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

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
1 September 2016 (01.09.2016)

WIPO | PCT

(10) International Publication Number
WO 2016/137623 A1

(51) International Patent Classification:
C04B 14/16 (2006.01) *C04B 24/16* (2006.01)
C04B 28/10 (2006.01) *C04B 16/06* (2006.01)
C04B 24/00 (2006.01) *C04B 41/45* (2006.01)

(21) International Application Number:
PCT/US2016/014690

(22) International Filing Date:
25 January 2016 (25.01.2016)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
14/634,764 28 February 2015 (28.02.2015) US

(71) Applicant: **HALLIBURTON ENERGY SERVICES, INC.** [US/US]; 3000 N. Sam Houston Parkway E., Houston, Texas 77032-3219 (US).

(72) Inventors: **PISKLAK, Thomas**; 14122 Cellini Drive, Cypress, Texas 77429 (US). **AGAPIOU, Kyriacos**; 1804 Anita Street, Houston, Texas 77004 (US). **MORGAN, Ronnie Glen**; 14069 North 2770 Road, Waurika, Oklahoma 73573 (US). **LEWIS, Samuel Jason**; 3 Dahlia Trail Pl., Spring, Texas 77382 (US). **BROTHERS, Lance E.**; 928 S. 8th Street, Chickasha, Oklahoma 73018 (US).

(74) Agent: **TUMEY, Corey**; Tumey LLP, P.O. Box 22188, Houston, Texas 77227 (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, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, 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, 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))*

— *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))*

(54) Title: SET-DELAYED CEMENT COMPOSITIONS COMPRISING PUMICE AND ASSOCIATED METHODS

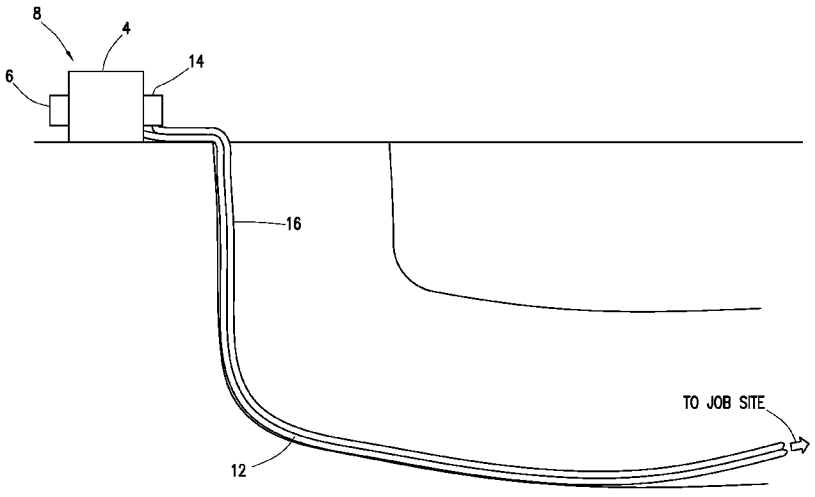


FIG. 4

(57) Abstract: Disclosed is a method of spraying a surface with a set-delayed cement. The method comprises providing a set-delayed cement composition comprising water, pumice, hydrated lime, and a set retarder; spraying a surface with the set-delayed cement composition; and allowing the set-delayed cement composition to set on the surface.

WO 2016/137623 A1

SET-DELAYED CEMENT COMPOSITIONS COMPRISING PUMICE AND ASSOCIATED METHODS

BACKGROUND

[0001] Examples relate to cementing operations and, in certain examples, to set-delayed cement compositions and methods of using set-delayed cement compositions in surface operations.

[0002] Cement compositions may be used in a variety of surface operations. For example, in spraying application, a cement handling system may spray cement into a pond, creek, or ditch, in order to line the structures with an impermeable barrier. Similarly, cement may be used to coat other structures such as walls, floors, or ceilings in order to provide support and in some applications, heat resistance. In construction applications, cement may be used to stabilize supports in a mine or attached to a pier.

[0003] A broad variety of cement compositions have been used in surface cementing operations. In some instances, set-delayed cement compositions have been used. Set-delayed cement compositions are characterized by being capable of remaining in a pumpable fluid state for at least about one day (e.g., at least about 7 days, about 2 weeks, about 2 years or more) at room temperature (e.g., about 80° F). When desired for use, the set-delayed cement compositions should be capable of being activated whereby reasonable compressive strengths are developed. For example, a cement set activator may be added to a set-delayed cement composition whereby the composition sets into a hardened mass. Among other things, the set-delayed cement composition may be suitable for use in surface applications, for example, where it is desired to prepare the cement composition in advance. This may allow, for example, the cement composition to be stored prior to its use. In addition, this may allow, for example, the cement composition to be prepared at a convenient location and then transported to the job site. Accordingly, capital expenditures may be reduced due to a reduction in the need for on-site bulk storage and mixing equipment. This may be particularly useful for applications where space and equipment may be limited.

[0004] While set-delayed cement compositions have been developed heretofore, challenges exist with their successful use in surface cementing operations. For example, set-delayed cement compositions prepared with Portland cement may have undesired gelation issues which can limit their use and effectiveness in cementing operations. Other set-delayed compositions that have been developed, for example, those comprising hydrated lime and

quartz, may be effective in some operations but may have limited use at lower temperatures as they may not develop sufficient compressive strength when used in applications where low temperature may be an issue.

BRIEF DESCRIPTION OF THE DRAWINGS

[0005] These drawings illustrate certain aspects of some of the embodiments of the present method, and should not be used to limit or define the method.

[0006] FIG. 1 illustrates a system for the preparation of a set-delayed cement composition and subsequent delivery of the composition to a cementing application site.

[0007] FIG. 2 illustrates the use of the set-delayed cement composition in a spray application for a pond.

[0008] FIG. 2A illustrates an enlarged perspective of a portion of the example illustrated in FIG. 2.

[0009] FIG. 3 illustrates a marine construction application, wherein a set-delayed cement composition may be pumped through a conduit to secure in place a beam to be used in the extension of pier.

[0010] FIG. 4 illustrates the use of a set-delayed cement composition in a mine operation.

DETAILED DESCRIPTION

[0011] Examples relate to cementing operations and, in certain examples, to set-delayed cement compositions and methods of using set-delayed cement compositions in surface operations. In particular examples, the set-delayed cement compositions may be used to line ponds, creeks, ditches, etc. In further examples, the set-delayed cement compositions may be used for marine construction, mine construction, or cement operations necessitating cement spraying. Additional examples may comprise using the set-delayed cement compositions to coat structures to amongst other reasons, impart heat resistance to the structures.

[0012] The set-delayed cement compositions may generally comprise water, pumice, hydrated lime, and a set retarder. Optionally, the set-delayed cement compositions may further comprise a dispersant and/or a cement set activator. The set-delayed cement compositions may be foamed. Advantageously, the set-delayed cement compositions may be capable of remaining in a pumpable fluid state for an extended period of time. For example, the set-delayed cement compositions may remain in a pumpable fluid state for at least about 1 day, about 2 weeks, about 2 years, or longer. Advantageously, the set-delayed cement compositions may develop reasonable compressive strengths after activation at relatively low temperatures. While the set-delayed cement compositions may be suitable for a number of cementing operations, they may be particularly suitable for use in applications in which alkali silicate reactions occur. Alkali silicate reactions may crack or deform concrete. The set-delayed cement compositions described herein may prevent alkali silicate reactions from occurring, thus mitigating cracks and deformations in any concrete in which the set-delayed cement composition is used.

