(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
19 September 2024 (19.09.2024)

WIPO | PCT

(10) International Publication Number
WO 2024/192251 A1

(51) International Patent Classification:
C04B 24/10 (2006.01) *C13K 1/06* (2006.01)
C04B 24/38 (2006.01) *C13B 50/00* (2011.01)

(21) International Application Number: PCT/US2024/019954

(22) International Filing Date: 14 March 2024 (14.03.2024)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
63/490,054 14 March 2023 (14.03.2023) US

(71) Applicant: SOLUGEN, INC. [US/US]; 14549 Minetta Street, Houston, TX 77035-6523 (US).

(72) Inventors: TAN, LoongYi; c/o Solugen, Inc., 14549 Minetta Street, Houston, TX 77035-6523 (US). AN, Jun Su; c/o Solugen, Inc., 14549 Minetta Street, Houston, TX 77035-6523 (US). HELANDER, Jason; c/o Solugen, Inc., 14549 Minetta Street, Houston, TX 77035-6523 (US). JEKNAVORIAN, Ara; c/o Solugen, Inc., 14549 Minetta Street, Houston, TX 77035-6523 (US). DESAI, Amit; c/o Solugen, Inc., 14549 Minetta Street, Houston, TX 77035-6523 (US).

(74) Agent: FALESKI, Thaddeus, J. et al.; Conley Rose, P.C., 777 North Eldridge Parkway, Suite 600, Houston, TX 77079 (US).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CV, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IQ, IR, IS, IT, JM, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, MG, MK, MN, MU, MW, MX, MY, MZ, NA,

(54) Title: MULTIFUNCTIONAL CEMENT ADDITIVES AND METHODS OF USING SAME

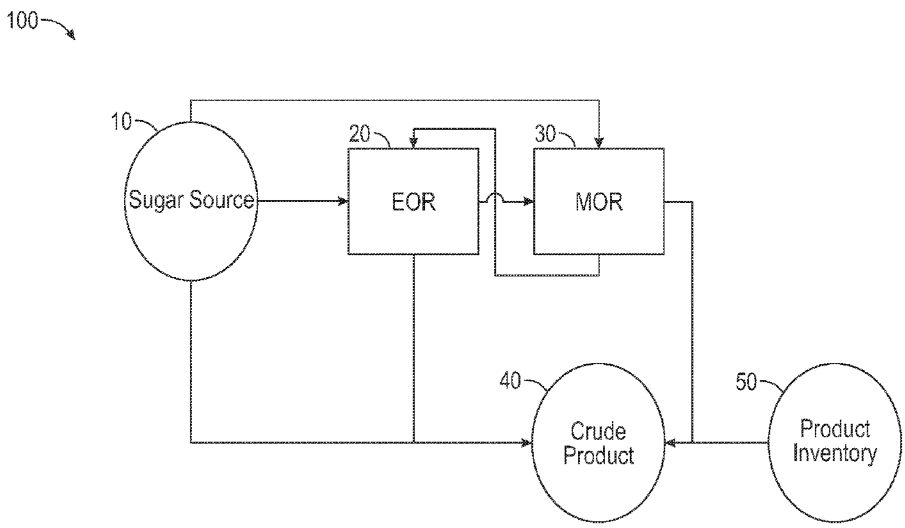

FIG. 1

(57) Abstract: A multifunctional cement additive including (i) a sugar derivative comprising glucaric acid, gluconic acid, glucuronic acid, glucose oxidation products, gluconic acid oxidation products disaccharides, oxidized disaccharides, uronic acid, aldaric acid, galactonic acid, galactaric acid, glutamic acid glucodialdose, 2-ketoglucose, salts thereof, lactones thereof, or a combination thereof and (ii) a solvent. A composition comprising (a) a cementitious material (b) a multifunctional additive comprising a sugar oxidation product and (c) a solvent wherein the multifunctional additive comprising a sugar oxidation product is a mixture of two compounds selected from the group consisting essentially of dextrose, glucose, fructose, sucrose, glucaric acid, glucodialdose, gluconic acid, erythorbic acid, galactaric acid, galacturonic acid, galactonic acid and 2-ketoglucose.

WO 2024/192251 A1

[Continued on next page]

NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, WS, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, CV, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SC, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, ME, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— *with international search report (Art. 21(3))*

MULTIFUNCTIONAL CEMENT ADDITIVES AND METHODS OF USING SAME

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims priority to U.S. Provisional Application No. 63/490,054 filed March 14, 2023 and entitled "Multifunctional Cement Additives and Methods of Using Same," which is hereby incorporated herein by reference in its entirety for all purposes.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

[0002] Not applicable.

FIELD

[0003] The present disclosure relates generally to compositions and methods for use with materials that form a hardened mass when hydrated. More particularly, the present disclosure relates to cement additives and methods of using same.

BACKGROUND

[0004] Investments in infrastructure are projected to increase significantly resulting in an increased demand for concrete, cement, and cement-based products. Cement, the powdery binder that holds the sand or crushed stone in concrete together, is one of the most energy-intensive products on the planet. Generally, limestone, which is used in in the production of cement, is baked at up to 1,450 °C (2,640 °F) in enormous kilns that are commonly fired with fossil fuels. The chemical reactions involved, such as the hydration of cement constituents, produce even more carbon dioxide as a by-product. Making one kilogram of cement sends one kilogram of CO_2 into the atmosphere. Considering that the trend for concrete usage is projected to increase in coming years, there is a growing need to mitigate the carbon dioxide emissions associated with the production of cement.

[0005] One avenue for mitigating the carbon dioxide emissions would involve the use of a reduced amount of cement for a given application. A challenge to the use of lower amounts of these materials is the potential for negative impacts on performance properties (e.g., mechanical) of the resultant concrete. Consequently, cement additives are included in cement compositions in order to influence one or more user and/or application-desired properties.

[0006] Cement additives are generally described as chemicals and/or materials added to a cement slurry to modify the characteristics of the slurry and/or the set cement. Cement additives may be broadly divided into six different categories that include: (i) water reducers, (ii) set retarders, (iii) accelerants, (iv) superplasticizers, (v) corrosion inhibitors, and (vi) air entrainers. Currently, many cement and/or concrete admixtures contain cement additives that are single or dual functionality products. For example, lignosulfonates are chemicals that are conventionally employed as both a set retarder and plasticizer. Another widely used chemical additive comprising gluconate, glucoheptonate, or both also exhibits dual functionality. A challenge to the use of these materials is that multiple additional compounds are needed to provide cementitious compositions having tailored, application-desired properties. Accordingly, an ongoing need exists for novel additives for use in cement and/or concrete that exhibit higher levels of functionality.

BRIEF DESCRIPTION OF THE DRAWINGS

[0007] For a detailed description of the aspects of the presently disclosed subject matter, reference will now be made to the accompanying drawings in which:

[0008] Figure 1 is an aspect of a process flow diagram for a chemoenzymatic process of the type disclosed herein.

SUMMARY

[0009] Disclosed herein is a multifunctional cement additive comprising (i) a sugar derivative comprising glucaric acid, gluconic acid, glucuronic acid, glucose oxidation products, gluconic acid oxidation products disaccharides, oxidized disaccharides, uronic acid, aldaric acid, galactonic acid, galactaric acid, glutamic acid glucodialdose, 2-ketoglucose, salts thereof, lactones thereof, or a combination thereof and (ii) a solvent.

