty acids and silanes are shown in Figure 24. Example specimens of each mix are shown in Figures 25 and 26 after sorptivity testing. Relative to the control mix, each of the mixes containing salts of fatty acids or silanes reduced the rate of water absorption and total quantity of water absorbed throughout the course of testing.

Example 9. Effect of admixtures on water absorption and freeze-thaw performance of CCSC concrete products

[00331] Concrete pavers were produced using CCSC and raw materials supplied by two industrial concrete producers. Mix proportions are specified in Table 21 below. Ca-stearate was added to the experimental batches during mixing with dosages ranging from 0.3 to 1.5 percent by weight of cement.

[00332] Pavers were tested for water absorption following procedures as specified in ASTM C140 Standard Test Methods for Sampling and Testing Concrete Masonry Units and Related Units. In this test method, samples are immersed for 24 hours with no less than 6 in. (152 mm) of water above the surface of the specimen. Following immersion in water,

samples are oven-dried at 100 to 115°C until two successive weightings at intervals of 2 hours show an increment of loss no greater than 0.2% of the last previously determined weight.

[00333] In addition to testing for water absorption, concrete pavers produced with and without Ca-stearate were installed according to industry specifications and evaluated for performance during service through wetting and drying cycles.

[00334] Durability of pavers with the addition of Ca-stearate was evaluated in comparison to reference concrete pavers with freeze-thaw testing in 3% saline solution following procedures as specified in CSA A231.2.

Table 21: CCSC Concrete Mix Designs

Mix Component	Concrete Mix A	Concrete Mix B
Cement	14.5%	17.0%
Sand	42.4%	72.0%
Coarse aggregate I	12.9%	10.6%
Coarse aggregate II	14.5%	-
Coarse aggregate III	3.15%	-
Coarse aggregate IV	12.4%	-
Pigment	0.15%	0.37%

[00335] Average water absorption percentages of CCSC Concrete pavers produced without Ca-stearate (Control) and with Ca-stearate (CS) are shown in Figure 27. At each of the tested dosages ranging from 0.3 to 1.5 percent by weight of cement, water absorption was significantly reduced in comparison to the control batches. As shown in Figure 28 and Figure 29, pavers produced with Ca-stearate exhibit reduced ingress and permeation of water in comparison to control pavers.

[00336] Freeze-thaw performance and durability assessment of concrete pavers in the presence of deicing salt is shown in Figure 30. Pavers produced with the addition of 1.0% calcium stearate (CS) show significant improvements in durability in comparison to pavers produced without calcium stearate during exposure to deicing salt and freeze-thaw cycling.

Example 10. Conductivity changes when admixtures are dissolved in the forming water of concrete mix

[00337] Comb-shaped polycarboxylic acid admixtures (SIKA HC-300, BASF Glenium-7500, or ConXL) when added to water were found to cause an increase in the electrical conductivity of the resultant solution. The electrical conductivity of the tap water

was at around 0.27 mS/cm and the polycarboxylate-based water-reducer/superplasticizer addition cause that conductivity to rise to around 5.9 mS/cm. These studies indicate that the degree of polarization was in connection with the molecular weight of the polyether macromolecules and the density of the polyether macromolecule arrangement in the comb-like polymers. The polarization of polycarboxylate admixtures to water molecules was caused by polyethylene glycol radicals in the side chains of the macromolecules such polyethylene glycol radicals were made to crystallize and observed even by routine XRD scans. Polyethylene glycol radicals were arranged in a zig-zag formation in water, thus forming a polarization body. The polarization body produced strong polarization to the water molecules, so the degree of ionization of the water increased; and accordingly, the electrical conductivity of the water will increase.

Example 11. Citric acid admixture used as a set retarder, besides being a very potent set-retarder, also causes crystallization of calcium citrate nanocrystals throughout the microstructure of cured concrete and leads to an improved water-proofing property

[00338] The use of citric acid anhydrous in Solidia Concrete^{TM} resulted in the total elimination of any water-reducer/superplasticizer usage and formed Ca-citrate crystals in the microstructure of the cured concrete (pavers) by forming nano-roughness (nano-texture) along the pore channels. Such nano-roughness as shown in the SEM photomicrographs help to increase the contact angle of water on such surfaces (like the Gecko anatomy). The Ca-stearate-based hydrophobe (Darapel by GCP Applied Technologies) used in such citric acid-sugar-Darapel admixture combinations has achieved quite low water absorption values as shown below.

Example 12

[00339] We have shown through numerous in-house paver-making and curing experiments that it is possible to use a pre-mixed single liquid admixture of carbonated water + HC-300 water-reducer,

[00340] use a pre-mixed single liquid admixture of carbonated water + sugar + HC-300 water-reducer,

[00341] use a pre-mixed single liquid admixture of carbonated water + sugar + Glenium-7500 water-reducer,

[00342] use a pre-mixed single liquid admixture of carbonated water + sugar + ConXL water-reducer,

[00343] use a pre-mixed single liquid admixture of carbonated water + sugar (set retarder) + HC-300 water-reducer +Mg-acetate sol (curing aid),

[00344] use a pre-mixed single liquid admixture of sugar (set retarder) + ConXL water-reducer +Mg-acetate sol (curing aid),

[00345] use a pre-mixed single liquid admixture of carbonated water + sugar + citric acid anhydrous (with no water-reducer),

[00346] use a pre-mixed single liquid admixture of water + sugar + citric acid anhydrous (with no water-reducer),

[00347] use a pre-mixed single liquid admixture of water + sugar + citric acid anhydrous (with no water-reducer) + silane-based, low viscosity hydrophobe solution.

[00348] By this way, it was made possible to add all the required admixtures as a single pre-mixed (by strictly observing the dosing of each component) cocktail into the concrete mixer at the very be-ginning of the mixing process, and thus let that single admixture act on the solid constituents (i.e., cement, sand, fine and/or coarse aggregates) for the entire duration of that 90-seconds of mixing allowed.

Example-13: Set-retarding or set-accelerator admixtures

[00349] The set-retarding or set-accelerator properties of admixtures were efficiently determined by using the Vicat needle data. Vicat data were generated in accordance with ASTM C305: Standard Practice for Mechanical Mixing of Hydraulic Cement Pastes and Mortars of Plastic Consistency and with ASTM C191: Standard Test Methods for Time of Setting of Hydraulic Cement by Vicat Needle. Masterset-R100 is a commercial set retarder supplied by BASF. As shown in Figure 31, for which data were only recorded until the 360th minute, Na_2CO_3 and acetic acid are good examples of accelerator admixtures, whereas, as shown in Figure 32, sucrose (grocery sugar, refined sugar), sucrose-acetic acid mixture and trisodium citrate (i.e., Na-citrate) are potent set retarders. Citric acid and citric acid-sucrose mixture are also quite potent set-retarders as shown in Figure 32, for which data were recorded beyond the 360th minute. Citric acid and citric acid-sucrose mixtures when used as the admixtures were also shown to result in excellent concrete strengths after carbonation-curing.

Example 14

[00350] Exemplary mix designs of such concrete mixes of item (b) above: 14.64% Solidia cement, 45.22% construction sand, 39.94% fine & coarse aggregates, 0.2% pigment, admixtures: sugar and SIKA HC-300 (see Table 7 concrete formulations, example ST-419). The set retarder (sugar) and the superplastizicer (SIKA HC-300) was first mixed in some of the forming water, then CO_2 was bubbled through the resultant "water-sugar-superplasticizer" solution, followed by adding that solution into the concrete mixer as a single admixture. 4x8" concrete pavers with 80 mm thickness were formed by using the paver press, followed by carbonation-curing indicated in Table 7. Compressive strength data for ST-419 is provided in Figure 33.

Example 15:

[00351] Exemplary mix design of such concrete mixes of item (f) above: 14.64% Solidia cement, 45.22% construction sand, 39.94% fine & coarse aggregates, 0.2% pigment, admixtures: sugar, Mg+acetate sol, ConXL, and Darapel.

[00352] Compressive strengths were above 7200 psi, as illustrated in Figure 34 (Table 7, example ST-1495).

Example 16:

[00353] Exemplary mix design of such concrete mixes of item (h) above: 14.5% Solidia cement, 46.55% construction sand, 38.8% fine & coarse aggregates, 0.15% pigment, admixtures: citric acid anhydrous, sugar and hydrophobe. Table 7, example ST-1742, Citric acid and sugar were first dissolved in some of the forming water, then added into the concrete mixer which already contained all the solid ingredients. No superplasticizer was used.

[00354] SEM image of Ca-citrate crystals in Solidia Concrete^{TM} is shown in Figure 35. As shown in Figure 36, water absorption data of pavers were below 3% after 10 days.

[00355] As illustrated in Figure 37, satisfactory compressive strengths, with low scatter were attained. Figures 35-37 belong to the example of ST-1742 of Table 7.

Example 17

[00356] A mix design of such concrete mixes as item (i) above: 14.5% Solidia cement, 46.55% construction sand, 38.8% fine & coarse aggregates, 0.15% pigment, admixtures: citric acid anhydrous, sugar and silane-based hydrophobe. Table 7, example ST-1840.

[00357] Citric acid anhydrous, sugar and the silane-based hydrophobe were first dissolved in some of the forming water, then added as a single admixture, complete with three different admixtures at the proper dosages, into the concrete mixer at once, while the mixer was having all the solid ingredients (cement, sand and aggregates) required for this concrete batch. No superplasticizer was used. ST-1840 compressive strength is illustrated in Figure 38. ST-1840 water absorption data is illustrated in Figure 39.

Example 18: Surface tension modification of the admixtures

[00358] Foaming of a superplasticizer can contribute to porosity buildup. Foaming can be mitigated or decreased by decreasing the surface tension of liquid admixtures. The single admixtures described above reduced the surface tension of the forming (mixing) water from 72 mN/m to around 28 to 40 mN/m. Surface tension, and, its effect on capillaries, is described by Jurin's law. This is a very significant surface tension reduction achieved by pre-mixing (e.g., in the automated dosing system of the industrial concrete mixers) the superplasticizer and the set retarder in some portion of the total forming/mixing water to be used in the concrete mixer. More than a 50% decrease in the entire liquid vehicle furthermore helps to remove water (*aka* interstitial or pore water) to a larger extent during carbonation-curing.

Example 19: Regulation of alkali sulphate crystallization by orthophosphate additions

[00359] Phosphoric acid seemed to be the best additive, at the optimum concentration level of 0.05 mM (over the concentration range of 0.01 to 1 mM), to inhibit the Ca-sulphate (gypsum) growth, whose presence may then act as a template for further unwanted alkali (Na and K) sulfate crystallizations, which causes severe hazing issues if the Na (and/or K) concentration of the ingredients (cement, sand and aggregates) of a concrete mix happens to be high. Therefore, we also practice caution in not to increase the alkali concentration of the concrete mixes even by properly selecting admixtures low in alkali ion concentration.

Example 20: Carbonate phases

[00360] Carbonate minerals of divalent cations (such as Ca^{2+}, Mg^{2+}, Sr^{2+}, Zn^{2+}, *etc.*) are usually divided into two classes; (1) rhombohedral (term related to crystallographic structure) carbonates and (2) orthorhombic carbonates. Calcite is a rhombohedral carbonate and the Ca^{2+}in calcite, like all other divalent cation-based rhombohedral carbonates exhibit, is nested among six O^{2-} anions (*i.e.*, six-fold coordination). Aragonite, on the other hand, is an orthorhombic carbonate and Ca^{2+} in aragonite is nested in a larger cation site among nine oxygens (*i.e.*, nine-fold coordination). To compare, Ca^{2+} cation has an ionic radius of 114 pm, whereas the smaller Mg^{2+} has the ionic radius of 86 pm.

[00361] Some examples of "rhombohedral" carbonate minerals of divalent cations less soluble than calcite (which can capture CO_2 up to 43.97wt%, ΔG_f from ions at 25°C: -48 kJ/mol – more negative, more stable):

(a) magnesite ($MgCO_3$, CO_2-capturing capacity (*CCC*) is 52.2 wt%, ΔG_f from ions at 25°C: -48 kJ/mol),

(b) dolomite ($CaMg(CO_3)_2$, CCC: 47.73 wt%, , ΔG_f from ions at 25°C: -57 kJ/mol),

(c) sphaerocobaltite ($CoCO_3$, CCC: 37 wt%, Co^{2+} radius: 88 pm, ΔG_f from ions at 25°C: -56 kJ/mol),

(d) smithsonite ($ZnCO_3$, CCC: 35.1 wt%, Zn^{2+} radius: 88 pm, ΔG_f from ions at 25°C: -57 kJ/mol),

(e) siderite ($FeCO_3$, CCC: 37.99 wt%, Fe^{2+} radius: 75 pm, ΔG_f from ions at 25°C: -60 kJ/mol),

(e) rhodochrosite ($MnCO_3$, CCC: 38.3 wt%, Mn^{2+} radius: 81 pm, ΔG_f from ions at 25°C: -60 kJ/mol)

(f) otavite ($CdCO_3$, CCC: 25.5 wt%, Cd^{2+} radius: 109 pm, ΔG_f from ions at 25°C: -70 kJ/mol).

[00362] Some examples of "orthorhombic" carbonate minerals of divalent cations less soluble than aragonite (which can capture CO_2 up to 43.97wt%, ΔG_f from ions at 25°C: -47 kJ/mol) are

(a) strontionite ($SrCO_3$, CCC: 29.81 wt%, Sr^{2+} radius: 132 pm, ΔG_f from ions at 25°C: -51 kJ/mol),

(b) alstonite ($BaCa(CO_3)_2$, CCC: 29.59 wt%, Ba^{2+} radius: 149 pm, ΔG_f from ions at 25°C: -50 kJ/mol),

(c) cerussite ($PbCO_3$, CCC: 16.47 wt%, Pb^{2+} radius: 133 pm, ΔG_f from ions at 25°C: -73 kJ/mol).

Example 21: Impact of sodium citrate on curing enhancement of CCSC Binder

[00363] In order to evaluate the impact of sodium citrate on the curing enhancement of CCSC Binder (Cement-P type), mortar cube batches were prepared using the mix designs shown in Table 22. Samples were demolded and cured in a CO_2 chamber at controlled temperature and humidity for 20 hours. After curing, samples were tested for compressive strength. The results of those tests are shown in Figure ____.

Table 22: CCSC Concrete Mix Designs

Mix Component	Quantity
CCSC Binder (Cement-P)	450 g
EN Standard Sand	1350 g
w/c ratio	0.33, 0.39
Admixture	
Water-reducer (PCE)	0.3% bwoc
Na-citrate (salt solution)	0-0.5% bwoc

[00364] The above means that if there may be any contamination, during concrete-making practices (from sand and aggregates), with divalent cations such as iron, zinc, manganese and strontium, these cations would help to produce, in part, carbonate phases different than calcite. For example, in some sand samples, dolomite is present due to geological contamination with lake waters and dolomitic limestone. Mg, Zn, Mn and Fe contamination from the sand and cement aggregates can happen, therefore, the detection of phases, with careful X-ray diffraction work, on cured Solidia Concrete™ products, such as magnesite, dolomite, smithsonite, siderite and rhodochrosite may be possible. These carbonate phases can be regarded as unique to the Solidia concrete curing processes, which is different than OPC concrete that does not involve any carbonation.

[00365] Applicant's disclosure is described herein in preferred embodiments with reference to the Figures, in which like numbers represent the same or similar elements. Reference throughout this specification to "one embodiment," "an embodiment," or similar language means that a particular feature, structure, or characteristic described in connection with the embodiment is included in at least one embodiment of the present invention. Thus,

appearances of the phrases “in one embodiment,” “in an embodiment,” and similar language throughout this specification may, but do not necessarily, all refer to the same embodiment.

[00366] The described features, structures, or characteristics of Applicant’s disclosure may be combined in any suitable manner in one or more embodiments. In the description herein, numerous specific details are recited to provide a thorough understanding of embodiments of the invention. One skilled in the relevant art will recognize, however, that Applicant’s composition and/or method may be practiced without one or more of the specific details, or with other methods, components, materials, and so forth. In other instances, well-known structures, materials, or operations are not shown or described in detail to avoid obscuring aspects of the disclosure.