[0013] The water may be from any source provided that it does not contain an excess of compounds that may undesirably affect other components in the set-delayed cement compositions. For example, a set-delayed cement composition may comprise fresh water or salt water. Salt water generally may include one or more dissolved salts therein and may be saturated or unsaturated as desired for a particular application. Seawater or brines may be suitable for use in embodiments. Further, the water may be present in an amount sufficient to form a pumpable slurry. In certain examples, the water may be present in the set-delayed cement composition in an amount in the range of from about 33% to about 200% by weight of the pumice. In certain examples, the water may be present in the set-delayed cement

compositions in an amount in the range of from about 35% to about 70% by weight of the pumice. One of ordinary skill in the art with the benefit of this disclosure will recognize the appropriate amount of water for a chosen application.

[0014] Pumice may be present in the set-delayed cement compositions. Generally, pumice is a volcanic rock that can exhibit cementitious properties in that it may set and harden in the presence of hydrated lime and water. The pumice may also be ground. Generally, the pumice may have any particle size distribution as desired for a particular application. In certain examples, the pumice may have a mean particle size in a range of from about 1 micron to about 200 microns. The mean particle size corresponds to d50 values as measured by particle size analyzers such as those manufactured by Malvern Instruments, Worcestershire, United Kingdom. In specific examples, the pumice may have a mean particle size in a range of from about 1 micron to about 200 microns, from about 5 microns to about 100 microns, or from about 10 microns to about 50 microns. In one particular example, the pumice may have a mean particle size of less than about 15 microns. An example of a suitable pumice is available from Hess Pumice Products, Inc., Malad, Idaho, as DS-325 lightweight aggregate, having a particle size of less than about 15 microns. It should be appreciated that particle sizes too small may have mixability problems while particle sizes too large may not be effectively suspended in the compositions. One of ordinary skill in the art, with the benefit of this disclosure, should be able to select a particle size for the pumice suitable for a chosen application.

[0015] Hydrated lime may be present in the set-delayed cement compositions. As used herein, the term "hydrated lime" will be understood to mean calcium hydroxide. In some embodiments, the hydrated lime may be provided as quicklime (calcium oxide) which hydrates when mixed with water to form the hydrated lime. The hydrated lime may be included in the set-delayed cement compositions, for example, to form a hydraulic composition with the pumice. The hydrated lime may be included in a pumice-to-hydrated-lime weight ratio of about 10:1 to about 1:1 or 3:1 to about 5:1. Where present, the hydrated lime may be included in the set-delayed cement compositions in an amount in the range of from about 10% to about 100% by weight of the pumice. In some examples, the hydrated lime may be present in an amount ranging between any of and/or including any of about 10%, about 20%, about 40%, about 60%, about 80%, or about 100% by weight of the pumice. In some examples, the cementitious components present in the set-delayed cement composition may consist essentially of the pumice and the hydrated lime. For example, the

cementitious components may primarily comprise the pumice and the hydrated lime without any additional components (e.g., Portland cement, fly ash, slag cement) that hydraulically set in the presence of water. One of ordinary skill in the art, with the benefit of this disclosure, will recognize the appropriate amount of the hydrated lime to include for a chosen application.

[0016] A set retarder maybe present in the set-delayed cement compositions. A broad variety of set retarders may be suitable for use in the set-delayed cement compositions. For example, the set retarder may comprise phosphonic acids, such as ethylenediamine tetra(methylene phosphonic acid), diethylenetriamine penta(methylene phosphonic acid), etc.; lignosulfonates, such as sodium lignosulfonate, calcium lignosulfonate, etc.; salts such as stannous sulfate, lead acetate, monobasic calcium phosphate, organic acids, such as citric acid, tartaric acid, etc.; cellulose derivatives such as hydroxyl ethyl cellulose (HEC) and carboxymethyl hydroxyethyl cellulose (CMHEC); synthetic co- or ter-polymers comprising sulfonate and carboxylic acid groups such as sulfonate-functionalized acrylamide-acrylic acid co-polymers; borate compounds such as alkali borates, sodium metaborate, sodium tetraborate, potassium pentaborate; derivatives thereof, or mixtures thereof. Examples of suitable set retarders include, among others, phosphonic acid derivatives. One example of a suitable set retarder is Micro Matrix® cement retarder, available from Halliburton Energy Services, Inc. Generally, the set retarder may be present in the set-delayed cement compositions in an amount sufficient to delay the setting for a desired time. In some examples, the set retarder may be present in the set-delayed cement compositions in an amount in the range of from about 0.01% to about 10% by weight of the pumice. In specific examples, the set retarder may be present in an amount ranging between any of and/or including any of about 0.01%, about 0.1%, about 1%, about 2%, about 4%, about 6%, about 8%, or about 10% by weight of the pumice. One of ordinary skill in the art, with the benefit of this disclosure, will recognize the appropriate amount of the set retarder to include for a chosen application.

[0017] As previously mentioned, examples of the set-delayed cement compositions may optionally comprise a dispersant. Examples of suitable dispersants include, without limitation, sulfonated-formaldehyde-based dispersants (e.g., sulfonated acetone formaldehyde condensate), examples of which may include Daxad® 19 dispersant available from Geo Specialty Chemicals, Ambler, Pennsylvania. Other suitable dispersants may be polycarboxylated ether dispersants such as Liquiment® 5581F and Liquiment® 514L

dispersants available from BASF Corporation Houston, Texas; or Ethacryl™ G dispersant available from Coatex, Genay, France. An additional example of a suitable commercially available dispersant is CFR™-3 dispersant, available from Halliburton Energy Services, Inc., Houston, Texas. The Liquiment® 514L dispersant may comprise 36% by weight of the polycarboxylated ether in water. While a variety of dispersants may be used, polycarboxylated ether dispersants may be particularly suitable for use. Without being limited by theory, it is believed that polycarboxylated ether dispersants may synergistically interact with other components of the set-delayed cement composition. For example, it is believed that the polycarboxylated ether dispersants may react with certain set retarders (e.g., phosphonic acid derivatives) resulting in formation of a gel that suspends the pumice and hydrated lime in the composition for an extended period of time.

[0018] The dispersant may be included in the set-delayed cement compositions in an amount in the range of from about 0.01% to about 5% by weight of the pumice. In specific examples, the dispersant may be present in an amount ranging between any of and/or including any of about 0.01%, about 0.1%, about 0.5%, about 1%, about 2%, about 3%, about 4%, or about 5% by weight of the pumice. One of ordinary skill in the art, with the benefit of this disclosure, will recognize the appropriate amount of the dispersant to include for a chosen application.

[0019] When desired for use, the set-delayed cement compositions may be activated (e.g., by combination with an activator) to set into a hardened mass. The term "cement set activator" or "activator", as used herein, refers to an additive that activates a set-delayed or heavily retarded cement composition and may also accelerate the setting of the set-delayed, heavily retarded, or other cement composition. By way of example, the set-delayed cement compositions may be activated to form a hardened mass in a time period in the range of from about 10 seconds to about 2 hours. For example, embodiments of the set-delayed cement compositions may set to form a hardened mass in a time period ranging between any of and/or including any of about 10 seconds, about 30 seconds, about 1 minute, about 10 minutes, about 30 minutes, about 1 hour, or about 2 hours.