[0010] Also disclosed herein is a composition comprising (a) a cementitious material (b) a multifunctional additive comprising a sugar oxidation product and (c) a solvent wherein the multifunctional additive comprising a sugar oxidation product is a mixture of two compounds selected from the group consisting essentially of dextrose, glucose, fructose, sucrose, glucaric acid, glucodialdose, gluconic acid, erythorbic acid, galactaric acid, galacturonic acid, galactonic acid and 2-ketoglucose.

DETAILED DESCRIPTION

[0011] Disclosed herein are compositions for use as cement additives. In some aspects, the cement additives of the present disclosure are multifunctional cement additives having at least three functionalities selected from the group consisting of water reducers, set retarders, accelerants, superplasticizers, corrosion inhibitors, strength enhancers, grinding aids, quality improvers, viscosity modifiers, shrinkage reducers and air entrainers. Herein, these materials are referred to as “cement additives with higher functionality” or CAHF. In one or more aspects, the CAHF comprises a sugar derivative and a solvent.

[0012] It is contemplated that the CAHF functions to modify the performance of any cementitious material. As used herein, "cementitious" materials include, but are not limited to, cement, concrete, shotcrete, mortar, grout, asphalt, and the like. Hereinafter reference will be made to cements and cementitious compositions although other compositions comprising materials that set and harden upon hydration are also contemplated.

[0013] In one or more aspects, the CAHF comprises at least one oxidized sugar or, additionally or alternatively, a mixture comprising sugars and at least one oxidized sugar. Additionally or alternatively, in some aspects, the CAHF comprises a sugar, an oxidized sugar, a partially-oxidized sugar, derivatives thereof, or a combination thereof.

[0014] In one or more aspects, the CAHF comprises a sugar oxidation product. For example, the sugar oxidation product may comprise an aldaric acid, uronic acid, glucaric acid, gluconic acid, glucuronic acid, glucose oxidation products, gluconic acid oxidation products, disaccharides, oxidized disaccharides, n-keto-acids, C2-C6 diacids, galactonic acid, galactaric acid, glutamic acid, glucodialdose, 2-ketoglucose, glucodiamine, glycolaldehyde, glyoxal, salts thereof, lactones thereof and a combination thereof.

[0015] In some aspects, a sugar oxidation product suitable for use in the CAHF comprises less than about 5 wt.% maltose, maltotriose, fructose, higher molecular weight polysaccharides, oxidation products thereof or a combination thereof based on the total weight of the sugar oxidation product.

[0016] In some aspects, the CAHF comprises aldonic acid, uronic acid, aldaric acid, or a combination thereof. For example, the CAHF is a mixture of aldaric acid, and uronic acids.

[0017] In some aspects, the CAHF comprises a glucose oxidation product, a gluconic acid oxidation product, a gluconate, or a combination thereof. In one or more aspects, the CAHF comprises glucaric acid, gluconic acid, glucuronic acid, glucose oxidation products, gluconic acid oxidation products or a combination thereof. In one or more aspects, the CAHF comprises disaccharides, oxidized disaccharides, uronic acid, aldaric acid or a combination thereof. In one or more aspects, the CAHF comprises gluconic acid, glucaric acid, glucuronic acid, n-keto-acids, C_2 to C_6 diacids or a combination thereof.

[0018] In one or more aspects, the CAHF comprises galactonic acid, galactaric acid, an oxidation product comprising predominantly (e.g., greater than about 50 weight percent) galactonic acid and/or galactaric acid with minor component species of n-keto-acids, C_2 to C_6 diacids or a combination thereof. In one or more aspects, the CAHF comprises glutamic acid. In one or more aspects, the CAHF comprises glucodialdose, 2-ketoglucose or a combination thereof.

[0019] Alternatively, the CAHF comprises a buffered glucose oxidation product, a buffered gluconic acid oxidation product, an oxidized glucuronolactone, a uronic acid oxidation product or a combination thereof. In such aspects, the buffered glucose oxidation product, the buffered gluconic acid oxidation product, or combinations thereof are buffered to a suitable pH.

[0020] The CAHF may comprise a mixture of sugars and sugar oxidation products. For example, the CAHF may comprise dextrose, glucose, fructose, sucrose, glucaric acid and, glucodialdose, gluconic acid, erythorbic acid, galactaric acid, galacturonic acid, galactonic acid, 2-ketoglucose, salts thereof, lactones thereof, or a combination thereof.

[0021] Any sugar oxidation product for use in the CAHF may comprise a counter-cation such as a Group 1 alkali metal, a Group 2 alkaline earth metal or a combination thereof. For example, the counter-cation may comprise silicates, borates, aluminum, calcium, magnesium, ammonium, sodium, potassium, cesium, strontium or a combination thereof.

[0022] In some aspects, the CAHF comprises dextrose, glucose, fructose, sucrose, glucaric acid, glucodialdose, gluconic acid erythorbic acid, galactaric acid, galacturonic acid, galactonic acid, 2-ketoglucose, salts thereof, lactones thereof, or a combination thereof.

[0023] In some aspects, the CAHF comprises a crude mixture of sugars and sugar oxidation products. In such aspects, the crude mixture may be a reaction product that contains at least 40 weight percent, alternatively at least 50 wt.%, alternatively at least 60 wt.% or alternatively from about 40 wt.% to about 60 wt.% of sugars and sugar oxidation products combined based on the total weight of the CAHF.

[0024] In some aspects, the crude mixture may be derived from a cellulose feedstock, for example, a waste cellulose feedstock. Nonlimiting examples of waste cellulose feedstocks include recycled cardboard, paperboard, fiberboard, paper, and cotton textiles. In some aspects, the cellulose feedstock comprises cardboard waste. For example, cardboard waste can be decomposed using enzymes such as cellulase and β-glucosidase in a process that leads to the formation of glucose. In one or more aspects, cardboard waste is decomposed to form a cellulose-derived reaction product comprising glucose which is subsequently subjected to conditions suitable for the formation of a reaction product comprising an oxidized glucose. In one or more aspects, the CAHF comprises a cellulose-derived reaction product comprising an oxidized glucose cellulose, glucose, and derivatives thereof.

[0025] In some aspects, the CAHF comprises a mixture of glucaric acid and gluconic acid where the sum total of glucaric acid and gluconic acid ranges from about 20 wt.% to about 80 wt.%, alternatively from about 25 wt.% to about 75 wt.% or alternatively from about 50 wt.% to about 75 wt.% based on the total weight of the CAHF. In one or more aspects, the CAHF comprises a mixture of two compounds selected from the group consisting essentially of dextrose, glucose, fructose, sucrose, glucaric acid an, glucodialdose, gluconic acid, erythorbic acid, galactaric acid, galacturonic acid, galactonic acid and 2-ketoglucose, where the ratio of the two compounds is from about 10:90 to about 90:10, alternatively from about 20:80 to about 80:20 or alternatively about 50:50.