[00367] In this specification and the appended claims, the singular forms “a,” “an,” and “the” include plural reference, unless the context clearly dictates otherwise.

[00368] Unless defined otherwise, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art. Although any methods and materials similar or equivalent to those described herein can also be used in the practice or testing of the present disclosure, the preferred methods and materials are now described. Methods recited herein may be carried out in any order that is logically possible, in addition to a particular order disclosed.

What is claimed is:

CLAIMS

1. A calcium silicate-based material comprising:

   grains of carbonatable phases selected from wollastonite or pseudowollastonite ($CaSiO_3$, CS), rankinite ($Ca_3Si_2O_7$, C3S2) and larnite (Ca_2SiO_4, C2S, belite); grains of partially reactive amorphous phases; or grains or particles of uncarbonatable phases selected from melilite ((Ca, Na, K)2[(Mg, Fe^{2+}, Fe^{3+}, Al, $Si)_3O_7$]) and crystalline silica (SiO_2); or a combination of any two or more types thereof; and

   a combination of one or more admixtures selected from: strength enhancers, hydrophobic compounds, set retarders, pH enhancing additives, efflorescence reducers, ettringite growth inhibitors, minerals, corrosion inhibitors, air-entraining admixtures, shrinkage-reducing admixtures, evaporation controlling admixtures, plasticizers, superplasticizers, and crystallization inhibitors.
2. The calcium silicate-based material of any of the above claims, wherein the calcium silicate-based material is curable by carbonation.
3. The calcium silicate-based material of any claim 2, wherein the calcium silicate-based material is curable by carbonation at a temperature of about 35°C to about 105°C to form $CaCO_3$ with a mass gain of about 10% or more.
4. The calcium silicate-based material of any of the above claims, wherein elemental Ca and elemental Si are present in the material at a molar ratio from about 0.8 to about 1.2; and metal oxides of Al, Fe and Mg are present in the material at about 30% or less by mass.
5. The calcium silicate-based material of any of the above claims, wherein at least one hydraulic species is present in an amount of 5% or less.
6. The calcium silicate-based material of any of the above claims, wherein the admixture comprises a set-retarding admixture, is present in an amount of about 0.1 to about 10 g per kg of the calcium silicate-based material, and is selected from one or more of: monosaccharides (xylose), disaccharides (sucrose), trisaccharides (raffinose), citric acid, tartaric acid, oxalic acid, malic acid, lignosulfonates, hydroxycarboxylic acids, gluconic acid, gluconic acid salts, boric acid, boric acid salts, orthophosphates, metaphosphates, zinc salts, sugar alcohols, salicylic acid, mucic acid, galactaric acid, sorbitol, heptonic acid salts, pentose sugars, arabinose.

7. The calcium silicate-based material of any of the above claims, wherein the admixture comprises a water-reducer, plasticizer, superplasticizer and dispersant admixture, is present in an amount of about 0.01 to 5 g per kg of the calcium silicate-based material, and is one or more of a polycarboxylate ether type polymer.
8. The calcium silicate-based material of claim 9, wherein the polycarboxylate ether type polymer comprises poly(oligo(ethylene glycol) methyl ether methacrylate/methacrylic acid, having a comb-like polymer built up with ionic hydrophilic carboxylate groups and long, elastic side nonionic hydrophilic oligo(ethylene oxide) chains, where the long ethylene oxide side chains exert steric hindrance that keeps the carbonatable calcium silicate grains away from each other to prevent agglomeration.
9. The calcium silicate-based material of claim 9, wherein the polycarboxylate ether type polymer is selected from one or more of: vinyl acetate, methyl acrylate, methacrylamide, 2-hydroxylethyl methacrylate, sodium 2-methyl-2-propene-1-sulphonate, sodium allyl sulfonate, 2-methacryloyloxy-ethyl-trimethyl-ammonium chloride, 3-trimethoxysilyl-propyl-methacrylate, 2-(methacryloyloxy)-ethyl phosphate, 2-acrylamido-2-methyl-1-propanesulfonic acid, β-cyclodextrin with meth-acrylic ester group, β-cyclodextrin with a maleic ester group, and octadecyl phosphate.
10. The calcium silicate-based material of any of the above claims, wherein the admixture comprises a water-proofing and hydrophobic admixture, is present in an amount of about 0.1 to about 10 g per kg of the calcium silicate-based material, and is selected from one or more of: silanes, siloxanes, alkaline earth stearates, stearic acid dissolved in alcohols, alkali oleates, oleic acid salts, fatty acids, valeric acid, archidic acid, palmitic acid, arachidonic acid, erucic acid, lionoleic acid, lauric acid and their respective salts.
11. The calcium silicate-based material of any of the above claims, wherein the admixture comprises a pH-regulating admixture, is present in an amount of about 0.1 to about 10 g per kg of the calcium silicate-based material, and is selected from one or more of: calcined alkaline earth oxides, dolomitic hydrated lime, alkali hydroxides, sodium silicate, water glass, high alkalinity recycled concrete, slag aggregate, Ordinary Portland Cement (OPC), calcium nitrite, calcium nitrate tetrahydrate, alkali carbonates and alkali bicarbonates.
12. The calcium silicate-based material of any of the above claims, wherein the admixture comprises a carbonation-curing enhancer, accelerator and $CaCO_3$ crystal structure-

controlling admixture, is present in an amount of about 0.1 to about10 g per kg of the carbonatable calcium silicate material, and is selected from one or more of: an aqueous solution of dilute acetic acid, an aqueous solution of alkaline earth oxides solubilized in acetic or citric acid, an aqueous suspension of alkaline earth hydroxides, water soluble salts of alkaline earth elements, triethanolamine, diethanolamine, triisopropanolamine, triehtylenepentamine, hydroxyethyldiethylenetriamine, and aminoethylethanolamine.

13. The calcium silicate-based material of claim 9, wherein the water-reducing admixture is selected from plasticizers based on naphthalene (PNS, polynaphthalene sulfonates) or lignosulfonates.
14. The calcium silicate-based material of any of the above claims, wherein forming/mixing water used in production of the material is pre-carbonated with CO_2 gas to increase the dissolved CO_2 concentration of the water from almost zero to around 1 to 6 g per liter, preferably to about 1.5 g per liter, at room temperature and pressure.
15. The calcium silicate-based material of any of the above claims, wherein the admixture comprises a combination of two or more of: a water-reducer, superplasticizer, a set retarder, a curing enhancer, an air-entrainer, an efflorescence control agent, and a liquid hydrophobe.
16. The calcium silicate-based material of any of claims 1-14, wherein the admixture is a combination of two or more of: strength enhancers, hydrophobic compounds, set retarders, pH enhancing additives, efflorescence reducers, ettringite growth inhibitors, minerals, corrosion inhibitors, air-entraining admixtures, shrinkage-reducing admixtures, evaporation controlling admixtures, plasticizers, superplasticizers, and crystallization inhibitors.
17. The calcium silicate-based material of either of claims 15 or 16, wherein the combination is premixed in water and then added and mixed with the calcium silicate-based material as a single liquid admixture.
18. The calcium silicate-based material of any of the above claims, wherein carbonation of the calcium silicate-based material results in the formation of one or more phases of calcium carbonates, such as amorphous and hydrated calcium carbonate, dry amorphous calcium carbonate, monohydrocalcite, $CaCO_3 \cdot H_2O$, calcium carbonate hexahydrate, $CaCO_3 \cdot 6H_2O$, calcite, vaterite and aragonite.

19. A composite material comprising the calcium silicate-based material of any of the previous claims, and one or more aggregate.

20. A calcium silicate-based material comprising:

grains of carbonatable phases selected from wollastonite or pseudowollastonite ($CaSiO_3$, CS), rankinite ($Ca_3Si_2O_7$, C3S2) and larnite (Ca_2SiO_4, C2S, belite); grains of partially reactive amorphous phases; or grains or particles of uncarbonatable phases selected from melilite ((Ca, Na, K)2[(Mg, Fe^{2+}, Fe^{3+}, Al, Si)$_3$O$_7$]) and crystalline silica (SiO_2); or a combination of any two or more types thereof; and

a curing enhancing admixture during carbonation process selected from: sucrose, glucose, fructose, sugar alcohols, acetic acid, malic acid, tartaric acid, citric acid, gluconic acid, hydroxycarboxylic acid, magnesium, magnesium compounds, and salts and combinations thereof.

21. The calcium silicate-based material of claim 20, wherein the admixture comprises magnesium oxide, magnesium hydroxide or a magnesium salt.

22. The calcium silicate-based material of any of claims 20-21, wherein the calcium silicate-based material comprises about 0.02% to about 20%, of the admixture, by weight.

23. A method of forming a CO_2-cured calcium silicate-based material, the method comprising:

forming a mixture of:

a carbonatable calcium silicate-based material;

a curing enhancing admixture selected from sucrose, glucose, fructose, acetic acid, malic acid, tartaric acid, citric acid, gluconic acid, hydroxycarboxylic acid, magnesium, magnesium compounds, and combinations thereof; and

water;

drying the mixture; and

curing the mixture by exposing the mixture to carbon dioxide to form the cured calcium silicate-based material;

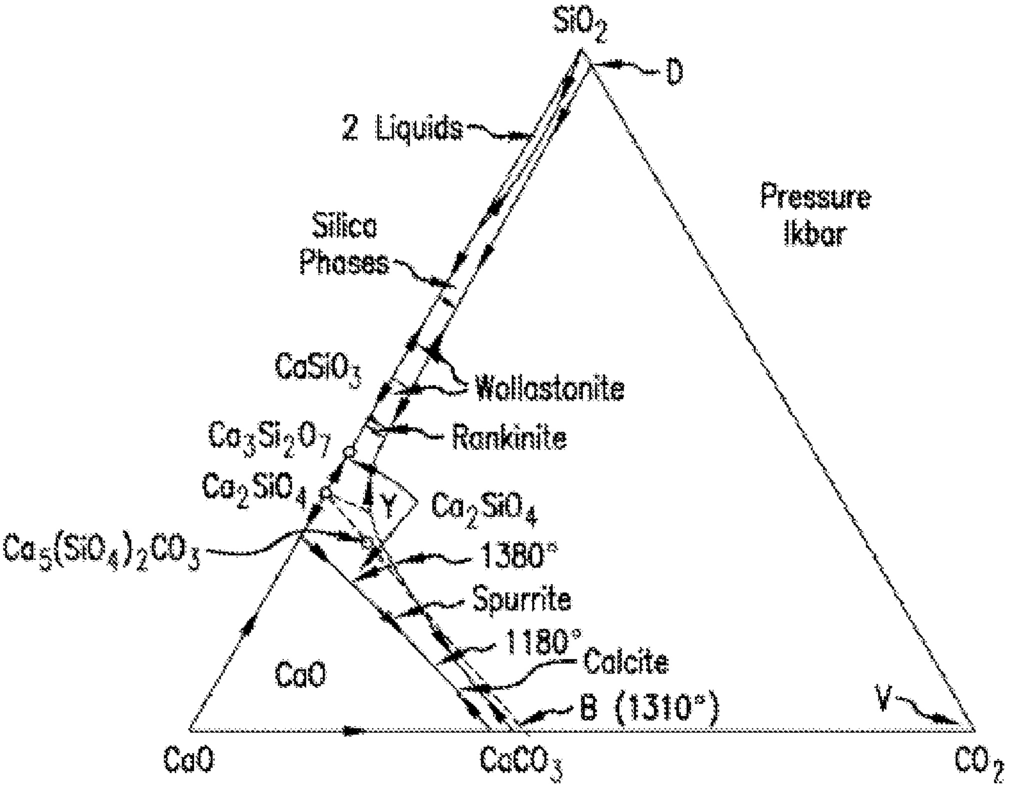
wherein the cured calcium silicate-based material has a compressive strength of at least 3,000 psi.

24. The method of claim 23, wherein the carbonatable calcium silicate-based material comprises grains of carbonatable phases selected from wollastonite or

pseudowollastonite ($CaSiO_3$, CS), rankinite ($Ca_3Si_2O_7$, C3S2) and larnite (Ca_2SiO_4, C2S, belite); grains of partially reactive amorphous phases; or grains or particles of uncarbonatable phases selected from melilite ((Ca, Na, K)2[(Mg, Fe^{2+}, Fe^{3+}, Al, $Si)_3O_7$]) and crystalline silica (SiO_2); or a combination of any two or more types thereof.

25. The method of claim 23 or 24, wherein the admixture comprises magnesium oxide, magnesium hydroxide or a magnesium salt.
26. The method of any of claims 23-25, wherein the mixture comprises about 0.02% to about 20%, of the admixture, by weight.
27. The method of any of claims 23-26, wherein the cured calcium silicate-based material has a compressive strength of at least 6,000 psi.
28. The method of any of claim 27, wherein the cured calcium silicate-based material has a compressive strength of at least 8,000 psi.

FIG. 1



PRIOR ART

FIG. 2

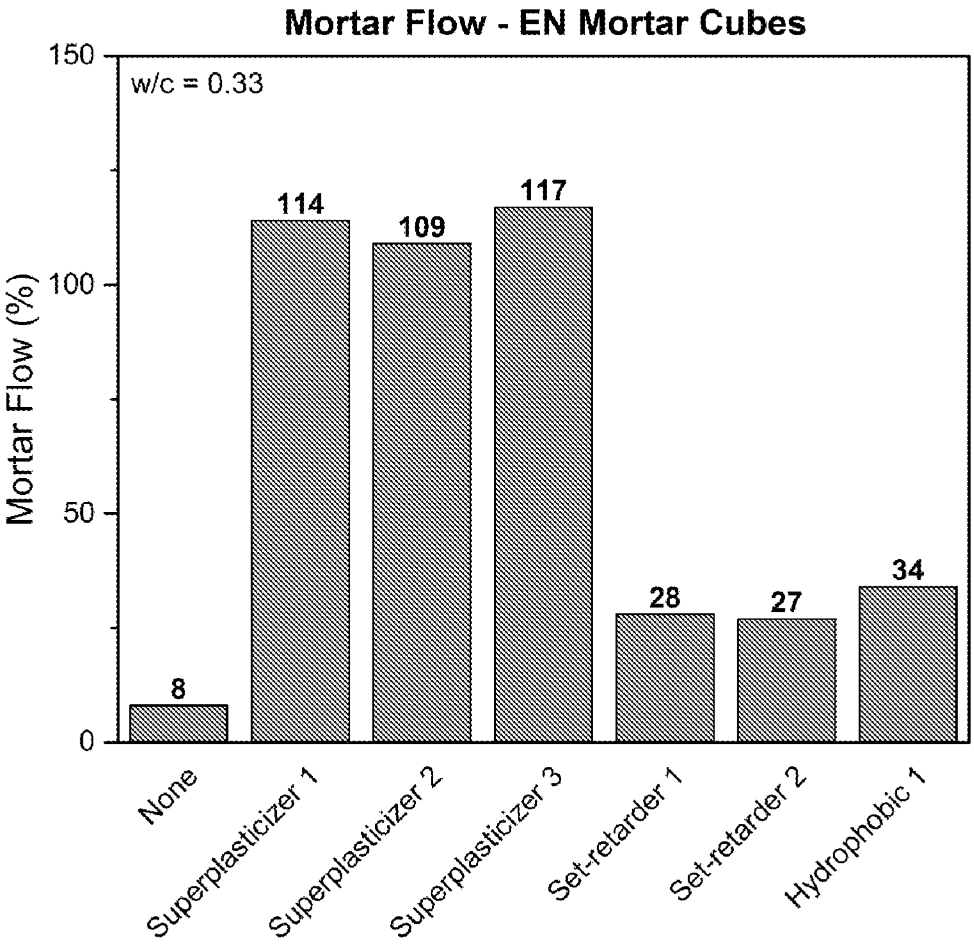

Mortar Flow - EN Mortar Cubes
w/c = 0.33
Mortar Flow (%)
0
50
100
150
8
114
109
117
28
27
34
None
Superplasticizer 1
Superplasticizer 2
Superplasticizer 3
Set-retarder 1
Set-retarder 2
Hydrophobic 1