[0020] One or more cement set activators may be added to the set-delayed cement compositions. Examples of suitable cement set activators include, but are not limited to: zeolites, amines such as triethanolamine, diethanolamine; silicates such as sodium silicate; zinc formate; calcium acetate; Groups IA and IIA hydroxides such as sodium hydroxide, magnesium hydroxide, and calcium hydroxide; monovalent salts such as sodium chloride;

divalent salts such as calcium chloride; nanosilica (i.e., silica having a particle size of less than or equal to about 100 nanometers); polyphosphates; and combinations thereof. In some embodiments, a combination of the polyphosphate and a monovalent salt may be used for activation. The monovalent salt may be any salt that dissociates to form a monovalent cation, such as sodium and potassium salts. Specific examples of suitable monovalent salts include potassium sulfate, and sodium sulfate. A variety of different polyphosphates may be used in combination with the monovalent salt for activation of the set-delayed cement compositions, including polymeric metaphosphate salts, phosphate salts, and combinations thereof. Specific examples of polymeric metaphosphate salts that may be used include sodium hexametaphosphate, sodium trimetaphosphate, sodium tetrametaphosphate, sodium pentametaphosphate, sodium heptametaphosphate, sodium octametaphosphate, and combinations thereof. A specific example of a suitable cement set activator comprises a combination of sodium sulfate and sodium hexametaphosphate. In a specific example, the activator may be provided and added to the set-delayed cement composition as a liquid additive, for example, a liquid additive comprising a monovalent salt, a polyphosphate, and optionally a dispersant.

[0021] Some embodiments may include a cement set activator comprising nanosilica. As used herein, the term "nanosilica" refers to silica having a particle size of less than or equal to about 100 nanometers ("nm"). The size of the nanosilica may be measured using any suitable technique. It should be understood that the measured size of the nanosilica may vary based on measurement technique, sample preparation, and sample conditions such as temperature, concentration, etc. One technique for measuring the particle size of the nanosilica is Transmission Electron Microscopy (TEM). An example of a commercially available product based on laser diffraction is the ZETASIZER Nano ZS particle size analyzer supplied by Malvern Instruments, Worcerstershire, UK. In some examples, the nanosilica may comprise colloidal nanosilica. The nanosilica may be stabilized using any suitable technique. In some examples, the nanosilica may be stabilized with a metal oxide, such as lithium oxide, sodium oxide, potassium oxide, and/or a combination thereof. Additionally the nanosilica may be stabilized with an amine and/or a metal oxide as mentioned above. Without limitation by theory, it is believed that the nanosilicas have an additional advantage in that they have been known to fill in pore space in cements which can result in superior mechanical properties in the cement after it has set.

[0022] Some examples may include a cement set activator comprising a combination of a monovalent salt and a polyphosphate. The monovalent salt and the polyphosphate may be combined prior to addition to the set-delayed cement composition or may be separately added to the set-delayed cement composition. The monovalent salt may be any salt that dissociates to form a monovalent cation, such as sodium and potassium salts. Specific examples of suitable monovalent salts include potassium sulfate and sodium sulfate. A variety of different polyphosphates may be used in combination with the monovalent salt for activation of the set-delayed cement compositions, including polymeric metaphosphate salts, phosphate salts, and combinations thereof, for example. Specific examples of polymeric metaphosphate salts that may be used include sodium hexametaphosphate, sodium trimetaphosphate, sodium tetrametaphosphate, sodium pentametaphosphate, sodium heptametaphosphate, sodium octametaphosphate, and combinations thereof. A specific example of a suitable cement set activator comprises a combination of sodium sulfate and sodium hexametaphosphate. Interestingly, sodium hexametaphosphate is also known in the art to be a strong retarder of Portland cements. Because of the unique chemistry of polyphosphates, polyphosphates may be used as a cement set activator for the set-delayed cement compositions disclosed herein. The ratio of the monovalent salt to the polyphosphate may range, for example, from about 5:1 to about 1:25 or from about 1:1 to about 1:10. In some examples the cement set activator may comprise the monovalent salt and the polyphosphate salt in a ratio (monovalent salt to polyphosphate) ranging between any of and/or including any of about 5:1, 2:1, about 1:1, about 1:2, about 1:5, about 1:10, about 1:20, or about 1:25.

[0023] In some examples, the combination of the monovalent salt and the polyphosphate may be mixed with a dispersant and water to form a liquid additive for activation of a set-delayed cement composition. Examples of suitable dispersants include, without limitation, the previously described dispersants, such as sulfonated-formaldehyde-based dispersants and polycarboxylated ether dispersants. One example of a suitable sulfonated-formaldehyde-based dispersant is a sulfonated acetone formaldehyde condensate, available from Halliburton Energy Services, Inc., as CFR-3™ dispersant. One example of a suitable polycarboxylated ether dispersant is Liquiment® 514L or 5581F dispersants, available from BASF Corporation, Houston, Texas.

[0024] The cement set activator may be added to the set-delayed cement composition in an amount sufficient to induce the set-delayed cement composition to set into a hardened

mass. For example, the cement set activator may be added to the set-delayed cement composition in an amount in the range of about 0.1% to about 20% by weight of the pumice. In specific examples, the cement set activator may be present in an amount ranging between any of and/or including any of about 0.1%, about 1%, about 5%, about 10%, about 15%, or about 20% by weight of the pumice. One of ordinary skill in the art, with the benefit of this disclosure, will recognize the appropriate amount of cement set activator to include for a chosen application.

[0025] Other additives suitable for use in subterranean cementing operations also may be included in examples of the set-delayed cement compositions. Examples of such additives include, but are not limited to: weighting agents, lightweight additives, mechanical-property-enhancing additives, fluid-loss-control additives, defoaming agents, foaming agents, and combinations thereof. One or more of these additives may be added to the set-delayed cement compositions after storing but prior to the placement of a set-delayed cement composition into a subterranean formation. A person having ordinary skill in the art, with the benefit of this disclosure, should readily be able to determine the type and amount of additive useful for a particular application and desired result.

[0026] Weighting agents may be included in the set-delayed cement compositions. Weighting agents are typically materials that weigh more than water and may be used to increase the density of the set-delayed cement compositions. By way of example, weighting agents may have a specific gravity of about 2 or higher (*e.g.*, about 2, about 4, etc.). Examples of weighting agents that may be used include, but are not limited to, hematite, hausmannite, barite, and combinations thereof. Specific examples of suitable weighting agents include HI-DENSE® weighting agent, available from Halliburton Energy Services, Inc.

[0027] Lightweight additives may be included in the set-delayed cement compositions, for example, to decrease the density of the set-delayed cement compositions. Examples of suitable lightweight additives include, but are not limited to, bentonite, coal, diatomaceous earth, expanded perlite, fly ash, gilsonite, hollow microspheres, low-density elastic beads, nitrogen, pozzolan-bentonite, sodium silicate, combinations thereof, or other lightweight additives known in the art. The resin compositions may generally have lower base densities than the set-delayed cement compositions, thus hollow glass beads and/or foam may be suitable lightweight additives for the set-delayed cement compositions, dependent upon the base densities of the set-delayed cement compositions.