[0026] In one or more aspects, the CAHF comprises a cellulose-derived reaction product which is present in an amount of from about 20 wt.% to about 80 wt.%, additionally or alternatively, from about 25 wt.% to about 75 wt.% or, additionally or alternatively, from about 50 wt.% to about 75 wt.% based on the total weight of the CAHF.In one or more aspects, the CAHF further comprises a solvent. Nonlimiting examples of solvent suitable for use in the CAHF include methanol, ethanol, water, acetonitrile, and combinations thereof. In one or more aspects, the solvent is water. Nonlimiting example of water suitable for use in the CAHF may be salt water, fresh water, brackish water, ground water, non-potable water (i.e., water that is not of drinking water quality), raw water (i.e., water that has not yet passed through a water treatment facility) and recycled water / reclaimed water. A solvent suitable for use is compatible with the components of the CAHF and able to solubilize the components at room temperature. In one or more aspects, the solvent constitutes the remainder of the CAHF once all other components are accounted for.

[0027] In some aspects, a method of the present disclosure comprises contacting a CAHF, a cementitious material and an aqueous fluid to form a homogenous slurry. Contacting of the components (CAHF, cementitious material, aqueous fluid) may be carried out by the mixing components using mixing equipment (e.g., a jet mixer, re-circulating mixer, a batch mixer, a blender, a mixing head of a solid feeding system) to form a pumpable slurry (e.g., a homogeneous fluid). Any container that is compatible with the components and has sufficient space can be used for mixing.

[0028] In some aspects, the cementitious material comprises a hydraulic cement. Hydraulic cements generally comprise calcium oxide, silicon dioxide, aluminum oxide, ferric oxide, and sulfur oxide, and harden by reaction with water. Nonlimiting examples of hydraulic cements suitable for use in the present disclosure include Portland cements (e.g., classes A, B, C, G, and H Portland cements), pozzolana cements, gypsum cements, phosphate cements, high alumina content cements, silica cements, high alkalinity cements, shale cements, acid/base cements, magnesia cements such as Sorel cements, fly ash cement, zeolite cement systems, kiln dust cement systems, slag cements, micro-fine cement, metakaolin, and combinations thereof. In some aspects, the cement is a Portland cement, which is a mixture of calcium oxide, silicon dioxide, aluminum oxide, ferric oxide, and sulfur oxide.

[0029] In one or more aspects, the cement is present in the slurry in an amount of from about 10 wt.% to about 90 wt.%, alternatively from about 20 wt.% to about 80 wt.% or alternatively from about 25 wt.% to about 80 wt.% based on the total weight of the cement slurry.

[0030] In one or more aspects, the CAHF is present in the slurry in a range of from about 0.01% to about 5% by weight of cementitious material (BWOC), additionally or alternatively, from about 0.1% to about 5%, additionally or alternatively, from about 0.1% to about 1% or, additionally or alternatively, from about 2% to about 10%.

[0031] In some aspects, the cementitious composition includes a sufficient amount of an aqueous fluid to form a pumpable cement slurry. The aqueous fluid may be fresh water or salt water, e.g., an unsaturated aqueous salt solution or a saturated aqueous salt solution such as brine or seawater. In some aspects, the aqueous fluid is present within the cement slurry in an amount of from about 20 % to about 180 % BWOC, alternatively from about 28 % to about 60 % BWOC, or alternatively from about 36 % to about 66 % BWOC.

[0032] In one or more aspects, the cementitious composition comprises one or more additives, in addition to the CAHF,to meet some user and/or process objective. The one or more additives can include a viscosifier, a rate of penetration enhancer, spotting fluid, a sweeping agent, a deflocculant, a degreaser, a pH buffer, a wetting agent, a lubricant, a shale inhibitor, a friction reducer, a strength-stabilizing agent, an emulsifier, an expansion agent, a salt, a fluid loss agent, a vitrified shale, a thixotropic agent, a dispersing agent, a weight reducing additive (e.g., hollow glass or ceramic beads), a heavyweight additive, a surfactant, a scale inhibitor, a clay stabilizer, a silicate-control agent, a biocide, a biostatic agent, a storage stabilizer, a filtration control additive, a suspending agent, a foaming surfactant, latex emulsions, a formation conditioning agent, elastomers, gas/fluid absorbing materials, resins, superabsorbers, mechanical property modifying additives (i.e. carbon fibers, glass fibers, metal fibers, minerals fibers, polymeric elastomers, latexes, etc.), inert particulates, a biopolymer, a polymer, a fume silica, a free fluid control additive, particulate materials, acids, bases, conventional breaking agents, lime, clay control agents, fluid loss control additives, flocculants, water softeners, foaming agents, oxidation inhibitors, thinners, scavengers, lubricants, bridging agents, a foam stabilizer, dispersants, breakers, emulsion thinner, emulsion thickener, pH control additive, lost circulation additives, stabilizers, chelating agents, oxidizers, a clay, reducers, consolidating agents, complexing agents, sequestration agents, or combinations thereof. The additives may be included singularly or in combination in effective amounts.

[0033] In some aspects, the cement slurry is formed at the jobsite or the site of intended use (e.g., at the well site where the completion operation is being performed). This site may include construction sites, mixing sites, or at an oil gas wellbore. Alternatively, the cementitious slurry is formed off-site and then later used at the site of intended use or jobsite (e.g., a well site). For example, the CAHF may be dry blended with the cement at a location remote from the jobsite, transported to the well site, formed into a pumpable slurry and placed. In another example, the cementitious slurry with the CAHF is placed in a construction location, or down a wellbore at the well site. Alternatively, the CAHF can be added as an aqueous solution (e.g., concentrate) to the mixed water that is later contacted with the cementitious material. Alternatively, the CAHF is formulated as an aqueous emulsions/dispersion that may be injected into the slurry during the cementing operation.

[0034] In some aspects, the CAHF when added to a cement slurry results in an increase in the compressive strength of the set cement when compared to a set cement lacking a CAHF. In some aspects, the compressive strength of the set cement comprising a CAHF is increased by from about 5% to about 100%, alternatively from about 10% to about 50% or, alternatively from about 5% to about 30%. In some aspects, the set cement comprising a CAHF of the type disclosed herein has a compressive strength of from about 500 psi to about 8000 psi, alternatively from about 5000 psi about 8000 psi, alternatively from about 500 psi to about 3000 psi or alternatively from about 2000 psi to about 6000 psi as determined in accordance with ASTM C39.

[0035] In some aspects, a cement slurry comprising a CAHF of the type disclosed herein has an increase in slump of from about 0.5 inches (in.) to about 9 in. alternatively from about 1 in. to about 5 in., alternatively from about 0.5 in. to about 3 in., or alternatively from about 3 in. to about 7 in. Slump is a measure of the consistency of a concrete mix, or its ability to flow, and is often used to evaluate how much water has been used in the mix. In some aspects, a cement slurry comprising a CAHF of the type disclosed herein has a slump of from about 5.6 in. to about 9 in., alternatively from about 7 in. to about 9 in., alternatively from about 6 in. to about 8 in., or alternatively from about 5.6 in. to about 7.2 in. as determined in accordance with ASTM C31.

[0036] CAHFs of the type disclosed herein may have at least three functionalities selected from the group consisting of water reducers, set retarders, accelerants, superplasticizers, corrosion inhibitors, strength enhancers, grinding aids, quality improvers, viscosity modifiers, shrinkage reducers and air entrainers.