FIG. 3

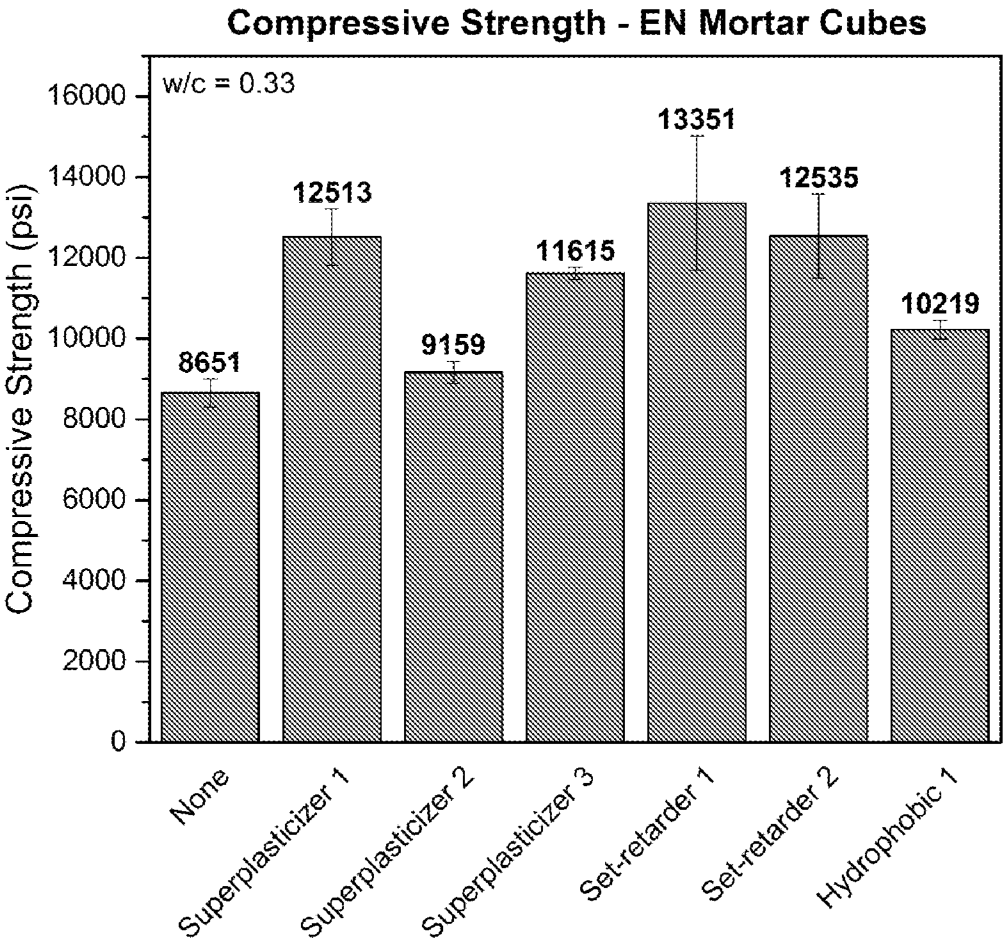

Compressive Strength - EN Mortar Cubes
w/c = 0.33
Compressive Strength (psi)
16000
14000
12000
10000
8000
6000
4000
2000
0
8651
12513
9159
11615
13351
12535
10219
None
Superplasticizer 1
Superplasticizer 2
Superplasticizer 3
Set-retarder 1
Set-retarder 2
Hydrophobic 1

FIG. 4

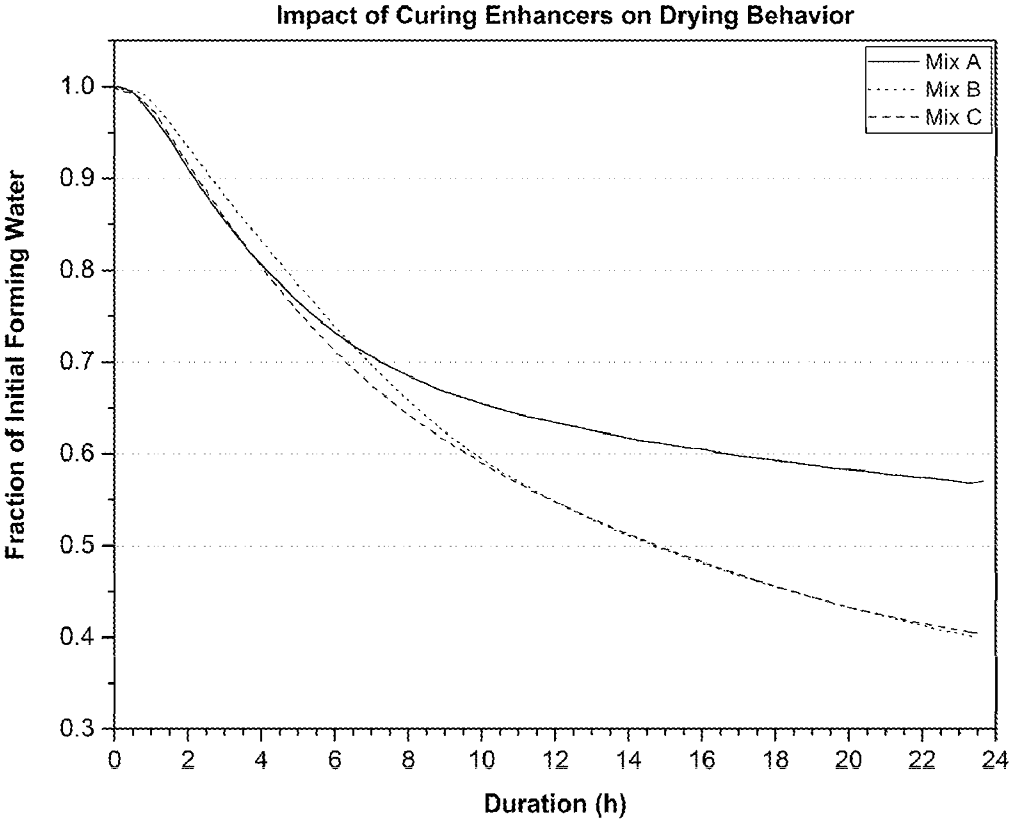

Impact of Curing Enhancers on Drying Behavior
Mix A
Mix B
Mix C
Fraction of Initial Forming Water
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0
2
4
6
8
10
12
14
16
18
20
22
24
Duration (h)

FIG. 5

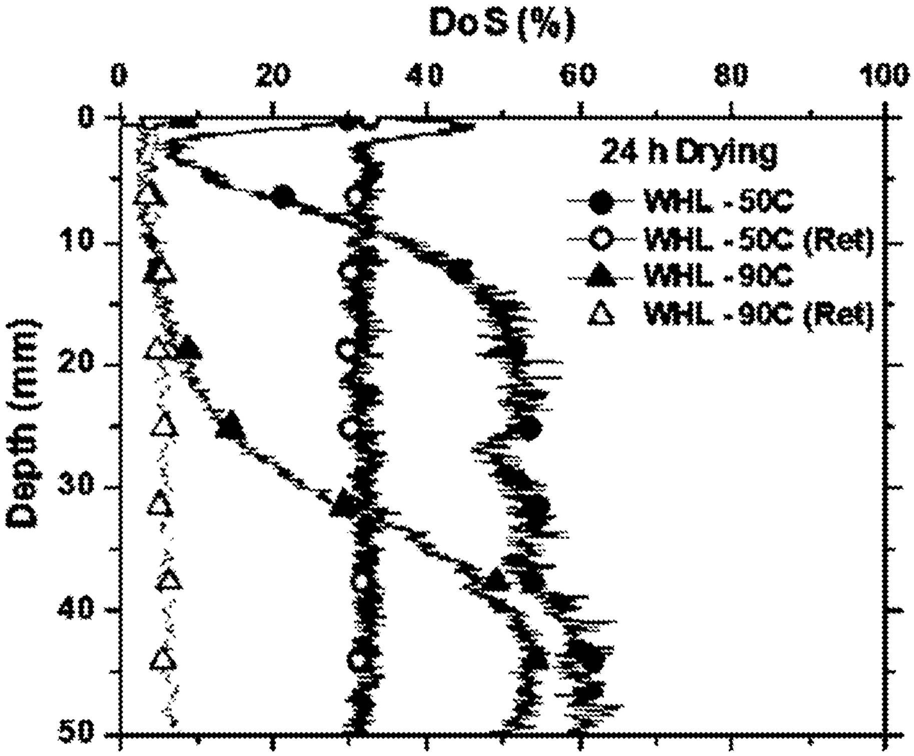

DoS (%)
0
20
40
60
80
100
Depth (mm)
0
10
20
30
40
50
24 h Drying
WHL - 50C
WHL - 50C (Ret)
WHL - 90C
WHL - 90C (Ret)

FIG. 6

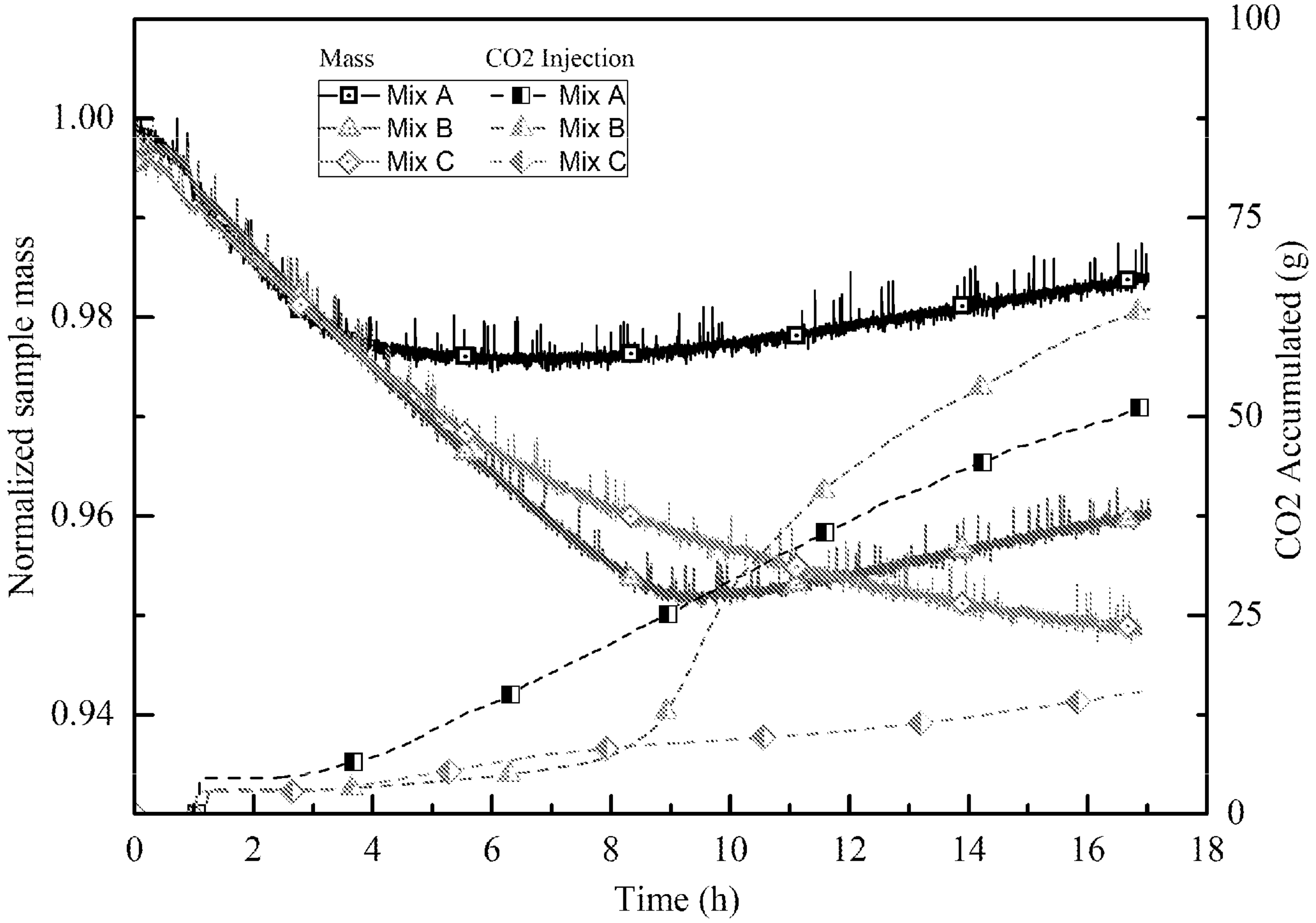

Mass
CO2 Injection
Mix A
Mix B
Mix C
Mix A
Mix B
Mix C
Normalized sample mass
1.00
0.98
0.96
0.94
CO2 Accumulated (g)
100
75
50
25
0
Time (h)
0
2
4
6
8
10
12
14
16
18

FIG. 7

FIG. 8

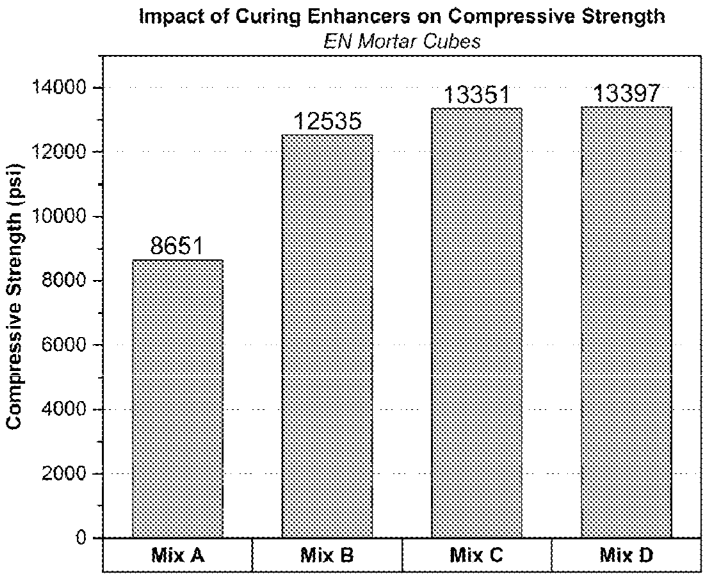
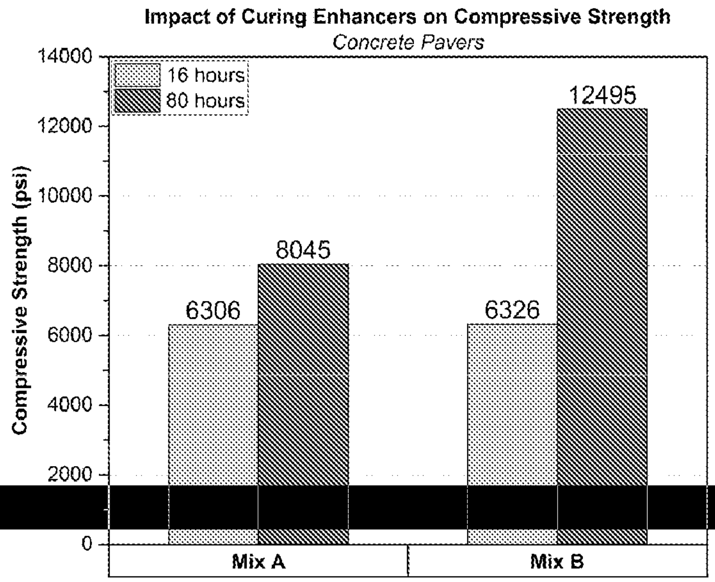

Impact of Curing Enhancers on Compressive Strength
EN Mortar Cubes
Compressive Strength (psi)
14000
12000
10000
8000
6000
4000
2000
0
8651
12535
13351
13397
Mix A
Mix B
Mix C
Mix D

FIG. 9



[redacted]