[0028] Optionally, cement foaming additives may be included in the set-delayed cement compositions, for example, to facilitate foaming and/or stabilize the resultant foam formed therewith. The foaming additive may include a surfactant or combination of surfactants that reduce the surface tension of the water. As will be appreciated by those of ordinary skill in the art, the foaming additives may be used in conjunction with a gas to produce a foamed set-delayed cement compositions. By way of example, the foaming agent may comprise an anionic, nonionic, amphoteric (including zwitterionic surfactants), cationic surfactant, or mixtures thereof. Examples of suitable foaming additives include, but are not limited to: betaines; anionic surfactants such as hydrolyzed keratin; amine oxides such as alkyl or alkene dimethyl amine oxides; cocoamidopropyl dimethylamine oxide; methyl ester sulfonates; alkyl or alkene amidobetaines such as cocoamidopropyl betaine; alpha-olefin sulfonates; quaternary surfactants such as trimethyltallowammonium chloride and trimethylcocoammonium chloride; C8 to C22 alkylethoxylate sulfates; and combinations thereof. Specific examples of suitable foaming additives include, but are not limited to: mixtures of an ammonium salt of an alkyl ether sulfate, a cocoamidopropyl betaine surfactant, a cocoamidopropyl dimethylamine oxide surfactant, sodium chloride, and water; mixtures of an ammonium salt of an alkyl ether sulfate surfactant, a cocoamidopropyl hydroxysultaine surfactant, a cocoamidopropyl dimethylamine oxide surfactant, sodium chloride, and water; hydrolyzed keratin; mixtures of an ethoxylated alcohol ether sulfate surfactant, an alkyl or alkene amidopropyl betaine surfactant, and an alkyl or alkene dimethylamine oxide surfactant; aqueous solutions of an alpha-olefinic sulfonate surfactant and a betaine surfactant; and combinations thereof. An example of a suitable foaming additive is ZONESEALANT™ 2000 agent, available from Halliburton Energy Services, Inc.

[0029] Optionally, set accelerators for the set-delayed cement compositions may be included in the set-delayed cement compositions, for example, to increase the rate of setting reactions. Control of setting time may allow for the ability to adjust to wellbore conditions or customize set times for individual jobs. Examples of suitable set accelerators may include, but are not limited to, aluminum sulfate, alums, calcium chloride, calcium sulfate, gypsum-hemihydrate, sodium aluminate, sodium carbonate, sodium chloride, sodium silicate, sodium sulfate, ferric chloride, or a combination thereof. For example, aluminum sulfate may be used to accelerate the setting time of the set-delayed cement compositions for surface uses which may require fast setting, for example, roadway repair, consumer uses, etc. The cement set accelerators may be added alongside any cement set activators when setting of the set-

delayed cement compositions is desired. Alternatively, the set accelerators may be added before the cement set activator if desired, and if the set accelerator does not induce premature setting. Without being limited by theory, aluminum sulfate may promote the formation of sulfate containing species (e.g., ettringite) which may modify the rheology of the matrix during hydration such that textural uniformity and adherence to a surface is improved. Set accelerators may produce a set-delayed cement composition with a thickening time of less than 10 minutes, alternatively less than 5 minutes, alternatively, less than 1 minute, or further alternatively less than 30 seconds.

[0030] Optionally, mechanical-property-enhancing additives for set-delayed cement compositions may be included in the set-delayed cement compositions, for example, to ensure adequate compressive strength and long-term structural integrity. These properties can be affected by the strains, stresses, temperature, pressure, and impact effects from a subterranean environment. Examples of mechanical-property-enhancing additives include, but are not limited to, carbon fibers, glass fibers, metal fibers, mineral fibers, silica fibers, polymeric elastomers, latexes, and combinations thereof.

[0031] Optionally, fluid-loss-control additives for cement may be included in the set-delayed cement compositions, for example, to decrease the volume of fluid that is lost. Properties of the set-delayed cement compositions may be significantly influenced by their water content. The loss of fluid can subject the set-delayed cement compositions to degradation or complete failure of design properties. Examples of suitable fluid-loss-control additives include, but not limited to, certain polymers, such as hydroxyethyl cellulose, carboxymethylhydroxyethyl cellulose, copolymers of 2-acrylamido-2-methylpropanesulfonic acid and acrylamide or N,N-dimethylacrylamide, and graft copolymers comprising a backbone of lignin or lignite and pendant groups comprising at least one member selected from the group consisting of 2-acrylamido-2-methylpropanesulfonic acid, acrylonitrile, and N,N-dimethylacrylamide.

[0032] Optionally, cement defoaming additives may be included in the set-delayed cement compositions, for example, to reduce the tendency of the set-delayed cement compositions to foam during mixing and pumping of the set-delayed cement compositions. Examples of suitable defoaming additives include, but are not limited to, polyol silicone compounds. Suitable defoaming additives are available from Halliburton Energy Services, Inc., under the product name D-AIR™ defoamers.

[0033] Optionally, fibers may be included in the set-delayed cement compositions, for example, to enhance the tensile and ductile properties the set-delayed cement compositions. Examples of suitable fibers include, but are not limited to, polyvinylalcohol, polypropylene, carbon, glass etc. Further, the fluidic nature and storage capabilities of the set-delayed cement composition allow for fibers which may, in other compositions, require high shear and high pressure pumping conditions for dispersion, to be dispersed using low. This is particularly advantageous in systems where the fibers may bridge and plug pumping equipment.

[0034] Optionally, refractory materials may be included in the set-delayed cement compositions, for example, to provide a set-delayed cement composition with higher heat resistance. Examples of suitable refractory materials include, but are not limited to, alumina, titanium, fire brick grog, etc. These refractory materials may be of particular importance in applications where fire and heat resistance is particularly important, for example, in consumer applications in the home.

[0035] The set-delayed cement compositions may possess properties beneficial for use in concrete applications. For example, in a typical concrete formulation, the aggregate (e.g., chert, quartzite, opal, strained quartz crystals, etc.) may be dissolved by the basic pore solution of the cement in what is known as an alkali silicate reaction. The dissolved portion of the aggregate may then react with calcium species present in the cement pore solution to form a calcium-silicate-hydrate gel. This alkali silicate reaction may be represented by Equation 1 below:

$$Ca(OH)_2 + H_4SiO_4 \rightarrow Ca^{2+} + H_2SiO_4^{2-} + 2H_2O \rightarrow CaH_2SiO_4 \cdot 2H_2O$$

(*Eq.* 1)

The calcium-silicate-hydrate gel formed from the aggregate, effectively increases the size of the aggregate. This increase in size may exert a force on the surrounding cement that consequently causes cracks or deformations in the surrounding cement. Without limitation by theory, it is believed that the set-delayed cement compositions may prevent or mitigate any alkali silicate reactions by binding the alkali materials present, increasing the tensile strength of the concrete, and/or by reducing the dissolution rate of the aggregate (e.g., the set-delayed cement compositions may have a pore solution pH of 12.5 as compared to a pH of 13.2 for standard concrete). Furthermore the set-delayed cement composition may be formulated such that the hydrated lime may be completely consumed by the pumice and thus prevent any initial dissolution of the aggregate.