[0037] In some aspects, a CAHF of the type disclosed herein increases the thickening time of the cement by from about 5% to about 400%, alternatively from about 100 % to about 400%, alternatively from about 5% to about 50% or alternatively from about 40% to about 200% when compared to an otherwise similar cementitious composition lacking a CAHF. In some aspects, a CAHF of the type disclosed herein has a thickening time of from about 2 hours (hrs) to about 34 hrs, alternatively from about 2 hrs to about 8 hrs, alternatively from about 4 hrs to about 30 hrs or alternatively from about 6 hrs to about 34 hrs. References herein to “thickening time” refers to the time required for the cementitious composition to achieve 70 Bearden units of Consistency (Bc) after preparation of the cementitious composition. At about 70 Bc, the cementitious composition undergoes a conversion from a pumpable fluid state to a non-pumpable gel. A measurement of Bc can be considered a thickening time test which is performed on a moving fluid. Thickening time can be measured in accordance with API RP 10B-2 clause 9 and ASTM C403.

[0038] The action of changing a cementitious composition from a fluid state to a solid state is called setting of cement and the time required for it to set is called the setting time of cement. In some aspects, a CAHF of the type disclosed herein reduces the setting time of the cementitious composition by from about 20% to about 90%, alternatively from about 40% to about 80%, alternatively from about 60% to about 90% or alternatively from about 20% to about 50% when compared to an otherwise similar cementitious composition lacking a CAHF as determined in accordance with a suitable standard reference such as API RP 10B-2 clause 9, ASTM C 150 , AASHTO T 131 or ASTM C 191.

[0039] In some aspects, a CAHF of the type disclosed herein functions as a corrosion inhibitor of the cement by reducing the conductivity of the cement by from about 10% to about 10000%, alternatively from about 400% to about 800%, alternatively from about 600% to about 10000% or alternatively from about 10% to about 500% when compared to an otherwise similar cementitious composition lacking a CAHF. In some aspects, a CAHF of the type disclosed herein has a conductivity of from about 0.1 μS/cm^2 to about 25 μS/cm^2, alternatively from about 0.1 μS/cm^2 to about 1 μS/cm^2, alternatively from about 2 μS/cm^2 to about 25 μS/cm^2 or alternatively from about 1 μS/cm^2 to about 20 μS/cm^{2}as determined in accordance with ASTM G180 Polarization Resistance Test.

[0040] In some aspects, the CAHF functions as a waterreducer. Herein, a water reducer refers to a material that reduces the water to cement ratio of a cementitious composition without adversely affecting the rheological properties of the slurry. Water reducers can decrease the concrete porosity, increase the concrete strength, increase the workability of the cement slurry, reduce the water permeability of the set cement, and reduce the diffusivity of aggressive agents in the concrete thereby improving the durability of concrete and providing a better surface finish.

[0041] In some aspects, the CAHF functions as a superplasticizer in the absence of other conventional superplasticizers. Herein, a superplasticizer, also known as a high range water reducer, refers to a material that (i) enables the production of cement with a reduction in water content of 30% or more and (ii) retards curing of the cement. Superplasticizers are used where a well-dispersed particle suspension is desired to improve the slurry rheology. Their addition to cementitious compositions allows the reduction of the water to cement ratio without negatively affecting the workability of the mixture, and enables the production of self-consolidating cementitious and high-performance cementitious compositions.

[0042] In one or more aspects, a cementitious composition comprising a CAHF has a water:cement ratio that is reduced by from about 5% to about 40%, alternatively by from about 10% to about 30% or alternatively by from about 10% to about 20% when compared to the water:cement ratio used for an otherwise identical cementitious composition lacking a CAHF. In some aspects, the CAHF is included in the cement with conventional superplasticizers such as phosphonic acid-terminated polyethers and naphthalenesulfonate/formaldehyde polymer or conventional water reducers such as lignosulfates and hydroxycarboxylic acids.

[0043] In some aspects, the CAHF functions as a set retarder in the absence of other conventional set retarders. Herein, a set retarder refers to a material used to increase the thickening time of cement slurries to enable proper placement. The need for cement retardation increases with depth due to the greater time required to complete the cementing operation and the effect of increased temperature on the cement-setting process. In one or more aspects, a cementitious composition comprising a CAHF has a set time that is increased by from about 20% to about 200%, additionally or alternatively, by from about 40% to about 150% or, additionally or alternatively, by from about 50% to about 100% when compared to the set time observed for an otherwise identical cementitious composition lacking a CAHF. In some aspects, the CAHF is included in the cement with conventional set retarders such as lignosulfonates, welan gum, xanthan gum, cellulose, polyanionic cellulose, organic acids, alkali metal salts of organic acids, carboxy hexoses and the corresponding lactones, polyvalent metal salts (e.g., polyvalent metal halides), and the like.

[0044] In some aspects, the CAHF functions as an accelerant in the absence of other conventional accelerants. Herein, an accelerant refers to a material used to reduce the time required for the set cement to develop compressive strength sufficient to enable operations to continue. Accelerators are generally used in near-surface applications in which the temperature is relatively low. In one or more aspects, a cementitious composition comprising a CAHF reduces the amount of time required for the set cement to develop compressive strength by from about 10% to about 100%, additionally or alternatively, by from about 20% to about 80% or, additionally or alternatively, by from about 25% to about 50% when compared to the set time observed for an otherwise identical cementitious composition lacking a CAHF. In some aspects, the CAHF is included in the cement with one or more conventional accelerants such as calcium nitrite, calcium nitrate, calcium chloride, calcium formate, or tricalcium silicate.

[0045] In some aspects, the CAHF functions as a corrosion inhibitor in the absence of other conventional corrosion inhibitors. Herein, a corrosion inhibitor refers to a material used to protect metal-containing components (e.g., iron-containing, steel-containing) in an operation from degradation by caustic materials. As the CAHF comprises a diacid, it may provide corrosion resistance to metal surfaces by binding to metal surfaces, and passivating and forming a corrosion resistant film. In one or more aspects, the CAHF may be effective to solubilize metal cations and/or to keep metal cations in solution, providing a higher concentration of metals in solution. A higher concentration of metal ions in solution may lead to a lower effective concentration gradient, which may thereby limit and decrease the mass transfer rate and corrosion rate from the solid metal to the aqueous or colloidal phase. For example, the CAHF may solubilize metals such iron, copper, manganese, and molybdenum and increase the solubility of these metals in solution by equal to or greater than about 10%, additionally or alternatively, equal to or greater than about 25%, additionally or alternatively, equal to or greater than about 50% or, additionally or alternatively, from about 10% to about 100% when compared to the solubility of the metal in the absence of a CAHF. The use of a CAHF of the type disclosed herein as a corrosion inhibitor may result in economic advantages such as reduction in material costs, increased batching time, and may display enhanced compatibility when carrying out operations in warmer climates. In some aspects, the CAHF is included in the cement with conventional corrosion inhibitors such as nitrites and nitrates.

[0046] In some aspects, the CAHF functions as an air entrainer in the absence of other conventional air entrainers. Herein, an air entrainer refers to a material that facilitates the intentional creation of air bubbles in the cementitious slurry. The air bubbles are created during mixing of the easy flowing, not hardened cementitious material, and most of them survive to be part of the hardened cementitious material. In some aspects, air entrainment may be effective to increase the durability of the hardened cementitious material, especially in climates subject to freeze-thaw cycles, and to increase workability of the concrete while in a plastic (flowing) state. In some aspects, the CAHF is combined with conventional air entrainers such as natural wood resins, animal fats, wetting agents, and water-soluble soaps of certain acids.