FIG. 10

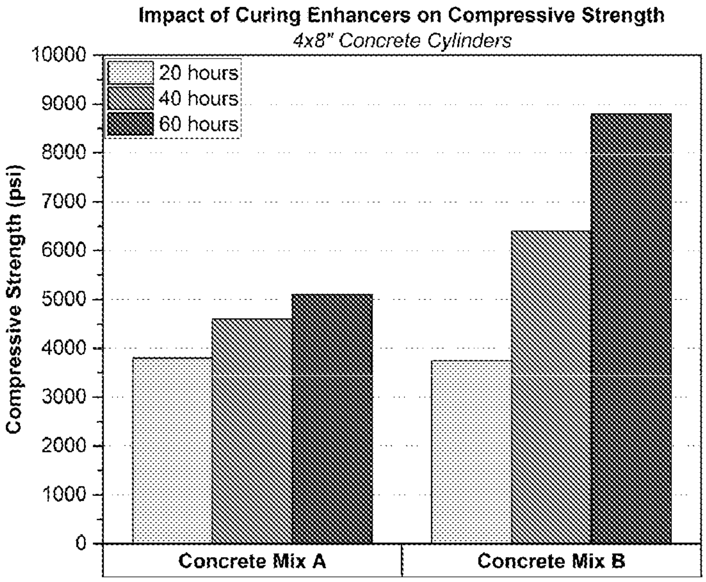

Impact of Curing Enhancers on Compressive Strength
4x8" Concrete Cylinders
Compressive Strength (psi)
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
20 hours
40 hours
60 hours
Concrete Mix A
Concrete Mix B

FIG. 11A

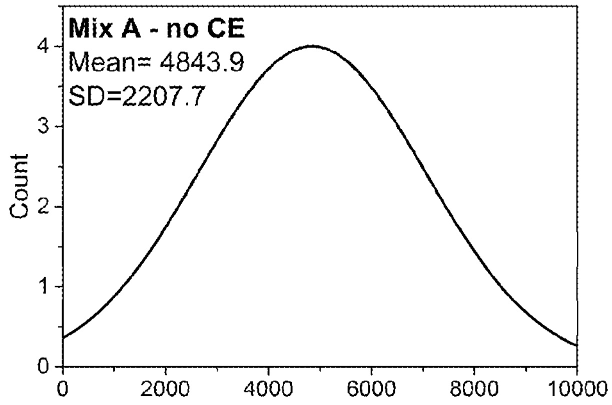


FIG. 11B

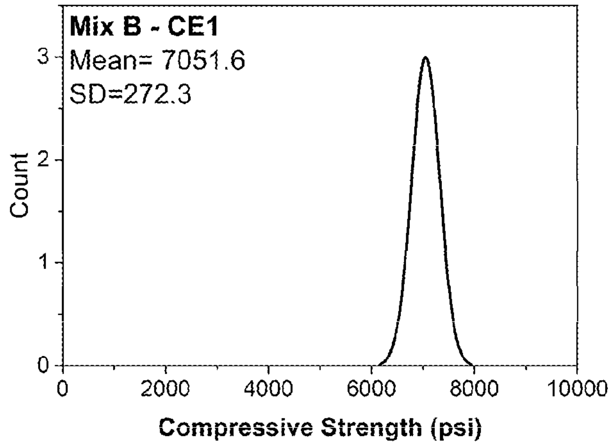


FIG. 12

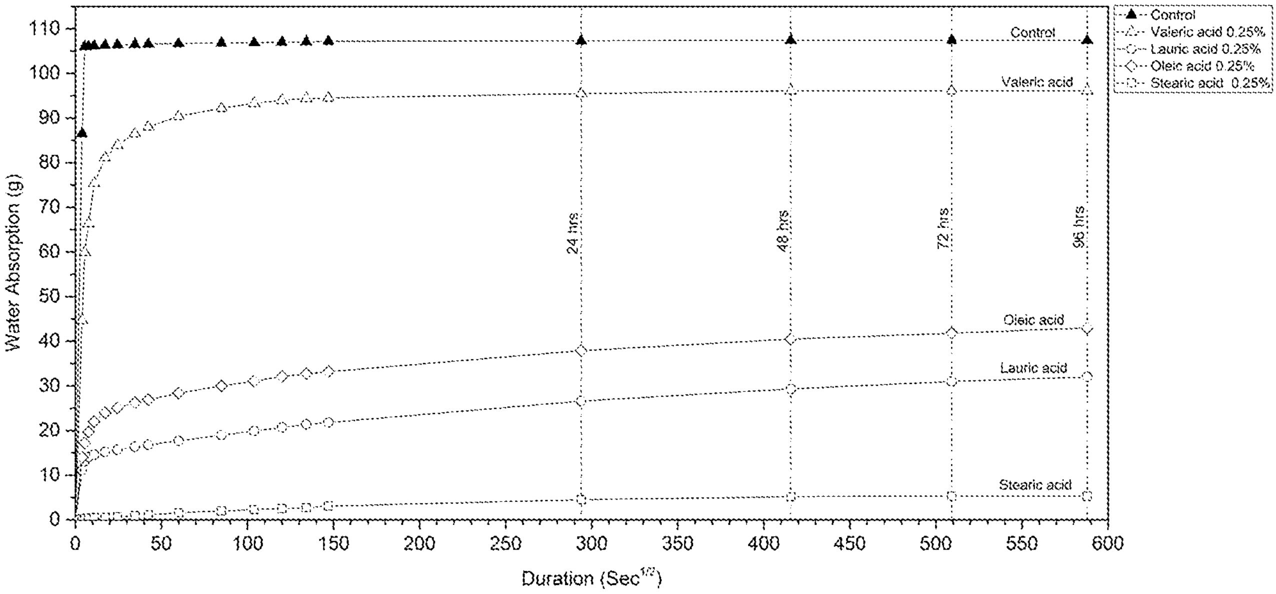

Control
Valeric acid 0.25%
Lauric acid 0.25%
Oleic acid 0.25%
Stearic acid 0.25%
Control
Valeric acid
Oleic acid
Lauric acid
Stearic acid
24 hrs
48 hrs
72 hrs
96 hrs
Water Absorption (g)
0
10
20
30
40
50
60
70
80
90
100
110
Duration (Sec$^{1/2}$)
0
50
100
150
200
250
300
350
400
450
500
550
600

FIG. 13

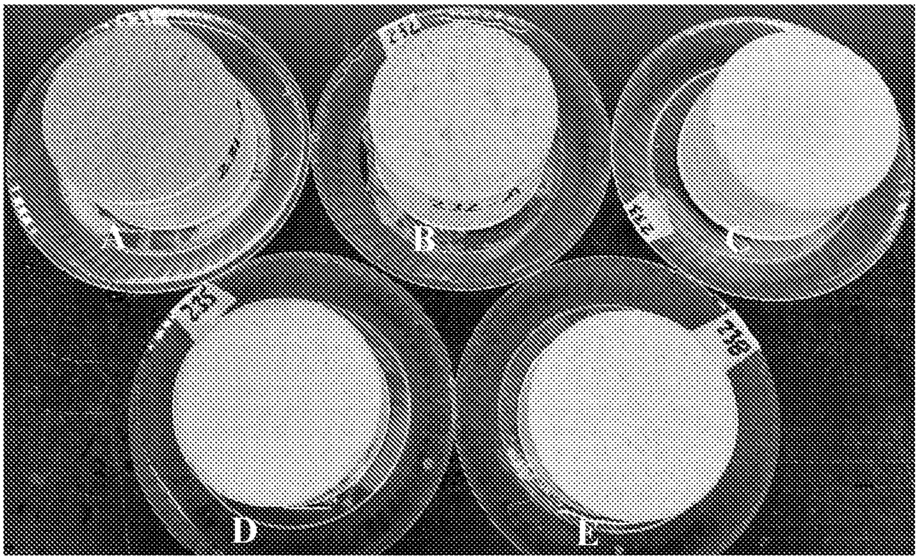


FIG. 14

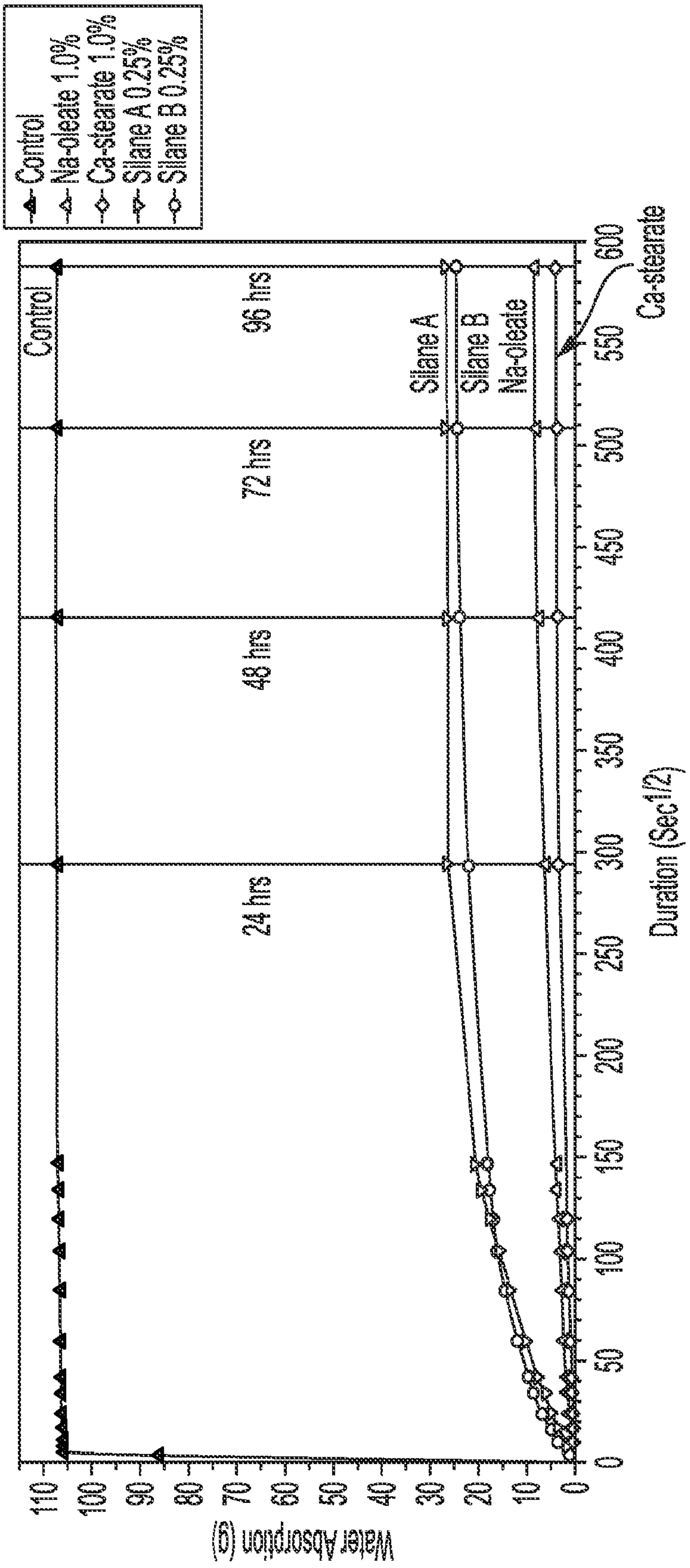

Control
Na-oleate 1.0%
Ca-stearate 1.0%
Silane A 0.25%
Silane B 0.25%
Water Absorption (g)
110
100
90
80
70
60
50
40
30
20
10
0
0
50
100
150
200
250
300
350
400
450
500
550
600
Duration (Sec1/2)
24 hrs
48 hrs
72 hrs
96 hrs
Control
Silane A
Silane B
Na-oleate
Ca-stearate