[0036] The set-delayed cement compositions may be used in applications of spray-applied cement and concrete. Spray-applied cement and concrete may be used through either a wet process or a dry process. The dry-mix process comprises pumping a dry cementitious material through a conduit and adding water at the exit of the conduit. In the wet-mix process, the cementitious material is mixed with water before being loaded into the conduit. When loaded into the conduit, the cement or concrete slurry is pumped to the exit of the conduit (e.g., a nozzle), where it may be sprayed onto a target area using compressed gas added at the conduit exit. The set-delayed cement compositions disclosed herein may be used in wet-mix spray-applications. In particular, the set-delayed cement composition may be spray-applied in cementing applications for tunnels, mines, reservoirs, swimming pools, repair works, fire damaged structures, retaining walls, refractory linings, zoological structures, bridges, dams, and the like. In a specific example, a set-delayed cement composition may be prepared in advance and then stored as a stable slurry until needed, whereby the set-delayed cement composition may be loaded into a cement spraying apparatus and sprayed onto a target area. In the aforementioned example, on-site mixing of the cement is no longer needed and thus the cement may be prepared off-site under stricter control standards and conditions.

[0037] As previously mentioned, the set-delayed cement compositions may have a delayed set in that they remain in a pumpable fluid state for at least one day (e.g., at least about 1 day, about 2 weeks, about 2 years or more) at room temperature (e.g., about 80 °F) in quiescent storage. For example, the set-delayed cement compositions may remain in a pumpable fluid state for a period of time from about 1 day to about 7 days or more. In some examples, the set-delayed cement compositions may remain in a pumpable fluid state for at least about 1 day, about 7 days, about 10 days, about 20 days, about 30 days, about 40 days, about 50 days, about 60 days, or longer. A fluid is considered to be in a pumpable fluid state where the fluid has a consistency of less than 70 Bearden units of consistency ("Bc"), as measured on a pressurized consistometer in accordance with the procedure for determining cement thickening times set forth in API RP Practice 10B-2, *Recommended Practice for Testing Well Cements*, First Edition, July 2005.

[0038] Those of ordinary skill in the art will appreciate that the set-delayed cement compositions should have a density suitable for a particular application. By way of example, the set-delayed cement compositions may have a density in the range of from about 4 pounds per gallon ("lb/gal") to about 20 lb/gal. In certain examples, the set-delayed cement compositions may have a density in the range of from about 8 lb/gal to about 17 lb/gal.

Examples of the set-delayed cement compositions may be foamed or unfoamed or may comprise other means to reduce their densities, such as hollow microspheres, low-density elastic beads, or other density-reducing additives known in the art. In examples, the density may be reduced after storing the composition, but prior to placement in a subterranean formation. Those of ordinary skill in the art, with the benefit of this disclosure, will recognize the appropriate density for a particular application. In some examples, the set-delayed cement compositions may set to have a desirable compressive strength after activation. Compressive strength is generally the capacity of a material or structure to withstand axially directed pushing forces. The compressive strength may be measured at a specified time after the set-delayed cement composition has been activated and the resultant composition is maintained under specified temperature and pressure conditions. Compressive strength can be measured by either destructive or non-destructive methods. The destructive method physically tests the strength of treatment fluid samples at various points in time by crushing the samples in a compression-testing machine. The compressive strength is calculated from the failure load divided by the cross-sectional area resisting the load and is reported in units of pound-force per square inch (psi). Non-destructive methods may employ a UCA™ ultrasonic cement analyzer, available from Fann Instrument Company, Houston, TX. Compressive strength values may be determined in accordance with API RP 10B-2, *Recommended Practice for Testing Well Cements*, First Edition, July 2005.

[0039] By way of example, the set-delayed cement compositions may develop a 24-hour compressive strength in the range of from about 50 psi to about 5000 psi, alternatively, from about 100 psi to about 4500 psi, or alternatively from about 500 psi to about 4000 psi. In some examples, the set-delayed cement compositions may develop a compressive strength in 24 hours of at least about 50 psi, at least about 100 psi, at least about 500 psi, or more. In some examples, the compressive strength values may be determined using destructive or non-destructive methods at a temperature ranging from 100 °F to 200 °F.

[0040] In some examples, the set-delayed cement compositions may have desirable thickening times after activation. Thickening time typically refers to the time a fluid, such as a set-delayed cement composition, remains in a fluid state capable of being pumped. A number of different laboratory techniques may be used to measure thickening time. A pressurized consistometer, operated in accordance with the procedure set forth in the aforementioned API RP Practice 10B-2, may be used to measure whether a fluid is in a pumpable fluid state. The thickening time may be the time for the treatment fluid to reach 70

Bc and may be reported as the time to reach 70 Bc. The thickening time may be modified for any temperature at atmospheric pressure by modification of the formula, concentration of additives (e.g. activator/accelerator), etc. In some examples, the set-delayed cement compositions may have a thickening time at atmospheric pressure and surface temperatures between about 30 seconds to about 10 hours. For example, the set-delayed cement compositions may have a thickening time of greater than about 30 seconds, greater than about 1 minute, greater than about 10 minutes, greater than about 1 hour, or greater than about 10 hours.

[0041] In some examples, a set-delayed cement composition may be provided that comprises water, pumice, hydrated lime, a set retarder, and optionally a dispersant. The set-delayed cement composition may be stored, for example, in a vessel or other suitable container. The set-delayed cement composition may be permitted to remain in storage for a desired time period. For example, the set-delayed cement composition may remain in storage for a time period of about 1 day or longer. For example, the set-delayed cement composition may remain in storage for a time period of about 1 day, about 2 days, about 5 days, about 7 days, about 10 days, about 20 days, about 30 days, about 40 days, about 50 days, about 60 days, or longer. In some examples, the set-delayed cement composition may remain in storage for a time period in a range of from about 1 day to about 7 days or longer. Thereafter, the set-delayed cement composition may be activated, for example, by addition of a cement set activator, used in a cementing or concrete application and allowed to set in the course of said application.

[0042] A method of spraying a surface with a set-delayed cement composition may be provided. The method may be used in conjunction with one or more of the methods, compositions, and/or systems illustrated in FIGs. 1-4. The method may comprise providing a set-delayed cement composition comprising water, pumice, hydrated lime, and a set retarder; spraying a surface with the set-delayed cement composition; and allowing the set-delayed cement composition to set on the surface. The set retarder may comprise at least one retarder selected from the group consisting of a phosphate, a phosphonate, a phosphonic acid, a phosphonic acid derivative, a lignosulfonate, a salt, an organic acid, a carboxymethylated hydroxyethylated cellulose, a synthetic co- or ter-polymer comprising sulfonate and carboxylic acid groups, a borate compound, and any mixture thereof. The set-delayed cement composition may further comprise a cement set activator selected from the group consisting of a zeolite, amine, silicate, Group IA hydroxide, Group IIA hydroxide, monovalent salt,

divalent salt, nanosilica, polyphosphate, and any combination thereof. The set-delayed cement composition comprising the cement set activator may further comprise a thickening time in a range between about 30 seconds to about 10 minutes. The set-delayed cement composition may further comprise a fiber. The set-delayed cement composition may further comprise a dispersant selected from the group consisting of a sulfonated-formaldehyde-based dispersant, a polycarboxylated ether dispersant, and any combination thereof. Prior to the spraying step, the set-delayed cement composition may be stored for a period of at least about 1 day. The surface may be disposed about, on, or within a mine, a pond, a creek, a river, the ocean floor, a beach shore, a wall, a ceiling, a floor, an attic, or a basement. The set-delayed cement composition may be disposed within a mine and wherein the set-delayed cement composition may be pumped from a vessel outside of the mine into the mine. The set-delayed cement composition may be foamed. The set-delayed cement composition may comprise refractory materials. The set-delayed cement composition may comprise a dye and/or beads.