[0047] In other aspects, the CAHF functioning as a water reducer, reduces the water needed to form a pumpable cementitious slurry having one or more user and/or application desired properties. The cementitious composition having a lower water to cement ratio may exhibit a decreased permeability when compared to a cementitious composition prepared in the absence of a CAHF. The permeability of the cementitious composition may be decreased by from about 5% to about 50%, additionally or alternatively, from about 10% to about 40% or, additionally or alternatively, from about 25% to about 40% when compared to the permeability of an otherwise identical cementitious composition lacking a CAHF. The cementitious composition exhibiting reduced permeability may display beneficial attributes such as improved freeze-thaw resistance and a reduced degree of chemical attack by species such as sulfates and chlorides. Low permeability cementitious compositions can also help reduce the potential for reinforcing steel to corrode when exposed to chlorides by limiting the permeation of those chlorides into the cementitious composition. When reinforcing steel comes into contact with a cementitious composition, a chemical reaction occurs between the steel and the concrete that causes a protective layer (a passive layer) to develop around the reinforcing steel. This passive layer protects against corrosion of the reinforcing steel. If the cementitious composition is exposed to de-icing salts, these salts can migrate down to the reinforcing steel through small pores in the cementitious composition. Not intending to be bound by theory, over time, the chlorides in these salts can react with the reinforcing steel, breaking down the passive layer and causing the steel to corrode. When reinforcing steel in concrete corrodes, the product of that corrosion (rust) takes up more volume than the original steel and causes the cementitious composition to crack. After cracks develop, the deterioration accelerates as chlorides allow easy ingress to the reinforcing steel. The deterioration of both the cementitious composition and reinforcing steel compromises the integrity of the structure.

[0048] Additionally, a cementitious composition comprising the CAHF may be generated using a lower ratio of water to cement without altering workability (slump). In such aspects, the amount of cement utilized is reduced without altering the compressive strength when compared to a concrete prepared in the absence of a CAHF.

[0049] Further, in such aspects the lower cement content may result in a cementitious composition having a decreased carbon (CO_2) footprint. For example, the CAHF may reduce the carbon footprint of the cementitious composition by from about 1% to about

10% or alternatively from about 1% to about 5% when compared to the carbon footprint of a cementitious composition lacking a CAHF.

[0050] Additionally or alternatively, in some aspects, the CAHF reduces shrinkage and increases the temperature-insensitive settling of concrete.

[0051] A schematic depiction of a system for the production of a CAHF is presented in Figure 1. With reference to Figure 1, a sugar source (e.g., a cellulose-derived reaction product) is provided as the reactant to tank 10 which is conveyed to an Enzyme Oxidation Reactor (EOR) 20. The EOR 20 contains one or more enzymes capable of oxidizing the sugar source. For example, the EOR may comprise an oxidizing enzyme (e.g., alcohol oxidase, a copper radical oxidase). The EOR 20 may be operated under any conditions suitable for the formation of an oxidized sugar source, hereinafter termed a first intermediate. The first intermediate from EOR 20 may then be conveyed to a Metal Oxidation Reactor (MOR) 30.

[0052] In some aspects, the MOR 30 comprises a metal catalyst, alternatively a transition metal catalyst, alternatively a noble metal catalyst, or alternatively a metal oxidation catalyst. In some aspects, the metal catalyst is a metal oxidation catalyst or a supported metal catalyst. In some aspects, the support comprises carbon, silica, alumina, titania (TiO_2), zirconia (ZrO_2), a zeolite, or any combination thereof, which contains less than about 1.0 weight percent (wt.%), additionally or alternatively, less than about 0.1 wt.% or, additionally or alternatively, less than about 0.01 wt.% SiO_2 binders based on the total weight of the support.

[0053] In one or more aspects, the metal comprises one or more noble metals, for example, a Group 8 metal (e.g., Re, Os, Ir, Pt, Ru, Rh, Pd, Ag), a 3d transition metal, an early transition metal, or combinations thereof. In some aspects, the metal oxidation catalyst comprises gold, Au. The intermediate may be contacted with a metal oxidation catalyst in the MOR 30 under conditions suitable for oxidation of the first intermediate to form a second intermediate that is further oxidized .

[0054] In one or more aspects, the first intermediate, the second intermediate or a combination thereof may be used without additional processing as the CAHF. In one aspect or more aspects, at least a portion of the sugar source in Figure 1 is from waste streams, such as recycled cardboard. Additionally or alternatively, the sugar source in Figure 1 may be cellulosic sugars.

[0055] In some aspects, a CAHF of the type disclosed herein is a readily biodegradable product obtained from a chemoenzymatic process. This is in sharp contrast to conventional cement additives such as lignosulfonates, which commonly go through a process where sulfuric or nitric acid is introduced, producing environmentally detrimental sulfate or nitrate-based waste.

[0056] Use of a CAHF of the type disclosed herein is anticipated to reduce the amount of nitrites, nitrates, and sulfate products that are manufactured, for example, for inclusion in a cementitious composition, leading to a lower carbon footprint, as well as ancillary benefits such as lower nitrate/nitrite wastewater discharge.

[0057] In some aspects, addition of a CAHF to a cementitious material result in a delayed setting of the cementitious material. Delayed setting of the cementitious can advantageously enable increased bleed water, which is beneficial for freshly poured concrete flatwork exposed to hot dry windy environment.

[0058] A CAHF may be used as a set retarder in gypsum plaster formulations. In gypsum formulations, CAHF can replace traditional retarders (e.g., tartaric acid).

[0059] In one or more aspects, the CAHF is present in the gypsum plaster formulation in an amount ranging from about 0.01 wt.% to about 10 wt.% by weight of gypsum, alternatively from about 0.01 wt.% to about 5 wt.%, alternatively from about 0.1 wt.% to about 5 wt.%, alternatively from about 0.1 wt.% to about 1 wt.% or alternatively from about 2 wt.% to about 10 wt.%.

[0060] Advantageously, a CAHF of the type disclosed herein is very flexible in terms of its compatibility and can also be combined with existing corrosion inhibitors, set retarders, water reducers, air entrainers, accelerators and superplasticizers, as desired to further enhance their performance. Additional benefits of the use of a CAHF with a cementitious material include enabled re-use of returned concrete; enablement of normal later age strength development under hot weather conditions; eliminating the discharge of truck wash water which could then be used as concrete batch water For example, using a CAHF as set retarders and water reducers may allow for the use of cementitious material that is a mixture used concrete and fresh concrete. Without wishing to be limited by theory, in hot weather conditions, concrete sets fast and becomes brittle. CAHFs of the type disclosed herein may delay this process and facilitate the development of compressive strength.

[0061] The following are additional aspects of the presently disclosed subject matter:

[0062] A first aspect which is a multifunctional cement additive comprising (i) a sugar derivative comprising glucaric acid, gluconic acid, glucuronic acid, glucose oxidation products, gluconic acid oxidation products disaccharides, oxidized disaccharides, uronic acid, aldaric acid, galactonic acid, galactaric acid, glutamic acid glucodialdose, 2-ketoglucose, salts thereof, lactones thereof, or a combination thereof and (ii) a solvent.

[0063] A second aspect which is the additive of the first aspect wherein the sugar derivative is sourced from a cellulose feedstock.