FIG. 15

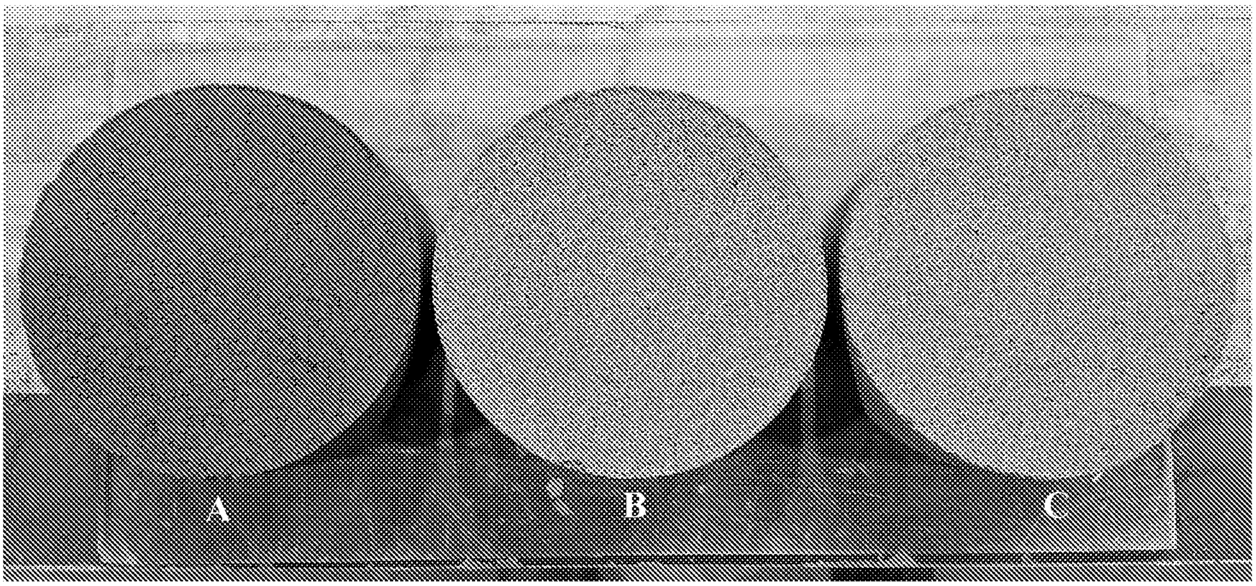


FIG. 16

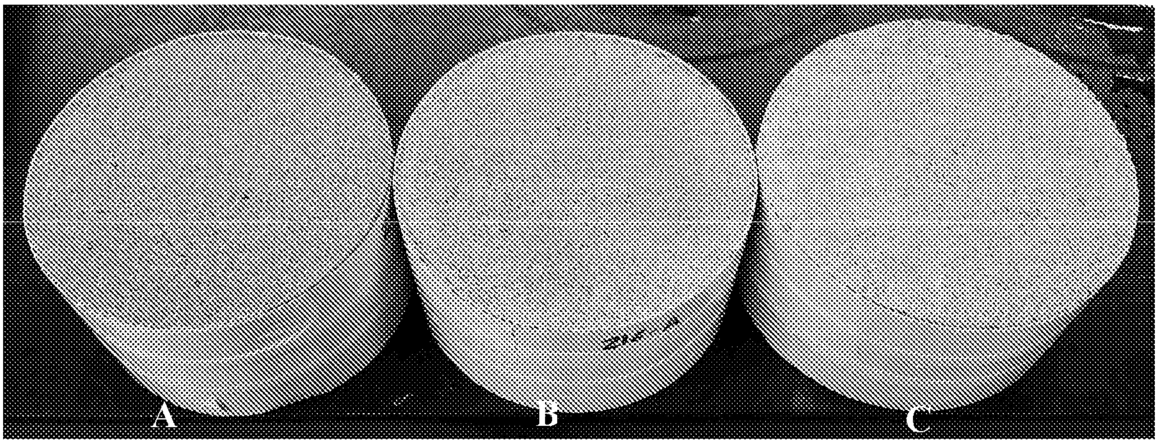


FIG. 17A

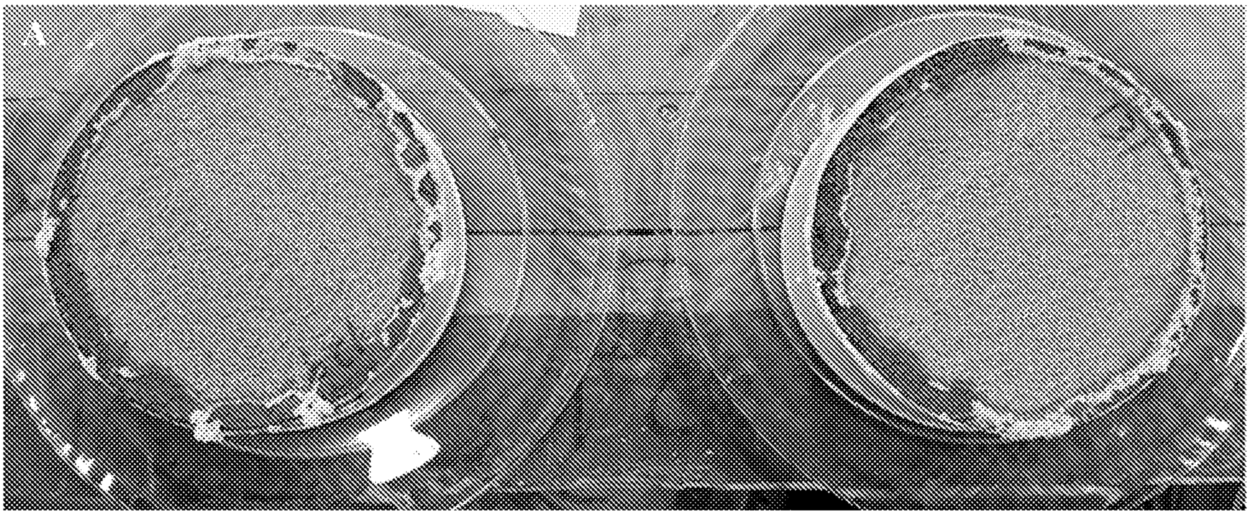


FIG. 17B

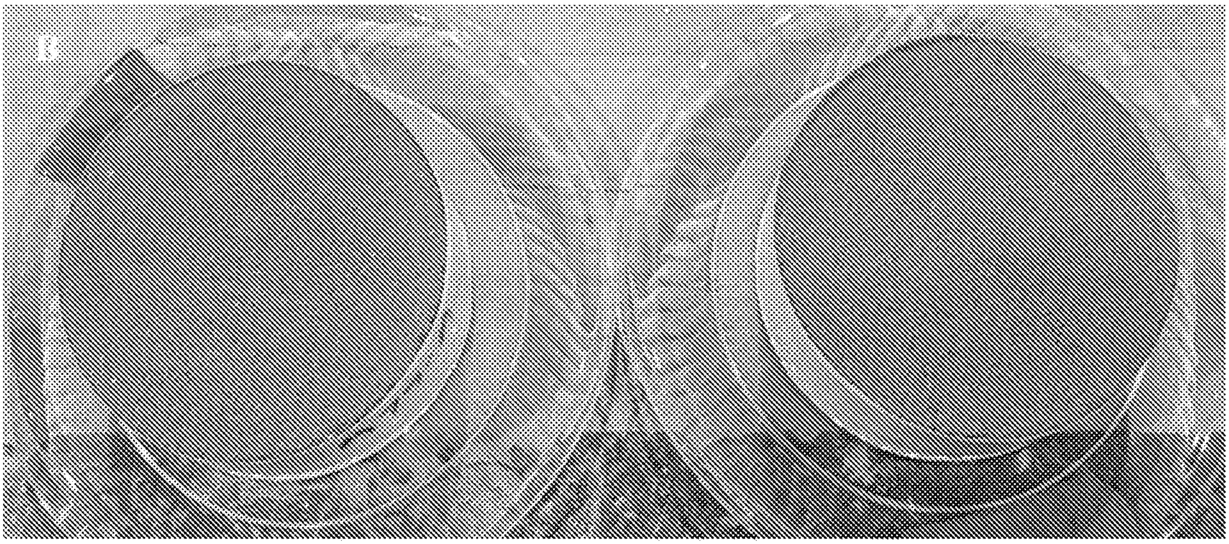


FIG. 18

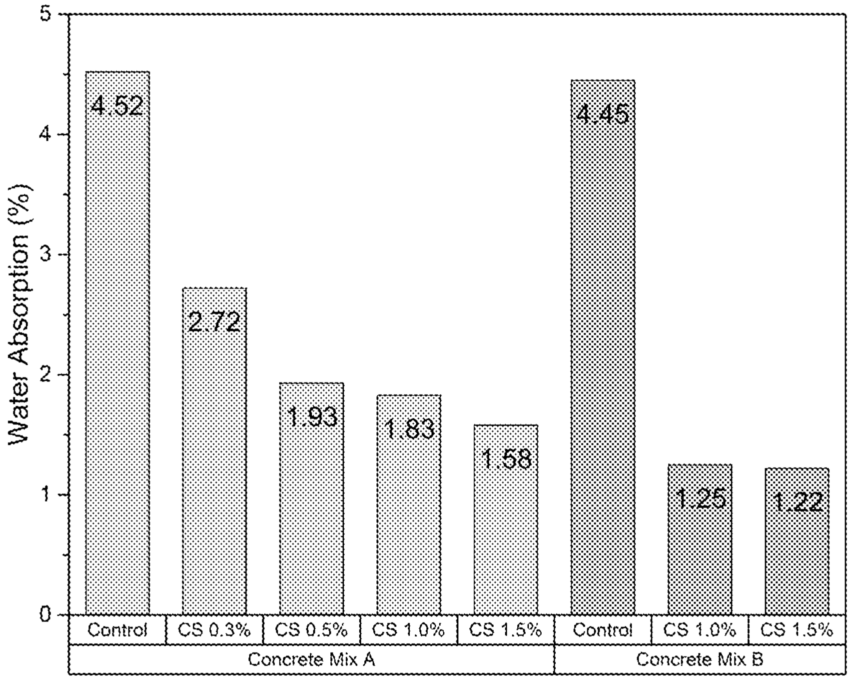

Water Absorption (%)
5
4
3
2
1
0
4.52
2.72
1.93
1.83
1.58
4.45
1.25
1.22
Control
CS 0.3%
CS 0.5%
CS 1.0%
CS 1.5%
Control
CS 1.0%
CS 1.5%
Concrete Mix A
Concrete Mix B

FIG. 19

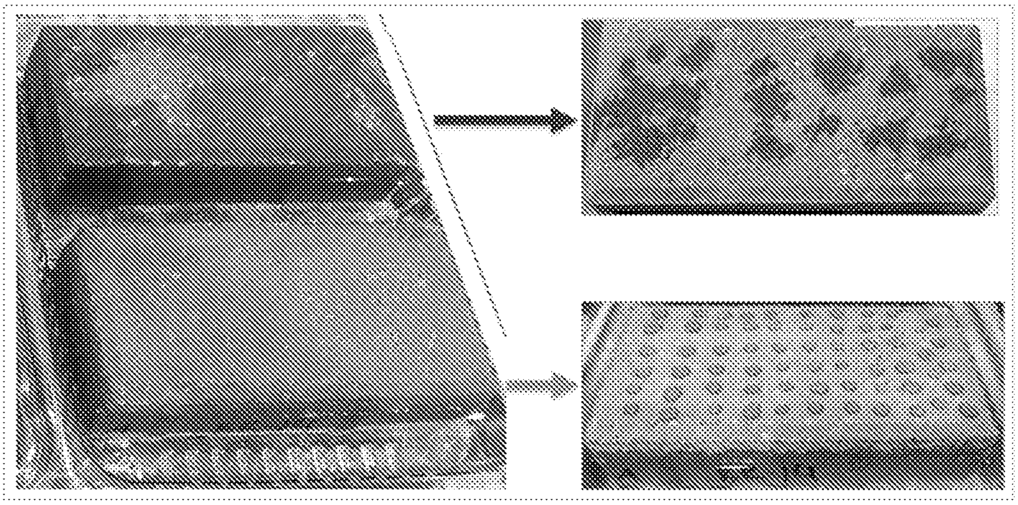


FIG. 20

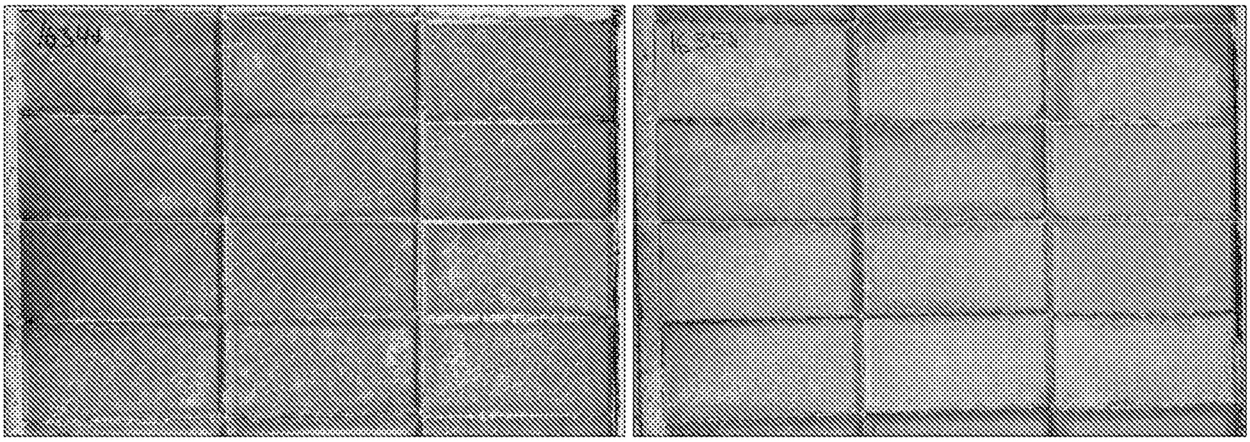


FIG. 21

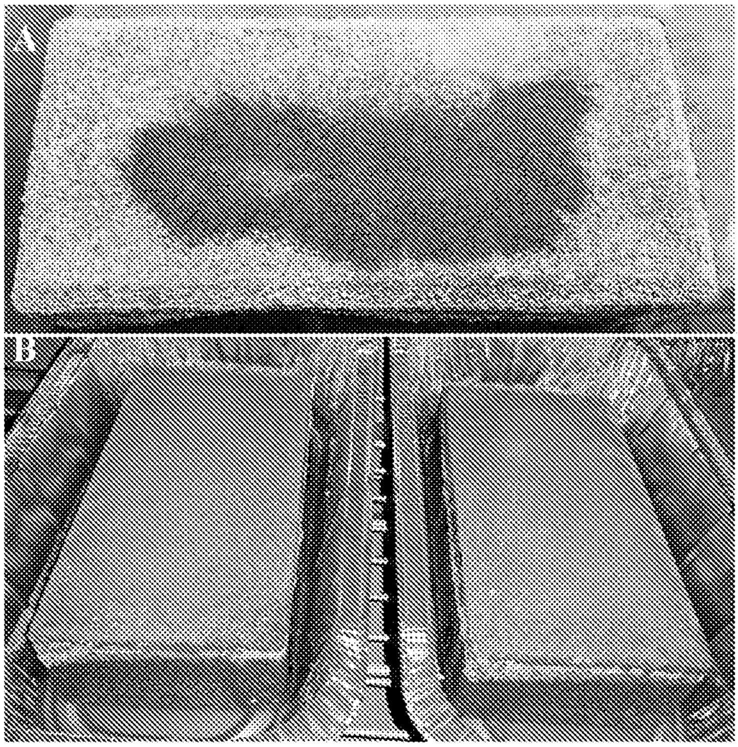


FIG. 22

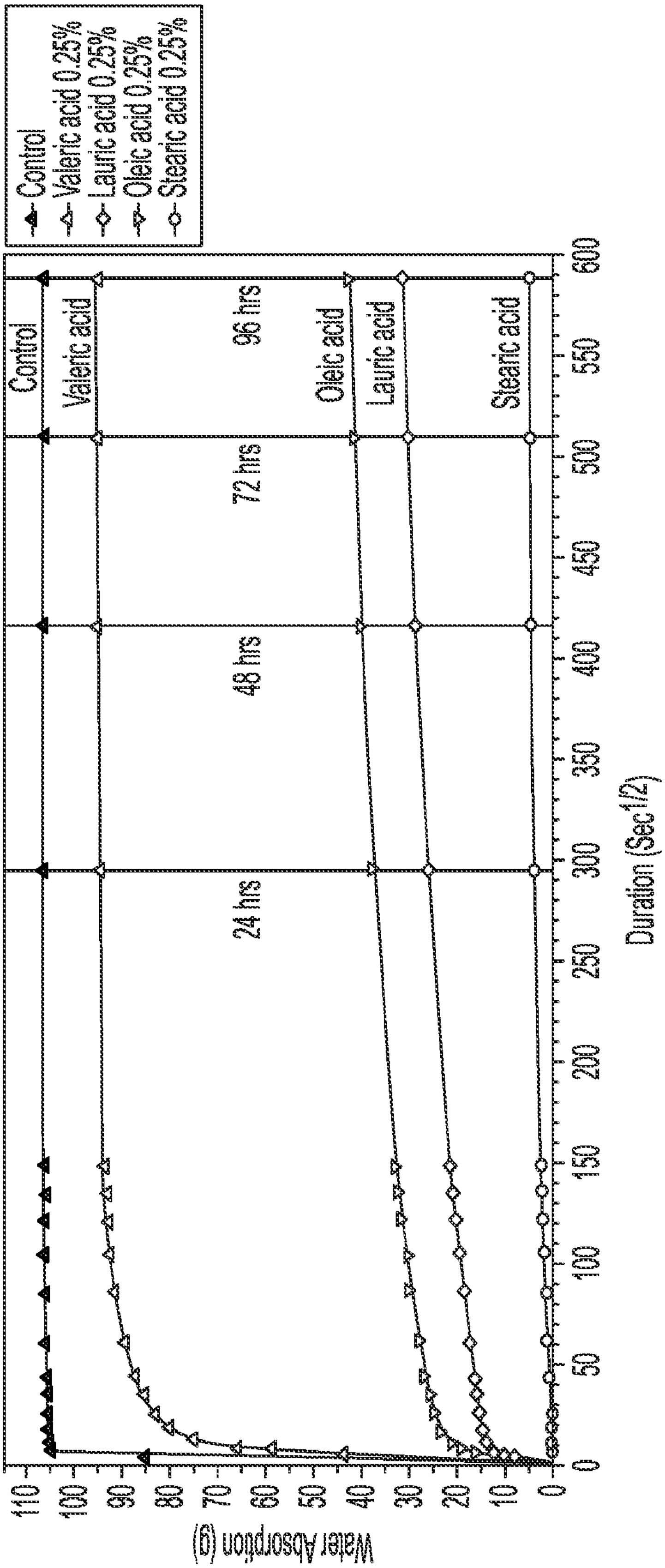

Control
Valeric acid 0.25%
Lauric acid 0.25%
Oleic acid 0.25%
Stearic acid 0.25%
Control
Valeric acid
96 hrs
Oleic acid
Lauric acid
Stearic acid
72 hrs
48 hrs
24 hrs
Water Absorption (g)
110
100
90
80
70
60
50
40
30
20
10
0
Duration (Sec1/2)
0
50
100
150
200
250
300
350
400
450
500
550
600