[0043] A method of coating a surface with a set-delayed cement composition may be provided. The method may be used in conjunction with one or more of the methods, compositions, and/or systems illustrated in FIGs. 1-4. The method may comprise providing a set-delayed cement composition comprising water, pumice, hydrated lime, and a set retarder; coating a surface with the set-delayed cement composition; and allowing the set-delayed cement composition to set on the surface. The set retarder may comprise at least one retarder selected from the group consisting of a phosphate, a phosphonate, a phosphonic acid, a phosphonic acid derivative, a lignosulfonate, a salt, an organic acid, a carboxymethylated hydroxyethylated cellulose, a synthetic co- or ter-polymer comprising sulfonate and carboxylic acid groups, a borate compound, and any mixture thereof. The set-delayed cement composition may further comprise a cement set activator selected from the group consisting of a zeolite, amine, silicate, Group IA hydroxide, Group IIA hydroxide, monovalent salt, divalent salt, nanosilica, polyphosphate, and any combination thereof. The set-delayed cement composition comprising the cement set activator may further comprise a thickening time in a range between about 30 seconds to about 10 minutes. The set-delayed cement composition may further comprise a fiber. The set-delayed cement composition may further comprise a dispersant selected from the group consisting of a sulfonated-formaldehyde-based dispersant, a polycarboxylated ether dispersant, and any combination thereof. Prior to the coating step, the set-delayed cement composition may be stored for a period of at least about 1 day. The surface may be disposed about, on, or within a mine, a pond, a creek, a river, the

ocean floor, a beach shore, a wall, a ceiling, a floor, an attic, or a basement. The set-delayed cement composition may be disposed within a mine and wherein the set-delayed cement composition may be pumped from a vessel outside of the mine into the mine. The set-delayed cement composition may be foamed. The set-delayed cement composition may comprise refractory materials. The set-delayed cement composition may comprise a dye and/or beads. Coating a surface with the set-delayed cement composition may comprise painting the surface with the set-delayed cement composition or dipping the surface into a vessel containing the set-delayed cement composition

[0044] A cementing system may be provided. The system may be used in conjunction with one or more of the methods, compositions, and/or systems illustrated in FIGs. 1-4. The system may comprise a set-delayed cement composition comprising: water, pumice, hydrated lime, and a set retarder, wherein the set-delayed cement composition is capable of remaining in a pumpable fluid state for at least about one day at 80° F; a cementing unit comprising: a vessel, a conduit; and a nozzle coupled to the conduit. The cementing unit may further comprise a pneumatic system comprising a gas compressor, a compressed gas, and a compressed gas conduit, wherein the compressed gas conduit is coupled to the nozzle, and wherein the compressed gas is capable of spraying the set-delayed cement composition. The nozzle may comprise an applicator capable of applying a cement set activator to the set-delayed cement composition. The cementing unit may further comprise a hydraulic system coupled to the nozzle, wherein the hydraulic system may be capable of spraying the set-delayed cement composition. The set retarder may comprise at least one retarder selected from the group consisting of a phosphate, a phosphonate, a phosphonic acid, a phosphonic acid derivative, a lignosulfonate, a salt, an organic acid, a carboxymethylated hydroxyethylated cellulose, a synthetic co- or ter-polymer comprising sulfonate and carboxylic acid groups, a borate compound, and any mixture thereof. The set-delayed cement composition may further comprise a cement set activator selected from the group consisting of a zeolite, amine, silicate, Group IA hydroxide, Group IIA hydroxide, monovalent salt, divalent salt, nanosilica, polyphosphate, and any combination thereof. The set-delayed cement composition comprising the cement set activator may further comprise a thickening time in a range between about 30 seconds to about 10 minutes. The set-delayed cement composition may further comprise a fiber. The set-delayed cement composition may further comprise a dispersant selected from the group consisting of a sulfonated-formaldehyde-based dispersant, a polycarboxylated ether dispersant, and any combination thereof. The set-delayed

cement composition may be foamed. The set-delayed cement composition may comprise refractory materials. The set-delayed cement composition may comprise a dye and/or beads.

[0045] Referring now to FIG. 1, the preparation of a set-delayed cement composition in accordance with the examples described herein will now be described. FIG. 1 illustrates a fluid handling system 2 for the preparation of a set-delayed cement composition and subsequent delivery of the composition to a cementing application site. As shown, the set-delayed cement composition may be mixed and/or stored in a vessel 4. Vessel 4 may be any such vessel suitable for containing and/or mixing the set-delayed cement composition, including, but not limited to drums, barrels, tubs, bins, jet mixers, re-circulating mixers, batch mixers, and the like. The set-delayed cement composition may then be pumped via pumping equipment 6. In some embodiments, the vessel 4 and the pumping equipment 6 may be disposed on one or more cementing units (e.g., cementing unit 8 as shown on FIG. 2) as will be apparent to those of ordinary skill in the art. In some embodiments, a jet mixer may be used, for example, to continuously mix the lime/settable material with the water as it is being pumped to the wellbore. In set-delayed embodiments, a re-circulating mixer and/or a batch mixer may be used to mix the set-delayed cement composition, and the activator may be added to the mixer as a powder prior to pumping the cement composition downhole. Additionally, batch mixer type units for the slurry may be plumbed in line with a separate tank containing a cement set activator. The cement set activator may then be fed in-line with the slurry as it is pumped out of the mixing unit. Further, in embodiments requiring a concrete, aggregate may be mixed with the set-delayed cement composition in vessel 4 before being pumped via pumping equipment 6

[0046] FIG. 2 illustrates the use of the set-delayed cement composition in a spraying application. Cementing unit 8, which may comprise vessel 4 and pumping equipment 6 as described in FIG. 1, may be used to spray a set-delayed cement composition on a rock lined pond bed 10. Cementing unit 8 may comprise a vessel capable of storing a set-delayed cement composition (e.g., vessel 4) and/or equipment used to deliver a set-delayed cement composition to a job site, illustrated by pumping equipment 6 and conduit 12. As illustrated by FIG. 2, rock lined pond bed 10 may comprise pores, voids, gaps, etc. that may make permeable and prone to erosion. Due to the inherent nature of the set-delayed cement composition, the set-delayed cement composition may be delivered through conduit 12 and sprayed onto rock lined pond bed 10 using a pneumatic system comprising gas compressor 14 and compressed gas conduit 16, which may be utilized to spray the set delayed cement