[0064] A third aspect which is the additive of any of the first through second aspects wherein the sugar derivative comprises a crude mixture of sugars and sugar oxidation products.

[0065] A fourth aspect which is the additive of the third aspect wherein the crude mixture is a reaction product that contains at least 40 wt.% sugars and sugar oxidation products based on the total weight of the additive.

[0066] A fifth aspect which is the additive of any of the first through fourth aspects wherein the sugar derivative comprises a mixture of glucaric acid and gluconic acid.

[0067] A sixth aspect which is the additive of fifth aspect wherein the amount of glucaric acid and gluconic acid ranges from about 20 wt.% to about 80 wt.% based on the total weight of the additive.

[0068] A seventh aspect which is the additive of any of the first through sixth aspects wherein the sugar derivative is a mixture of two compounds selected from the group consisting essentially of dextrose, glucose, fructose, sucrose, glucaric acid, glucodialdose, gluconic acid, erythorbic acid, galactaric acid, galacturonic acid, galactonic acid and 2-ketoglucose.

[0069] An eighth aspect which is the additive of any of the seventh aspect where a ratio of the two compounds is from about 10:90 to about 90:10.

[0070] A ninth aspect which is the additive of any of the first through ninth aspects wherein the solvent comprises methanol, ethanol, water, acetonitrile, or a combination thereof.

[0071] A tenth aspect which is a composition comprising (a) a cementitious material (b) a multifunctional additive comprising a sugar oxidation product and (c) a solvent wherein the multifunctional additive comprising a sugar oxidation product is a mixture of two compounds selected from the group consisting essentially of dextrose, glucose, fructose, sucrose, glucaric acid, glucodialdose, gluconic acid, erythorbic acid, galactaric acid, galacturonic acid, galactonic acid and 2-ketoglucose.

[0072] An eleventh aspect which is the composition of the tenth aspect wherein the multifunctional additive comprising a sugar oxidation product comprises a mixture of glucaric acid and gluconic acid.

[0073] A twelfth aspect which is the composition of any of the tenth through eleventh aspects wherein the amount of glucaric acid and gluconic acid ranges from about 0.1% to about 5% based on the total weight of cementitious material.

[0074] A thirteenth aspect which is the composition of any of the tenth through twelfth aspects wherein the cementitious material comprises cement, concrete, shotcrete, mortar, grout, asphalt, or a combination thereof.

[0075] A fourteenth aspect which is the composition of any of the tenth through thirteenth aspects wherein the cementitious material comprises Portland cements, pozzolana cements, gypsum cements, phosphate cements, high alumina content cements, silica cements, high alkalinity cements, shale cements, acid/base cements, magnesia cements, fly ash cement, zeolite cement systems, cement kiln dust cement systems, slag cements, micro-fine cement, metakaolin, limestone cements or a combination thereof.

[0076] A fifteenth aspect which is the composition of any of the tenth through fourteenth aspects having a water: cement ratio that is reduced by from about 5% to about 40% when compared to an otherwise identical composition lacking a multifunctional additive comprising a sugar oxidation product.

[0077] A sixteenth aspect which is the composition of any of the tenth through fifteenth aspects having a set time that is increased by from about 20% to about 200% when compared to the set time observed for an otherwise identical cementitious composition lacking a multifunctional additive comprising a sugar oxidation product.

[0078] A seventeenth aspect which is the composition of any of the tenth through sixteenth aspects having a permeability that is decreased by from about 5% to about 50% when compared to an otherwise identical cementitious composition lacking a multifunctional additive comprising a sugar oxidation product.

[0079] An eighteenth aspect which is the composition of any of the tenth through seventeenth aspects having an increase in slump of from about 0.5 inches (in.) to about 9 in. when compared to an otherwise identical cementitious composition lacking a multifunctional additive comprising a sugar oxidation product.

[0080] A nineteenth aspect which is the composition of any of the tenth through eighteenth aspects having a thickening time that is increased by from about 5% to about 400% when compared to an otherwise identical cementitious composition lacking a multifunctional additive comprising a sugar oxidation product.

[0081] A twentieth aspect which is the composition of any of the tenth through nineteenth aspects having a compressive strength of from about 500 psi to about 8000 psi when set.

EXAMPLES

[0082] The subject matter having been generally described, the following examples are given as particular aspects of the disclosure and are included to demonstrate the practice and advantages thereof, as well as aspects and features of the presently disclosed subject matter. It should be appreciated by those of skill in the art that the techniques disclosed in the examples which follow represent techniques discovered by the inventors to function well in the practice of the present subject matter, and thus can be considered to constitute suitable modes for its practice. However, those of skill in the art should, in light of the present disclosure, appreciate that many changes can be made in the specific aspects which are disclosed and still obtain a like or similar result without departing from the scope of the instant disclosure. It is understood that the examples are given by way of illustration and are not intended to limit the specification or the claims to follow in any manner.

[0083] In these examples, two CAHF formulations of the type disclosed herein were evaluated as concrete additives or admixtures. The first formulation was designated, LG60, and was a mixture of sodium gluconate, gluconic acid, and water with a solids amount of 60 weight percent. The second formulation was designated GOGA, which was mixture of gluconic acid, glucaric acid, and water with a solids amount of 40 weight percent.

EXAMPLE 1

[0084] The ability of a CAHF of the type disclosed herein to function as a set retarder was evaluated. The CAHF formulations investigated contained as indicated below: LAFARGE ALPENA Type II low alkali 0.54% 517 cement (LA Cement), ST MARY'S Type II Medium Alkali cement (MA Cement), Agg. Resources Midway PIT 2NS SAND (Sand), CARMEUSE L & ST. CEDARVILLE #67 stone (Stone), LG60, GOGA and water. Cement compositions were produced according to ASTM C1810, Method B. The various compositions that were evaluated are listed in Table 1 for low alkali cement and Table 2 for medium alkali cement. In Table 1 and Table 2 'oz/cwt' stands for ounces of admixture per 100 lbs of cement. Slump, set time, and compression strength were measured according to ASTM C31, ASTM C403, and ASTM C39 (on 4"X8" cylinders), respectively.

Table 1

	Formulations			
	Control	**LG60 - 4**	**GOGA - 4**	**GOGA - 6**
LA Cement (lbs/yd^3)	517	517	517	517
Sand (lbs/yd^3)	1528	1569	1569	1569
Stone (lbs/yd^3)	1825	1825	1825	1825
Water (lbs/yd^3)	286	272	272	262
LG60 (oz/cwt)	0	4	0	0
GOGA (oz/cwt)	0	0	4	6
	Properties			
Slump (in), ASTM C31	5.25	6.5	8	8.25
Initial set time (hr:min), ASTM C403	4:20	8:32	16:35	31:14
Final set time (hr:min), ASTM C403	5:57	13:23	18:41	33:44
Compression strength at 28 days (psi), ASTM C39	5650	6250	6580	7730

Table 2

	Formulations			
	Control	**LG60 - 4**	**GOGA - 4**	**GOGA - 6**
MA Cement (lbs/yd^3)	517	517	517	517
Sand (lbs/yd3)	1528	1569	1569	1569
Stone (lbs/yd3)	1825	1825	1825	1825
Water (lbs/yd3)	297	279	279	267
LG60 (oz/cwt)	0	4	0	0
GOGA (oz/cwt)	0	0	4	6
	Properties			
Slump (in), ASTM C31	5.5	6.75	7.25	7
Initial set time (hr:min), ASTM C403	4:29	7:20	17:34	26:06
Final set time (hr:min), ASTM C403	6:02	8:25	20:12	28:07
Compression strength at 28 days (psi), ASTM C39	5240	6130	6410	6760

[0085] The results presented in Table 1 and Table 2 indicate that LG60 and GOGA act as set retarders (increase set time) and improve compressive strength of the cementitious composition.