FIG. 23

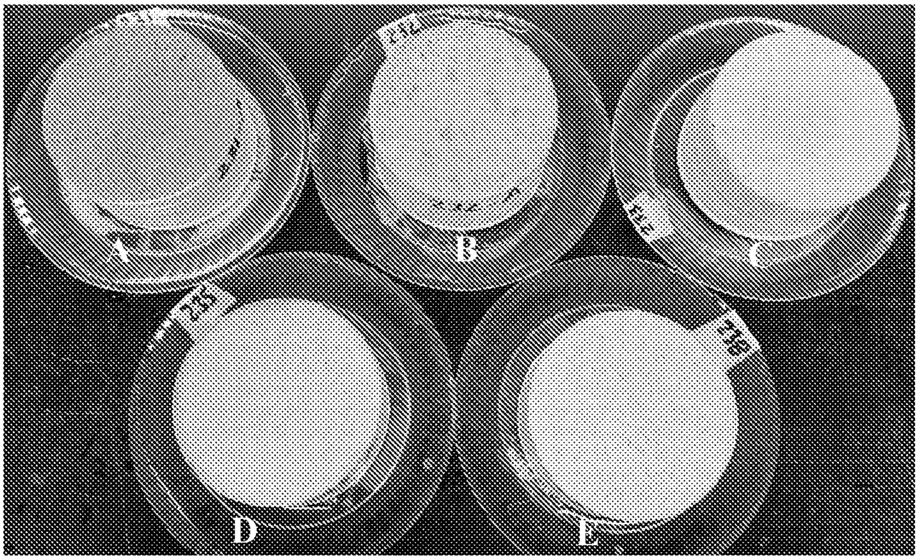


FIG. 24

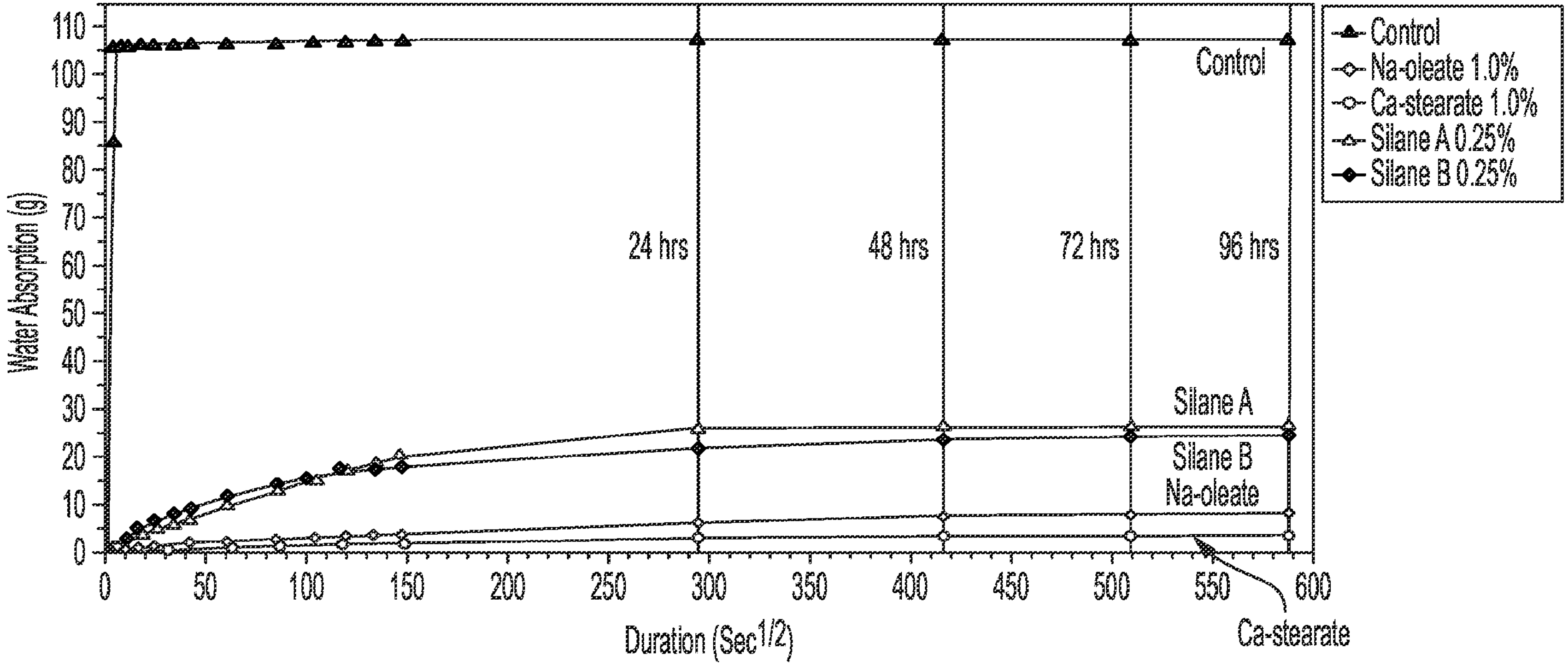

Water Absorption (g)
110
100
90
80
70
60
50
40
30
20
10
0
0
50
100
150
200
250
300
350
400
450
500
550
600
Duration (Sec$^{1/2}$)
24 hrs
48 hrs
72 hrs
96 hrs
Control
Silane A
Silane B
Na-oleate
Ca-stearate
Control
Na-oleate 1.0%
Ca-stearate 1.0%
Silane A 0.25%
Silane B 0.25%

FIG. 25

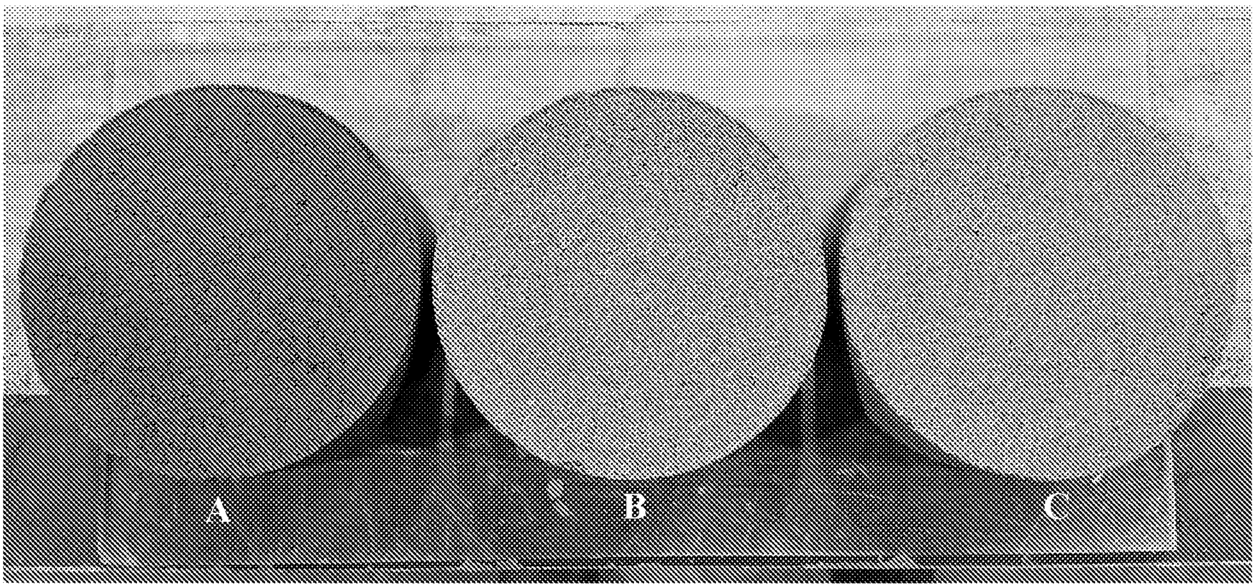


FIG. 26

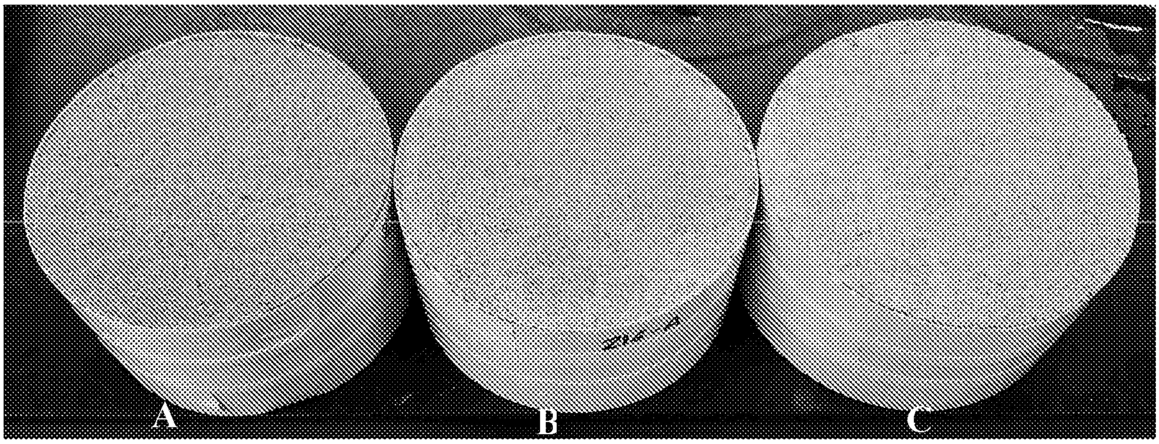


FIG. 27

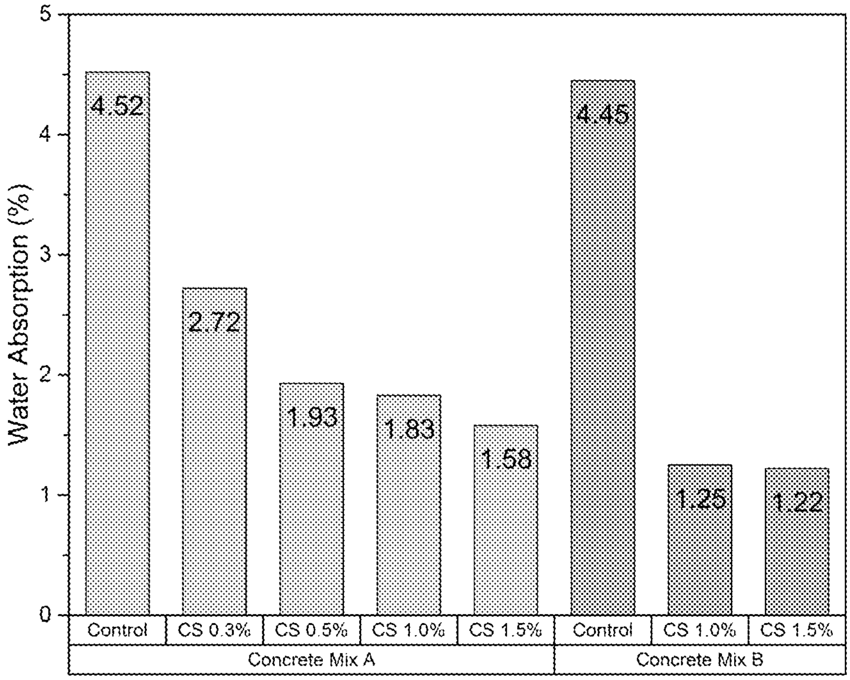

Water Absorption (%)
0
1
2
3
4
5
4.52
2.72
1.93
1.83
1.58
4.45
1.25
1.22
Control
CS 0.3%
CS 0.5%
CS 1.0%
CS 1.5%
Control
CS 1.0%
CS 1.5%
Concrete Mix A
Concrete Mix B

FIG. 28

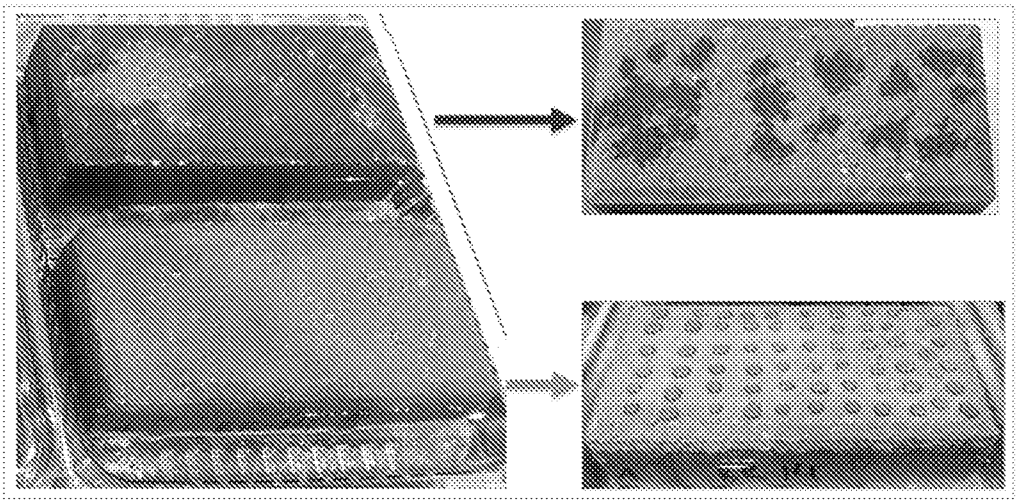


FIG. 29

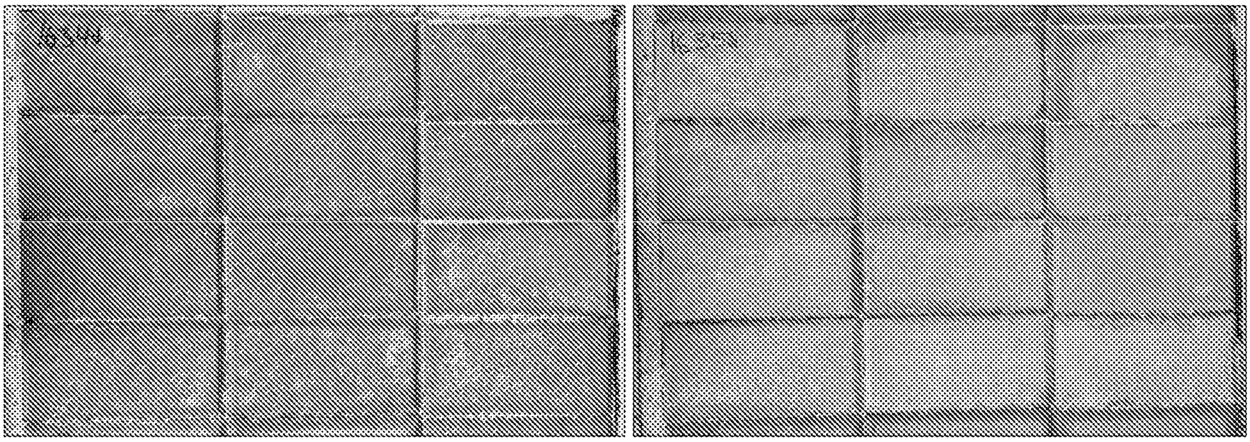


FIG. 30

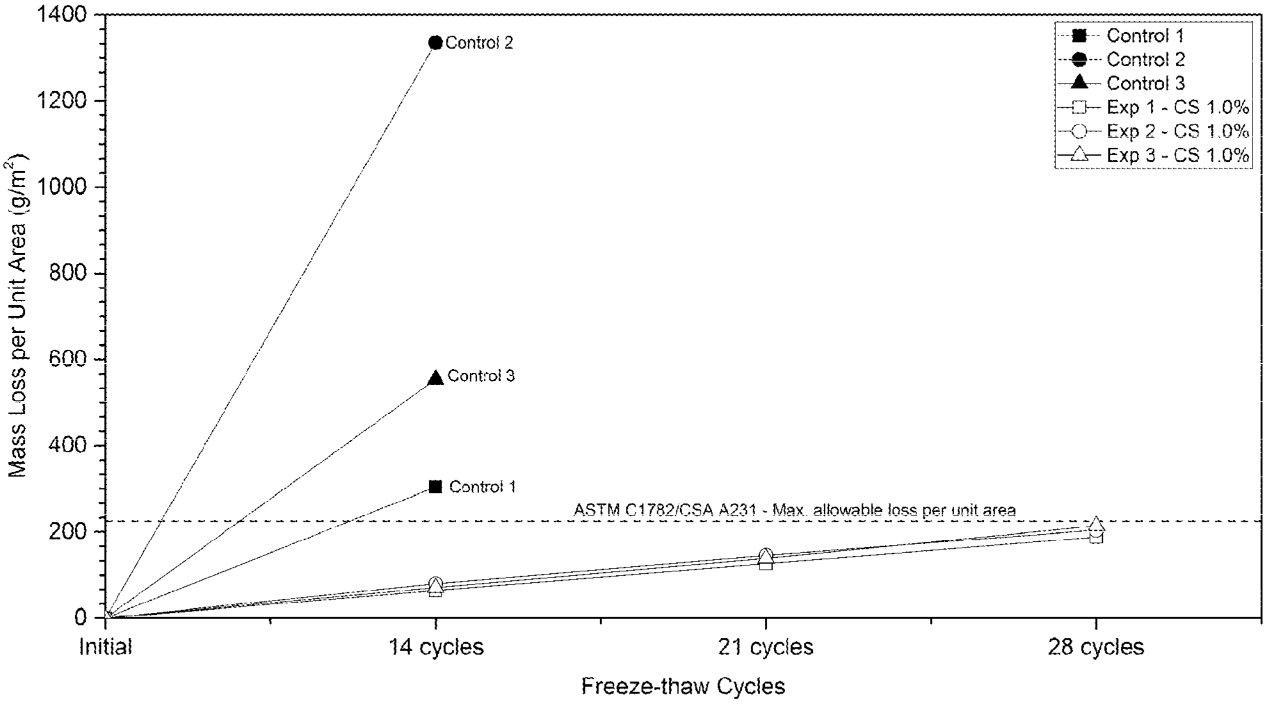

1400
1200
1000
800
600
400
200
0
Mass Loss per Unit Area (g/m²)
Initial
14 cycles
21 cycles
28 cycles
Freeze-thaw Cycles
Control 1
Control 2
Control 3
Exp 1 - CS 1.0%
Exp 2 - CS 1.0%
Exp 3 - CS 1.0%
Control 2
Control 3
Control 1
ASTM C1782/CSA A231 - Max. allowable loss per unit area