composition from nozzle 18. Alternatively, the spraying may be accomplished by a hydraulic system (not shown), for example, comprising an incompressible liquid to exert a direct or indirect force on the set-delayed cement composition such that the set-delayed cement composition may be sprayed from an exit in the conduit 12. Once sprayed, the set-delayed cement composition may be activated for use by a cement set activator, alternatively an applicator within the nozzle 18 of conduit 12 may apply the cement set activator as it exits nozzle 18 as shown in the inset of FIG. 2. Applicator 20 may comprise an opening and a valve through which activator conduit 22 may convey cement set activator to nozzle 18 where it may mix with a set-delayed cement composition in conduit 12. Additionally, activator pump 24 my pump cement set activator through activator conduit 22. The activated set-delayed cement composition may then be sprayed from the nozzle 18 using the compressed gas carried to nozzle 18 via compressed gas conduit 16. The strength of the cement set activator may be adjusted to adjust the thickening time of the set-delayed cement composition. The strength may be adjusted by using a relatively stronger cement set activator and/or also by increasing the cement set activator concentration. For example, a higher concentration of more reactive cement set activator may be used to induce setting of the set-delayed cement as soon as it is applied to a surface. Similarly, the set-delayed cement composition may be used in applications where the lining of porous or erosion prone structures would be desired. For example, the set-delayed cement composition may be used on ponds, reservoirs, drainage ditches, creek beds, rivers banks, and the like. Once set, the set-delayed cement composition may prevent leakage and/or erosion through and within the covered surfaces.

[0047] FIG. 3 illustrates a marine construction application, wherein a set-delayed cement composition may be pumped through conduit 12 to secure in place a beam 28 to be used in the extension of pier 26. The set-delayed cement composition may be sprayed from nozzle 18 using a pneumatic system, for example, one comprising compressed gas from compressed gas conduit 16. Alternatively, the spraying may be accomplished by a hydraulic system (not shown), for example, comprising an incompressible liquid to exert a direct or indirect force on the set-delayed cement composition such that the set-delayed cement composition may be sprayed from an exit in the conduit 12. As discussed above, the set-delayed cement composition is capable of extended storage wherein it remains in a stable fluid, slurry state until activated by the addition of a suitable cement set activator and allowed to set to form set cement 30. Set cement 30 is a set-delayed cement composition that has been

activated and allowed to set in place. As such, the set-delayed cement composition may be placed near a location or removed to a logistically convenient position and pumped to a desired area. The cement set activator may be added while mixing the set-delayed cement composition prior to pumping, or may added while pumping the set-delayed cement composition, for example, through an applicator within the nozzle of conduit 10. Set-delayed cement composition may be well suited for marine environments and may be particularly advantageous in deep-water scenarios due to its simplified delivery mechanism, reduced transport risk, and easier logistics since powder transport and mixing are not required.

[0048] FIG. 4 illustrates the use of a set-delayed cement composition for mine construction/repair. Cementing unit 8, which may comprise vessel 4, pumping equipment 6, and conduit 12, may be used to store, mix, and transport a set-delayed cement composition into a mine or other underground structure where it may be difficult to transport equipment. As illustrated by FIG. 4, the bulk of the cementing equipment and the set-delayed cement composition may be stored above ground. When desired, the set-delayed cement composition may be pumped by cementing unit 8 via conduit 12 to the underground job site where the set-delayed cementing composition may be used to consolidate, seal, or reinforce the tunnel/mine structure. Thus, transport time and or size constraint issues of the cementing equipment may be reduced or eliminated. The set-delayed cement composition may be poured from conduit 12 or it may be sprayed using a pneumatic system, for example, one comprising compressed gas from gas compressor 14 and compressed gas conduit 16. Alternatively, the spraying may be accomplished by a hydraulic system (not shown), for example, comprising an incompressible liquid to exert a direct or indirect force on the set-delayed cement composition such that the set-delayed cement composition may be sprayed from an exit in the conduit 12. With the benefit of this disclosure, one of ordinary skill in the art will be able to determine the best method of applying a set-delayed cement and/or concrete.

[0049] Additional examples may comprise using the set-delayed cement composition for coating applications. In these examples, a coating may be applied by spraying, painting, rolling-on dipping, etc. The coating may be applied to decorative or structural purposes. The set-delayed cement composition may be easily dyed and can be formulated to provide a fast-setting adhesive coating of a desirable color. The coating may be used to aesthetically enhance walls, floors, ceilings, sculptures, or any such desirable structure. Further, ornamental aggregate may be added to the set-delayed cement composition for additional aesthetic effects. Ornamental aggregate may comprise glitter, beads, and the like.

[0050] Additionally, the set-delayed cement compositions may provide a heat resistant coating to a surface. The disclosed set-delayed cement composition is stable up to temperatures as high as 400 °F. Therefore, coating a surface with the set-delayed cement compositions disclosed herein may impart a heat resistant coating to the surface. Further, as discussed above, heat refractory materials may be added to the set-delayed cement compositions to increase the heat resistance of the set-delayed cement compositions. Such materials may comprise, but are not limited to, alumina, titanium, fire brick grog, and the like.

[0051] Further, the set-delayed cement compositions may be foamed. The set-delayed cement composition may be formed using a foaming additive as described above or a pressurized gas. Equipment, such as fluid handling system 2 (as shown in FIG. 1) or cementing unit 8 (as shown in FIGs. 2 and 4), may be used to continuously produce foamed set-delayed cement composition that may be sprayed or coated onto a targeted surface where it may remain in place due to the rheology of the foamed set-delayed cement composition. Optionally, the foamed set-delayed cement composition may be passed through a heat exchanger and/or supplied a cement set accelerator to accelerate the setting process. The foamed set-delayed cement composition may be used in many applications. An example of an application comprises a fire retardant insulation which may be applied to many types of surfaces.

[0052] The exemplary set-delayed cement compositions disclosed herein may directly or indirectly affect one or more components or pieces of equipment associated with the preparation, delivery, recapture, recycling, reuse, and/or disposal of the disclosed set-delayed cement compositions. For example, the disclosed set-delayed cement compositions may directly or indirectly affect one or more mixers, related mixing equipment, mud pits, storage facilities or units, composition separators, heat exchangers, sensors, gauges, pumps, compressors, and the like used generate, store, monitor, regulate, and/or recondition the exemplary set-delayed cement compositions. The disclosed set-delayed cement compositions may also directly or indirectly affect any transport or delivery equipment used to convey the set-delayed cement compositions to a well site or downhole such as, for example, any transport vessels, conduits, pipelines, trucks, tubulars, and/or pipes used to compositionally move the set-delayed cement compositions from one location to another, any pumps, compressors, or motors (e.g., topside or downhole) used to drive the set-delayed cement compositions into motion, any valves or related joints used to regulate the pressure or flow

rate of the set-delayed cement compositions, and any sensors (i.e., pressure and temperature), gauges, and/or combinations thereof, and the like. The disclosed set-delayed cement compositions may also directly or indirectly affect the various downhole equipment and tools that may come into contact with the set-delayed cement compositions such as, but not limited to, wellbore casing, wellbore liner, completion string, insert strings, drill string, coiled tubing, slickline, wireline, drill pipe, drill collars, mud motors, downhole motors and/or pumps, cement pumps, surface-mounted motors and/or pumps, centralizers, turbolizers, scratchers, floats (e.g., shoes, collars, valves, etc.), logging tools and related telemetry equipment, actuators (e.g., electromechanical devices, hydromechanical devices, etc.), sliding sleeves, production sleeves, plugs, screens, filters, flow control devices (e.g., inflow control devices, autonomous inflow control devices, outflow control devices, etc.), couplings (e.g., electro-hydraulic wet connect, dry connect, inductive coupler, etc.), control lines (e.g., electrical, fiber optic, hydraulic, etc.), surveillance lines, drill bits and reamers, sensors or distributed sensors, downhole heat exchangers, valves and corresponding actuation devices, tool seals, packers, cement plugs, bridge plugs, and other wellbore isolation devices, or components, and the like.