EXAMPLE 2

[0086] The ability of a CAHF of the type disclosed herein to function as a corrosion inhibitor was evaluated. The CAHF containing cement compositions investigated contained as indicated below: HOLCIM ST GENEVIEVE PLT. Type II Cement (Cement); Agg. Resources Midway PIT 2NS (Sand); STONECO Ottawa Lake 1/2" Limestone (Limestone); BASF MASTERAIR VR, air entrainer; LG60; GOGA and water. Cement compositions were produced according to ASTM C1810, Method B. The various cement compositions that were evaluated are listed in Table 3. In Table 3, 'oz/cwt' stands for ounces of admixture per 100 lbs of cement. The corrosion performance is characterized by measuring electrical conductivity (μS/cm^2) according to ASTM G180 and a lower value means a cement composition with higher corrosion resistance.

Table 3

	Formulations		
	Control	**LG60**	**GOGA**
Cement (lbs/yd^3)	550	550	550
Sand (lbs/yd^3)	1239	1239	1239
Limestone (lbs/yd^3)	1800	1800	1800
Water (lbs/yd^3)	275	275	275
Air entrainer (oz/cwt)	0.8	0.5	0.5
LG60 (oz/cwt)	0	0.23	0
GOGA (oz/cwt)	0	0	0.23
	Properties		
Electrical conductance (μS/cm^2)	82	29	22

[0087] The results presented in Table 3 indicate that LG60 and GOGA act as corrosion inhibitors in cement compositions.

EXAMPLE 3

[0088] The ability of a CAHF of the type disclosed herein to function as a water reducer was evaluated. The CAHF-containing cement compositions investigated contained as indicated below: LAFARGE ALPENA Type IL (10) (Cement); AGG. RESOURCES MIDWAY PIT 2NS sand (Sand); CARMEUSE L & ST. CEDARVILLE #67 stone (Stone); LG60; 53% calcium/sodium lignosulfonate (Ligno); LG60 blend - 16% LG60 + 4% triethanolamine + 1% sodium thiocyanate + 3% corn syrup; Ligno blend - 30% Ligno + 5% triethanolamine + 5% corn syrup and water. CAHF-containing cement compositions were produced according to ASTM C1810, Method B. The various compositions that were evaluated are listed in Table 4. In Table 4 'oz/cwt' stands for ounces of admixture per 100 lbs of cement. Slump, air entrainment, and compression strength were measured according to ASTM C31, ASTM C231, and ASTM C39 (on 4"X8" cylinders), respectively.

Table 4

	Formulations				
	Control	**LG60**	**Ligno**	**LG60 blend**	**Ligno blend**
Cement (lbs/yd^3)	517	517	517	517	517
Sand (lbs/yd3)	1525	1570	1570	1570	1570
Stone (lbs/yd3)	1750	1750	1750	1750	1750
Water (lbs/yd3)	286	269	269	269	269
20 wt.% LG60 (oz/cwt)	0	4	0	0	0
40 wt.% Ligno (oz/cwt)	0	0	4	0	0
LG60 blend (oz/cwt)	0	0	0	4	0
Ligno blend (oz/cwt)	0	0	0	0	4
	Properties				
Slump (in), ASTM C31	5.5	4.5	4.25	3.75	4.25
Air (%), ASTM C231	1.9	2.1	3.5	2.2	3.2
Compression strength at 28 days (psi), ASTM C39	5400	6340	5960	6210	5960

[0089] The results presented in Table 4 indicate that compositions containing the CAHF LG60 displayed comparable water reduction to lignosulfonate which lead to lower air entrainment (lower porosity) and higher compressive strength. The result demonstrates the CAHF is an effective water reducer.

[0090] The subject matter having been shown and described, modifications thereof can be made by one skilled in the art without departing from the spirit and teachings of the subject matter. The aspects described herein are exemplary only and are not intended to be limiting. Many variations and modifications of the subject matter disclosed herein are possible and are within the scope of the disclosed subject matter. Where numerical ranges or limitations are expressly stated, such express ranges or limitations should be understood to include iterative ranges or limitations of like magnitude falling within the expressly stated ranges or limitations (e.g., from about 1 to about 10 includes, 2, 3, 4, etc.; greater than 0.10 includes 0.11, 0.12, 0.13, etc.). Use of the term "optionally" with respect to any element of a claim is intended to mean that the subject element is required, or alternatively, is not required. Both alternatives are intended to be within the scope of the claim. Use of broader terms such as comprises, includes, having, etc. should be understood to provide support for narrower terms such as consisting of, consisting essentially of, comprised substantially of, etc.

[0091] Accordingly, the scope of protection is not limited by the description set out above but is only limited by the claims which follow, that scope including all equivalents of the subject matter of the claims. Each and every claim is incorporated into the specification as an aspect of the present disclosure. Thus, the claims are a further description and are an addition to the aspects of the present invention. The discussion of a reference herein is not an admission that it is prior art to the presently disclosed subject matter, especially any reference that may have a publication date after the priority date of this application. The disclosures of all patents, patent applications, and publications cited herein are hereby incorporated by reference, to the extent that they provide exemplary, procedural or other details supplementary to those set forth herein.

CLAIMS

What is claimed is:

1. A multifunctional cement additive, comprising:

(i) a sugar derivative comprising glucaric acid, gluconic acid, glucuronic acid, glucose oxidation products, gluconic acid oxidation products disaccharides, oxidized disaccharides, uronic acid, aldaric acid, galactonic acid, galactaric acid, glutamic acid glucodialdose, 2-ketoglucose, salts thereof, lactones thereof, or a combination thereof; and

(ii) a solvent.

2. The additive of claim 1, wherein the sugar derivative is sourced from a cellulose feedstock.

3. The additive of claim 1, wherein the sugar derivative comprises a crude mixture of sugars and sugar oxidation products.

4. The additive of claim 3, wherein the crude mixture is a reaction product that contains at least 40 wt.% sugars and sugar oxidation products based on the total weight of the additive.

5. The additive of claim 1, wherein the sugar derivative comprises a mixture of glucaric acid and gluconic acid.

6. The additive of claim 5, wherein the amount of glucaric acid and gluconic acid ranges from about 20 wt.% to about 80 wt.% based on the total weight of the additive.

7. The additive of claim 1, wherein the sugar derivative is a mixture of two compounds selected from the group consisting essentially of dextrose, glucose, fructose, sucrose, glucaric acid, glucodialdose, gluconic acid, erythorbic acid, galactaric acid, galacturonic acid, galactonic acid, and 2-ketoglucose.

8. The additive of claim 7, where a ratio of the two compounds is from about 10:90 to about 90:10.

9. The additive of claim 1, wherein the solvent comprises methanol, ethanol, water, acetonitrile, or a combination thereof.