FIG. 31

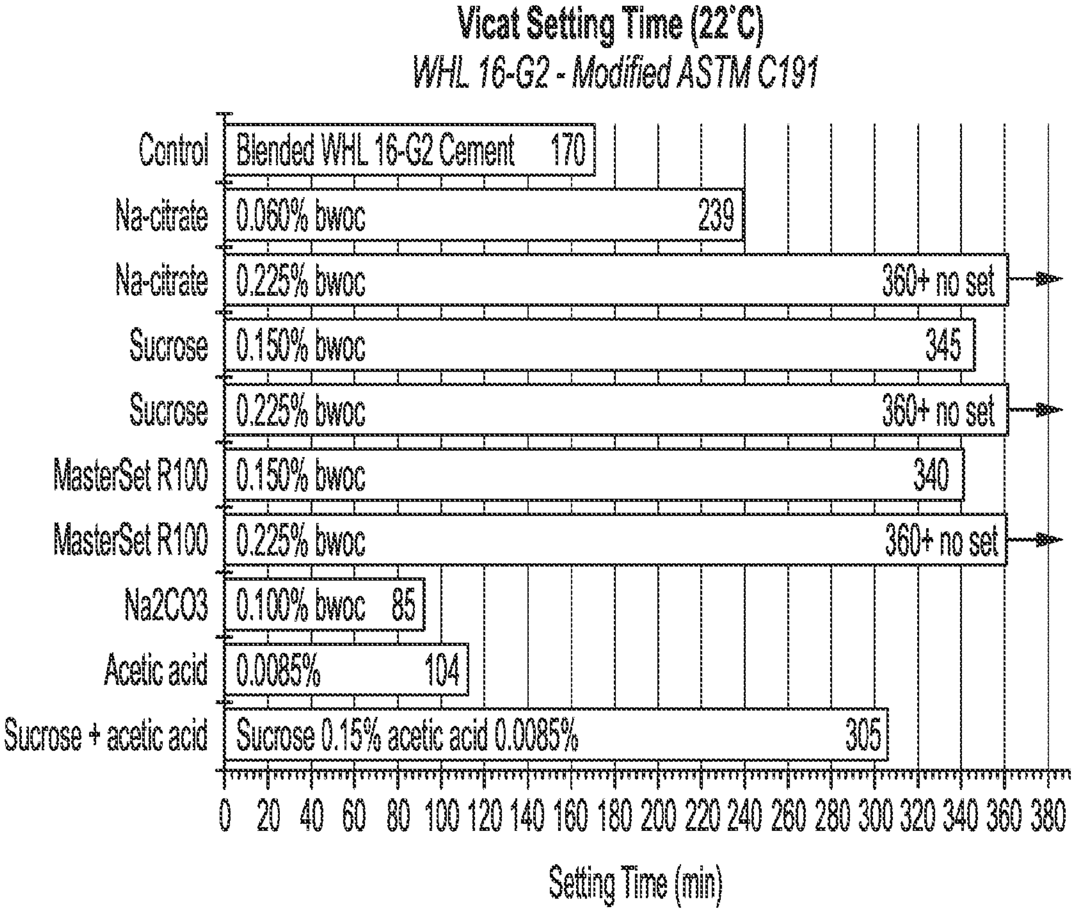

Vicat Setting Time (22˚C)
WHL 16-G2 - Modified ASTM C191
Control
Blended WHL 16-G2 Cement 170
Na-citrate
0.060% bwoc 239
Na-citrate
0.225% bwoc 360+ no set
Sucrose
0.150% bwoc 345
Sucrose
0.225% bwoc 360+ no set
MasterSet R100
0.150% bwoc 340
MasterSet R100
0.225% bwoc 360+ no set
Na2CO3
0.100% bwoc 85
Acetic acid
0.0085% 104
Sucrose + acetic acid
Sucrose 0.15% acetic acid 0.0085% 305
0
20
40
60
80
100
120
140
160
180
200
220
240
260
280
300
320
340
360
380
Setting Time (min)

FIG. 32

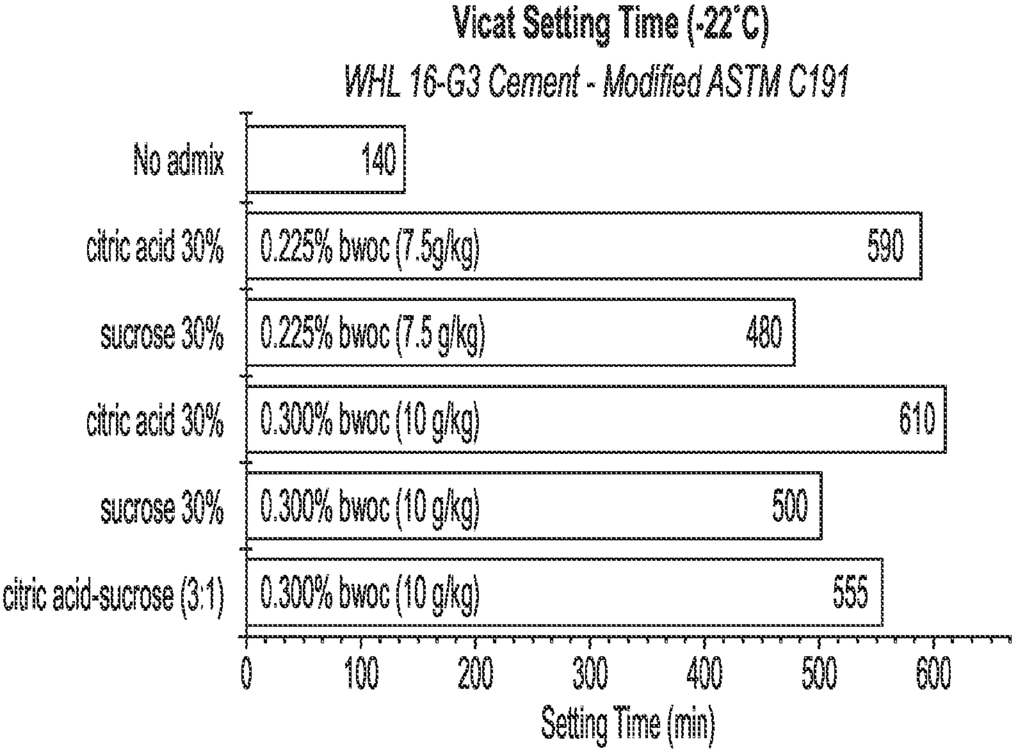

Vicat Setting Time (-22°C)
WHL 16-G3 Cement - Modified ASTM C191
No admix
140
citric acid 30%
0.225% bwoc (7.5g/kg)
590
sucrose 30%
0.225% bwoc (7.5 g/kg)
480
citric acid 30%
0.300% bwoc (10 g/kg)
610
sucrose 30%
0.300% bwoc (10 g/kg)
500
citric acid-sucrose (3:1)
0.300% bwoc (10 g/kg)
555
0
100
200
300
400
500
600
Setting Time (min)

FIG. 33

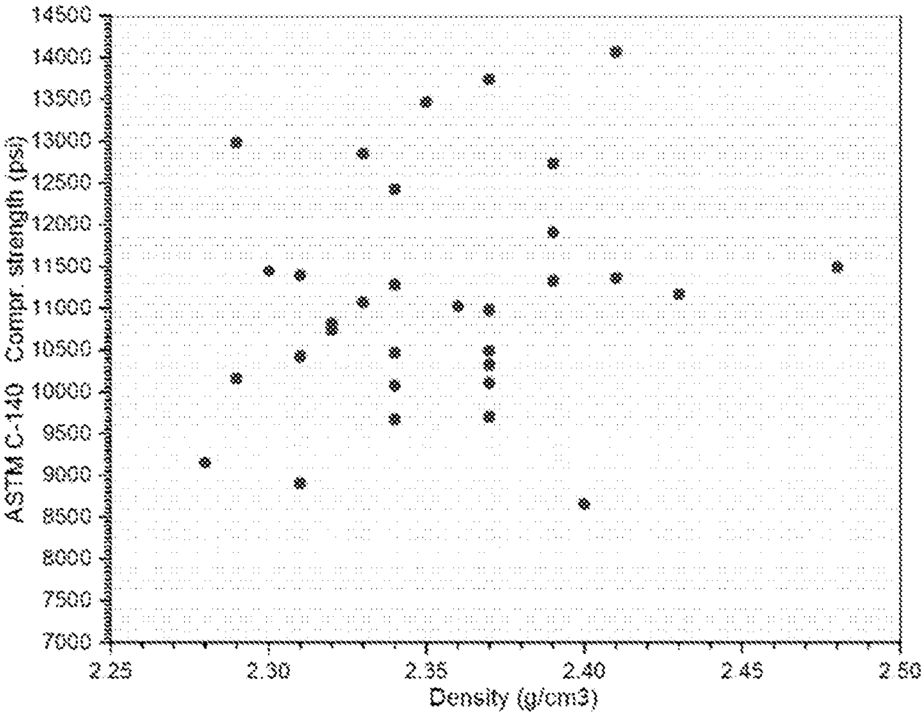

ASTM C-140 Compr. strength (psi)
14500
14000
13500
13000
12500
12000
11500
11000
10500
10000
9500
9000
8500
8000
7500
7000
2.25
2.30
2.35
2.40
2.45
2.50
Density (g/cm3)

FIG. 34

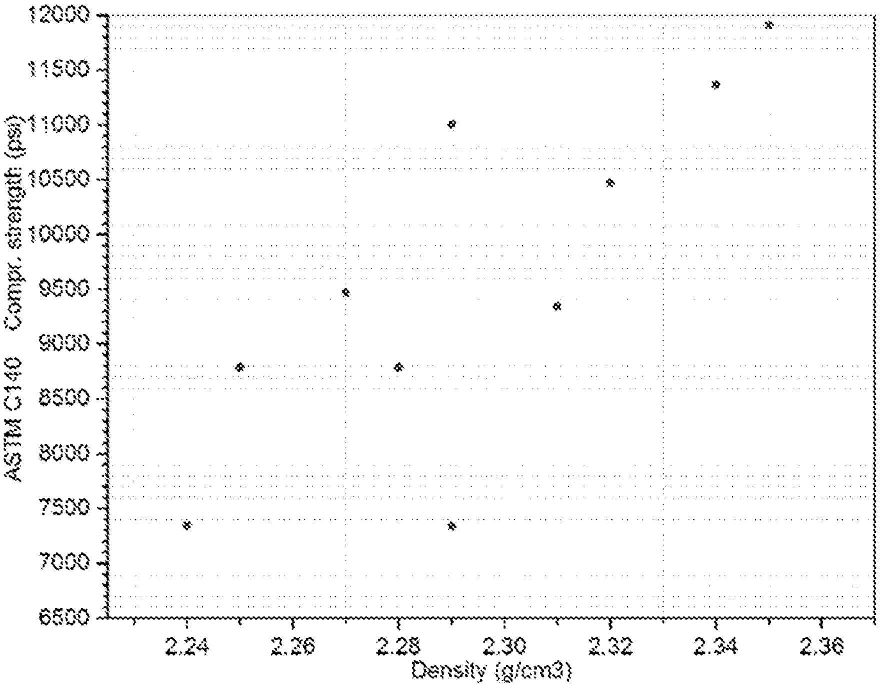

12000
11500
11000
10500
10000
9500
9000
8500
8000
7500
7000
6500
ASTM C140 Compr. strength (psi)
2.24
2.26
2.28
2.30
2.32
2.34
2.36
Density (g/cm3)

FIG. 35

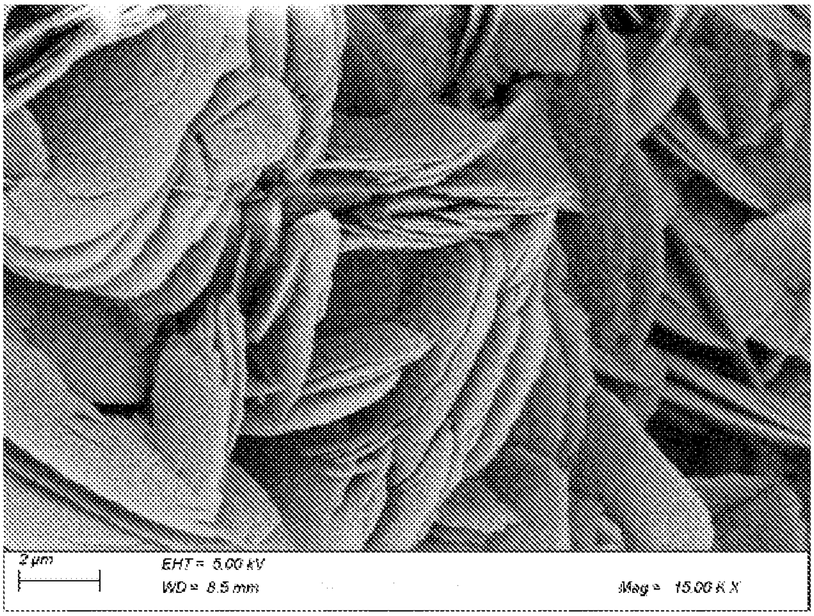


FIG. 36

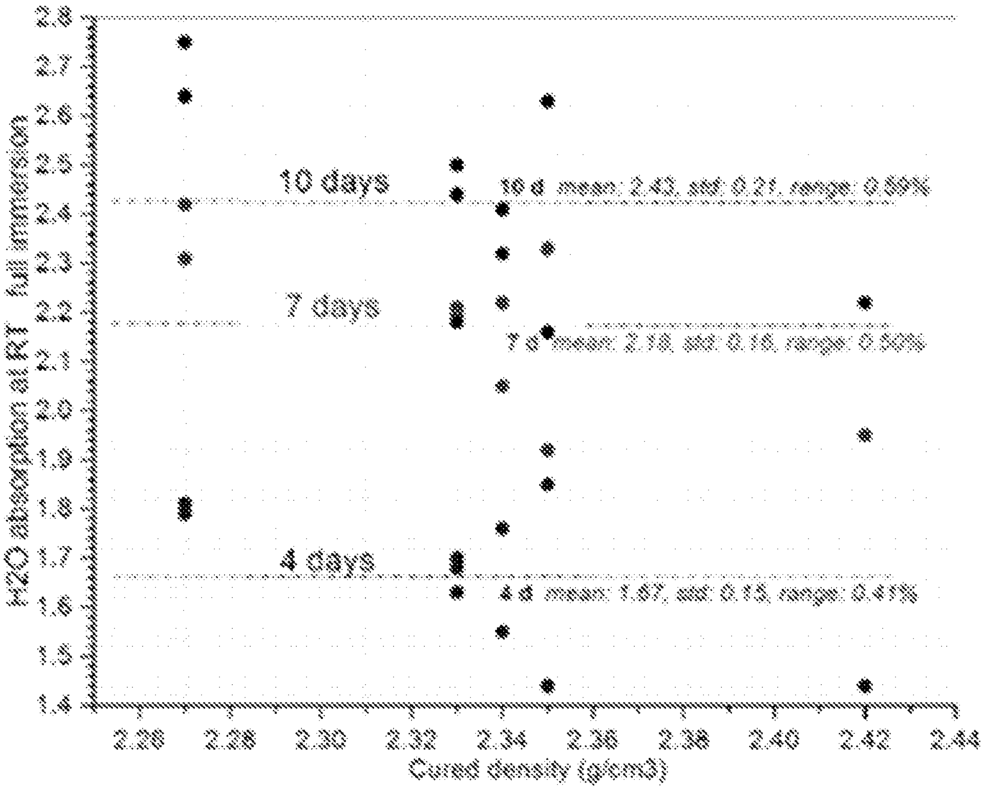

H2O absorption at RT full immersion
2.8
2.7
2.6
2.5
2.4
2.3
2.2
2.1
2.0
1.9
1.8
1.7
1.6
1.5
1.4
10 days
10 d mean: 2.43, std: 0.21, range: 0.59%
7 days
7 d mean: 2.18, std: 0.16, range: 0.50%
4 days
4 d mean: 1.67, std: 0.15, range: 0.41%
2.26
2.28
2.30
2.32
2.34
2.36
2.38
2.40
2.42
2.44
Cured density (g/cm3)