10. A composition, comprising:

(a) a cementitious material;

(b) a multifunctional additive comprising a sugar oxidation product; and

(c) a solvent;

wherein the multifunctional additive comprising a sugar oxidation product is a mixture of two compounds selected from the group consisting essentially of dextrose, glucose, fructose, sucrose, glucaric acid, glucodialdose, gluconic acid, erythorbic acid, galactaric acid, galacturonic acid, galactonic acid, and 2-ketoglucose.

11. The composition of claim 10, wherein the multifunctional additive comprising a sugar oxidation product comprises a mixture of glucaric acid and gluconic acid.

12. The composition of claim 11, wherein the amount of glucaric acid and gluconic acid ranges from about 0.1% to about 5% based on the total weight of cementitious material.

13. The composition of claim 10, wherein the cementitious material comprises cement, concrete, shotcrete, mortar, grout, asphalt, or a combination thereof.

14. The composition of claim 10, wherein the cementitious material comprises Portland cements, pozzolana cements, gypsum cements, phosphate cements, high alumina content cements, silica cements, high alkalinity cements, shale cements, acid/base cements, magnesia cements, fly ash cement, zeolite cement systems, cement kiln dust cement systems, slag cements, micro-fine cement, metakaolin, limestone cements or a combination thereof.

15. The composition of claim 10, having a water:cement ratio that is reduced by from about 5% to about 40% when compared to an otherwise identical composition lacking a multifunctional additive comprising a sugar oxidation product.

16. The composition of claim 10, having a set time that is increased by from about 20% to about 200% when compared to the set time observed for an otherwise identical cementitious composition lacking a multifunctional additive comprising a sugar oxidation product.

17. The composition of claim 10, having a permeability that is decreased by from about 5% to about 50% when compared to an otherwise identical cementitious composition lacking a multifunctional additive comprising a sugar oxidation product.

18. The composition of claim 10, having an increase in slump of from about 0.5 inches (in.) to about 9 in. when compared to an otherwise identical cementitious composition lacking a multifunctional additive comprising a sugar oxidation product.

19. The composition of claim 10, having a thickening time that is increased by from about 5% to about 400% when compared to an otherwise identical cementitious composition lacking a multifunctional additive comprising a sugar oxidation product.

20. The composition of claim 10, having a compressive strength of from about 500 psi to about 8000 psi when set.

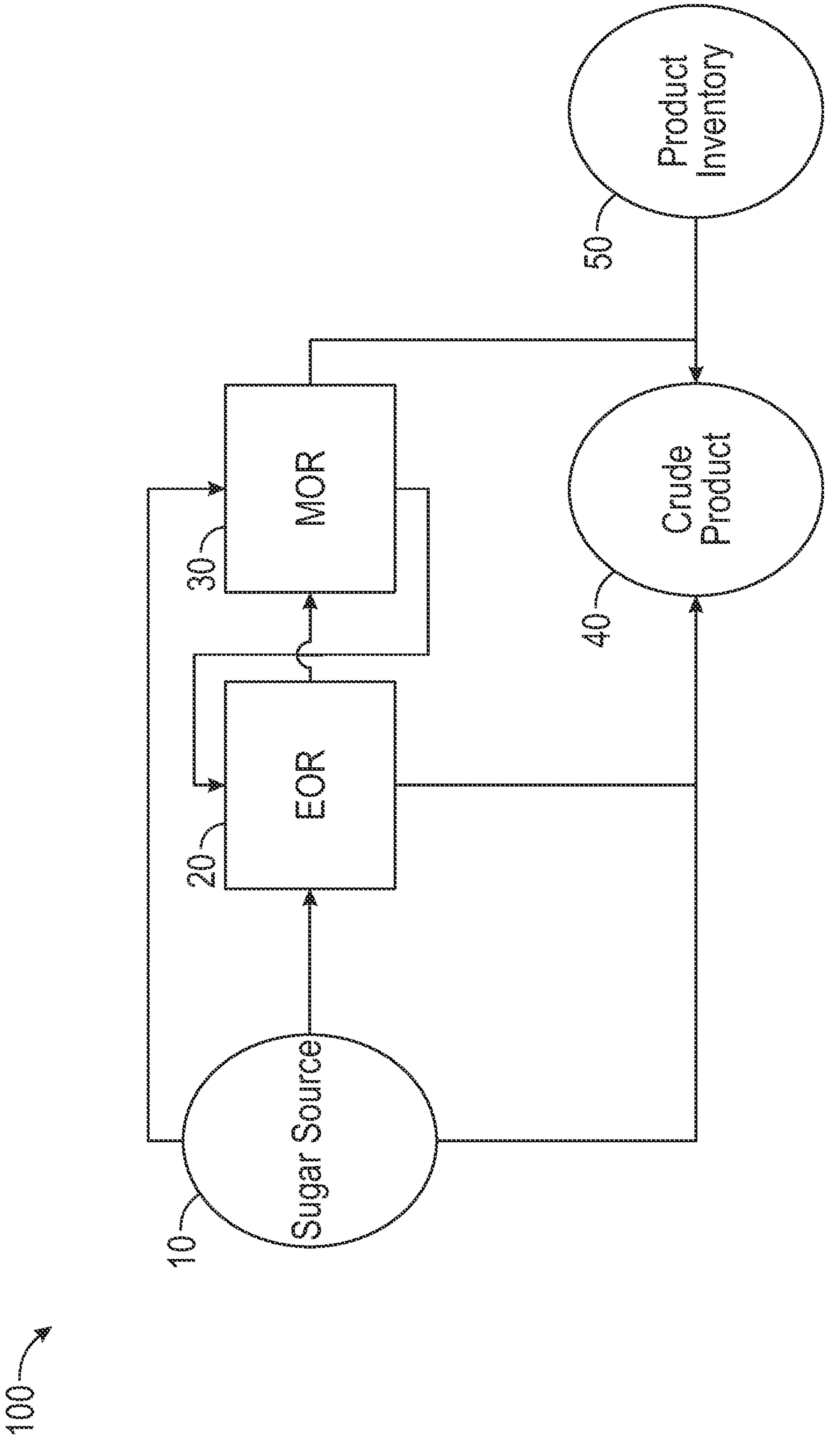
100
10
Sugar Source
20
EOR
30
MOR
40
Crude Product
50
Product Inventory

FIG. 1

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 24/19954

A. CLASSIFICATION OF SUBJECT MATTER

IPC - INV. C04B 24/10, C04B 24/38, C13K 1/06 (2024.01)
ADD. C13B 50/00 (2024.01)

CPC - INV. C04B 24/10, C04B 24/38, C13K 1/06

ADD. C13B 50/006

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 --- Y	WO 2022/010962 A1 (Solugen, Inc.) 13 January 2022 (13.01.2022) Para [0005]; [0006]; [0021]; [0022]; [0023]; [0024]; [0025]; [0027]; [0038]; [0078]	1 and 3-20 --------- 2
Y	US 2015/0010969 A1 (Asahi Kasei Chemicals Corporation) 08 January 2015 (08.01.2015) Para [0001]; [0025]; [0027]	2
A	WO 2000/044487 A1 (W.R. Grace & CO.-CONN) 26 January 2000 (26.01.2000) entire document	1-20
A	US 4,466,834 A (Dodson et al.) 21 August 1984 (21.08.1984) entire document	1-20

☐ 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	Date of mailing of the international search report
14 May 2024	JUN 24 2024

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