FIG. 37

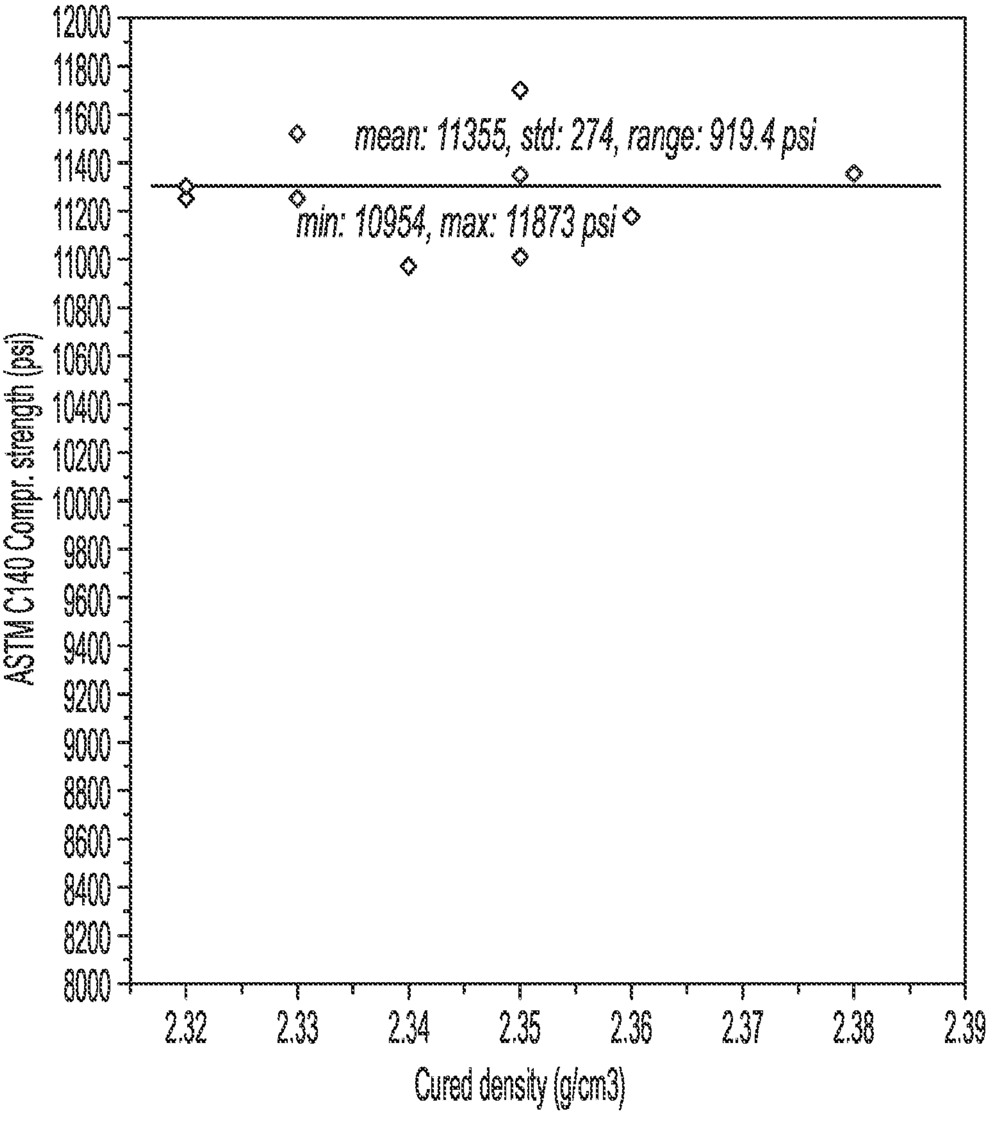

mean: 11355, std: 274, range: 919.4 psi
min: 10954, max: 11873 psi
ASTM C140 Compr. strength (psi)
12000
11800
11600
11400
11200
11000
10800
10600
10400
10200
10000
9800
9600
9400
9200
9000
8800
8600
8400
8200
8000
2.32
2.33
2.34
2.35
2.36
2.37
2.38
2.39
Cured density (g/cm3)

FIG. 38

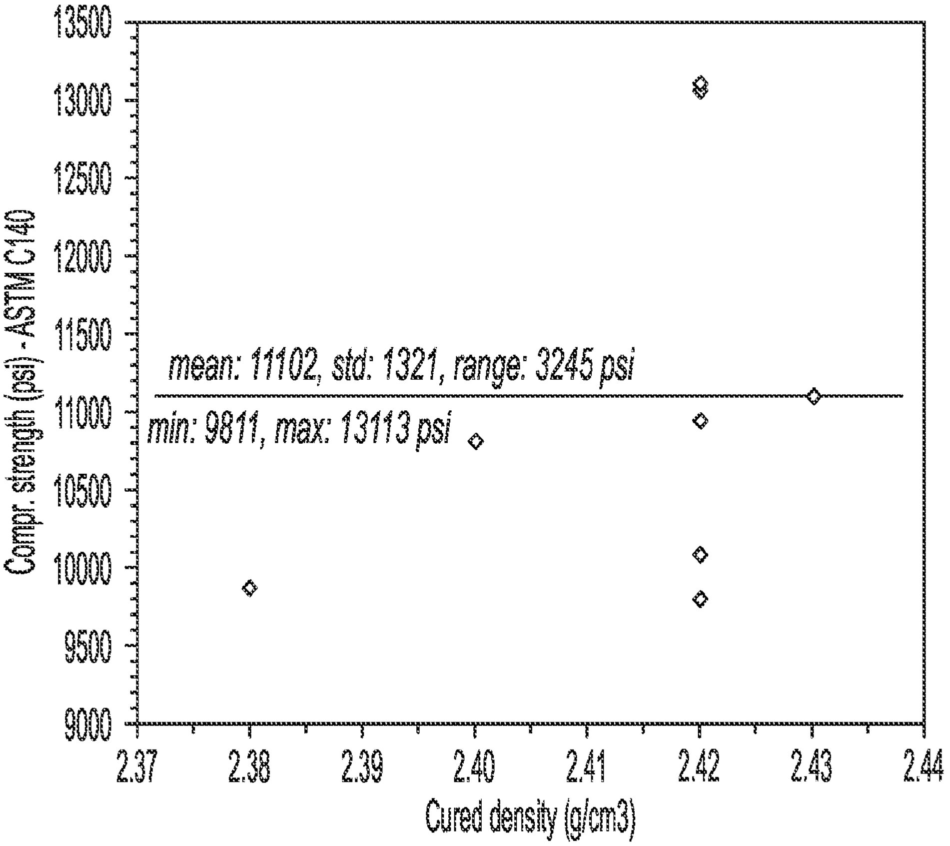

Compr. strength (psi) - ASTM C140
13500
13000
12500
12000
11500
11000
10500
10000
9500
9000
mean: 11102, std: 1321, range: 3245 psi
min: 9811, max: 13113 psi
2.37
2.38
2.39
2.40
2.41
2.42
2.43
2.44
Cured density (g/cm3)

FIG. 39

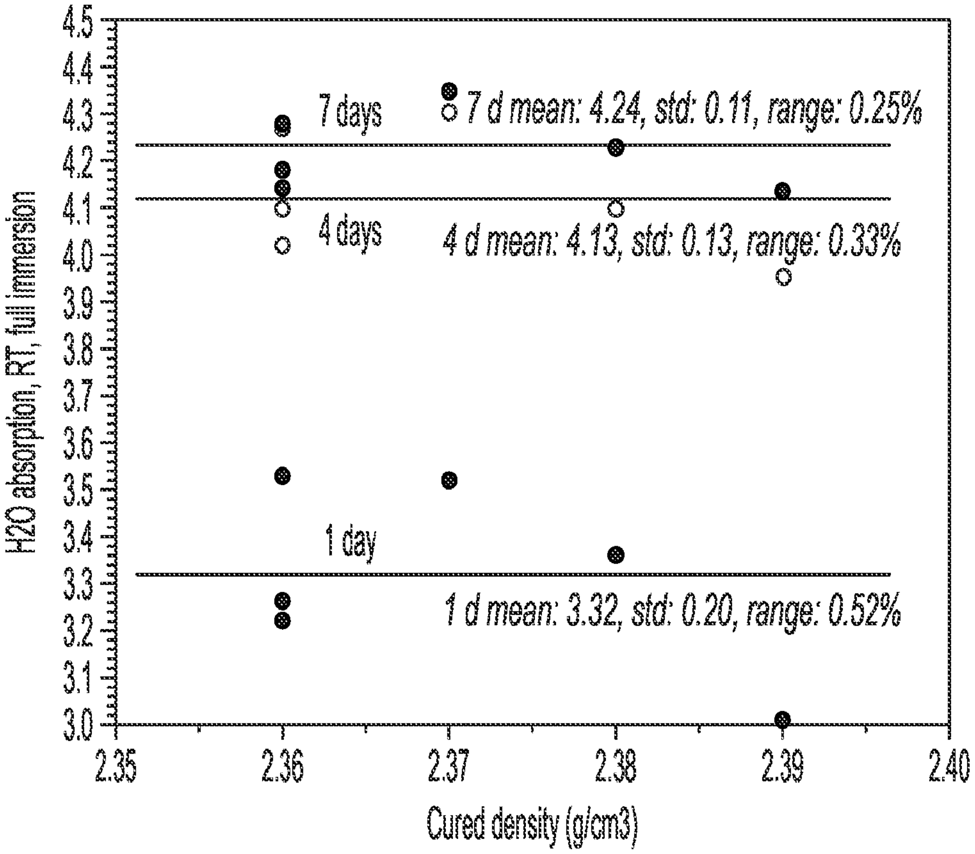
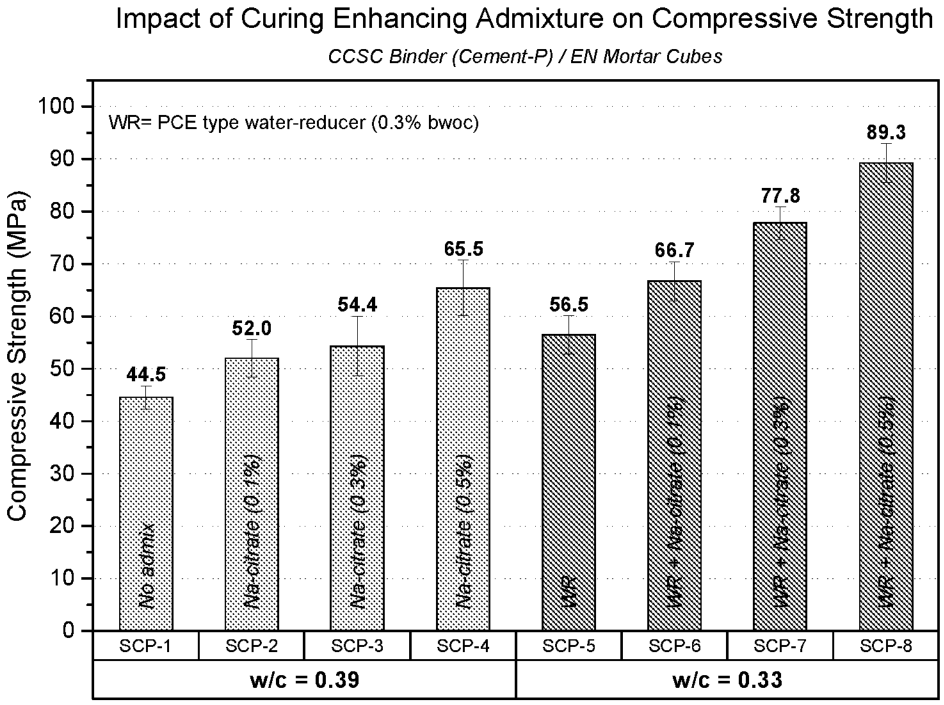

4.5
4.4
4.3
4.2
4.1
4.0
3.9
3.8
3.7
3.6
3.5
3.4
3.3
3.2
3.1
3.0
H2O absorption, RT, full immersion
2.35
2.36
2.37
2.38
2.39
2.40
Cured density (g/cm3)
7 days
7 d mean: 4.24, std: 0.11, range: 0.25%
4 days
4 d mean: 4.13, std: 0.13, range: 0.33%
1 day
1 d mean: 3.32, std: 0.20, range: 0.52%

FIG. 40


Impact of Curing Enhancing Admixture on Compressive Strength
CCSC Binder (Cement-P) / EN Mortar Cubes
WR= PCE type water-reducer (0.3% bwoc)
Compressive Strength (MPa)
0
10
20
30
40
50
60
70
80
90
100
44.5
52.0
54.4
65.5
56.5
66.7
77.8
89.3
No admix
Na-citrate (0.1%)
Na-citrate (0.3%)
Na-citrate (0.5%)
WR
WR + Na-citrate (0.1%)
WR + Na-citrate (0.3%)
WR + Na-citrate (0.5%)
SCP-1
SCP-2
SCP-3
SCP-4
SCP-5
SCP-6
SCP-7
SCP-8
w/c = 0.39
w/c = 0.33

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 21/37717

A. CLASSIFICATION OF SUBJECT MATTER

IPC - C04B 7/00; C04B 12/00; C04B 22/06; C04B 24/06; C04B 28/04 (2021.01)

CPC - C04B 12/007; C04B 22/066; C04B 28/188; C04B 28/24; C04B 35/22; C04B 35/64; C04B 40/0231

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
See Search History document

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
See Search History document

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
See Search History document

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2018/0273430 A1 (SOLIDIA TECHNOLOGIES INC), 27 September 2018 (27.09.2018), figures 10-18, para [0008]-[0010], [0036], [0039]-[0041], [0046], [0059], [0077], [0090]-[0091], [0114], [0121].	1-4, 20-25
A/D	US 2016/0096773 A1 (SOLIDIA TECHNOLOGIES INC), 7 April 2016 (07.04.2016), entire document.	1-4, 20-25
A	WO 2018/175769 A1 (SOLIDIA TECHNOLOGIES INC), 27 September 2018 (27.09.2018), entire document.	1-4, 20-25
A	US 2004/0216644 A1 (MORIOKA et al), 4 November 2004 (04.11.2004), entire document.	1-4, 20-25
A	MO et al, 'Effects of accelerated carbonation on the microstructure of Portland cement pastes containing reactive MgO', Cement and Concrete Research, volume 42, 20 March 2012 (20.03.2012), pg 769-777.	1-4, 20-25

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"D" document cited by the applicant in the international application

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search 20 August 2021 (20.08.2021)	Date of mailing of the international search report OCT 14 2021
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-8300	Authorized officer Kari Rodriquez Telephone No. PCT Helpdesk: 571-272-4300

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 21/37717

Box No. II **Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)**

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☒ Claims Nos.: 5-19, 26-28
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III **Observations where unity of invention is lacking (Continuation of item 3 of first sheet)**

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.