EXAMPLES

[0053] To facilitate a better understanding of the present embodiments, the following examples of certain aspects of some embodiments are given. In no way should the following examples be read to limit, or define, the entire scope of the embodiments.

Example 1

[0054] The following series of tests was performed to evaluate the force resistance properties of comparative cement compositions comprising pumice and hydrated lime. Three different comparative sample settable compositions, designated Samples 1-3, were prepared using pumice (DS-325 lightweight aggregate), hydrated lime, Liquiment® 514L dispersant, and water, as indicated in the table below. After preparation, the samples were placed in an UCA and cured at 140°F and 3,000 psi for 24 hours. The cured cement was then removed from the UCA and crushed to yield the compressive strength values provided in Table 1 below.

Table 1
Compressive Strength Tests

Sample		1	2	3
Density	lb/gal	14.3	14.3	14.3

Pumice:Lime Wt. Ratio		3:1	4:1	5:1
Pumice	g	400	400	400
Lime	g	134	103	100
Dispersant	g	12	4	13
Water	g	196	187	220
24-Hr Crush Strength	psi	2,240	1,960	2,130

[0055] Example 1 thus indicates that cement compositions that comprise pumice and lime in a weight ratio ranging from 3:1 to 5:1 may develop compressive strengths suitable for particular applications.

Example 2

[0056] A sample set-delayed cement composition, designated Sample 4, having a density of 13.3 lb/gal was prepared that comprised 500 grams of pumice (DS-325 lightweight aggregate), 100 grams of hydrated lime, 13 grams of Liquiment® 514L dispersant, 24 grams of Micro Matrix® cement retarder, and 300 grams of water. The rheological properties of the sample were measured after storing at room temperature and pressure for periods of 1 day and 6 days. After preparation, the rheological properties of the sample were determined at room temperature (e.g., about 80°F) using a Model 35A Fann Viscometer and a No. 2 spring, in accordance with the procedure set forth in API RP Practice 10B-2, *Recommended Practice for Testing Well Cements*. The results of this test are set forth in the table below.

TABLE 2
Viscosity Tests

Age of Sample (days)	Fann Readings						Yield Point ($lb/100ft^2$)	Plastic Viscosity (centipoise)
	600	300	200	100	6	3		
1	560	322	244	170	46	38	84	238
6	498	310	228	136	24	20	122	188

[0057] Example 2 thus indicates that set-delayed cement compositions that comprise pumice, hydrated lime, a dispersant, a set retarder, and water can remain fluid after 6 days.

Example 3

[0058] A sample set-delayed cement composition, designated Sample 5, having a density of 13.4 lb/gal was prepared that comprised 500 grams of pumice (DS-325 lightweight aggregate), 100 grams of hydrated lime, 7 grams of Liquiment® 514L dispersant, 6.3 grams of Micro Matrix® cement retarder, and 304 grams of water. The rheological properties of the sample were measured after storing at room temperature and pressure for periods of from 1 day to 19 days. The rheological properties were measured at room temperature (e.g., about

80°F) using a Model 35A Fann Viscometer and a No. 2 spring, in accordance with the procedure set forth in API RP Practice 10B-2, *Recommended Practice for Testing Well Cements*. The results of this test are set forth in the table below.

Table 3
Viscosity Tests

Age of Sample (Days)	Fann Readings				
	300	**200**	**100**	**6**	**3**
1	462	300	130	12	8
2	458	282	122	6	4
5	420	260	106	3	2
8	446	270	110	4	1
12	420	252	100	3	2
19	426	248	94	2	1

[0059] After 7 days, calcium chloride in the amount indicated in Table 4 below was added to a separately prepared sample of the same formulation as above. The sample was then placed in an UCA and the initial setting time, which is the time for the composition to reach a compressive strength of 50 psi while maintained at 3,000 psi was determined in accordance with API RP Practice 10B-2, *Recommended Practice for Testing Well Cements*. The initial setting time of the sample was also determined without addition of the calcium chloride. The samples with and without the calcium chloride were heated to a temperature of 140°F in 30 minutes and then maintained at that temperature throughout the test.

Table 4
Compressive Strength Tests

Age of Sample (Days)	Test Temperature (°F)	$CaCl_2$ (% by wt of Pumice & Lime)	Initial Setting Time (hr:min)
7	140	0	no set after 4 days
7	140	10	5:11

[0060] Example 3 thus indicates that the set-delayed cement compositions that comprise pumice, hydrated lime, a dispersant, a set retarder, and water will not set for a period of at least 19 days at ambient temperature and over 4 days at 140°F. Example 3 further indicates that sample set-delayed cement compositions may be activated at a desired time by addition of a suitable activator.

Example 4

[0061] A sample set-delayed cement composition, designated Sample 6, having a density of 13.4 lb/gal was prepared that comprised pumice (DS-325 lightweight aggregate), 20% hydrated lime, 1.4% Liquiment® 514L dispersant, 1.26% Micro Matrix® cement retarder, and 62% of water (all by weight of pumice, referred to in the table below as "% bwop"). After 45 days in storage at ambient conditions, the sample was mixed with 6% calcium chloride. At 140°F, the sample had a thickening time (time to 70 BC) of 2 hours and 36 minutes and an initial setting time (time to 50 psi) of 9 hours and 6 minutes as measured using an UCA while maintained at 3000 psi. After 48 hours, the sample was crushed with a mechanical press which gave a compressive strength of 2,240 psi. The thickening time and initial setting time were both determined in accordance with API RP Practice 10B-2, *Recommended Practice for Testing Well Cements*. The results of this test are set forth in the table below.

Table 5
Compressive Strength Tests

Age of Sample (Days)	Test Temperature (°F)	Calcium Chloride (% bwop)	Thickening Time (hr:min)	Initial Setting Time (hr:min)	48 Hr Crush Strength (psi)
45	140	6	2:36	9:36	2,240

[0062] Example 4 thus indicates that the set-delayed cement compositions that comprise pumice, hydrated lime, a dispersant, a set retarder, and water will not set for a period of at least 45 days at ambient temperature. Example 4 further indicates that sample set-delayed cement compositions may be activated at a desired time by addition of a suitable activator.

Example 5

[0063] This example was performed to evaluate the ability of sodium hydroxide and sodium sulfate to activate a set-delayed cement composition that comprised pumice (DS-325 lightweight aggregate), hydrated lime, Liquiment® 514L dispersant, Micro Matrix® cement retarder, and water. Four sample set-delayed cement compositions, designated Samples 7-10, were prepared having concentrations of components as indicated in the table below. The samples were monitored via an UCA. After the samples were placed in the UCA, the pressure was increased to 3,000 psi, and the temperature was increased to 100°F over a 15-minute time period and held for the duration of the test. A portion of the slurry was retained

and poured into a plastic cylinder to monitor the slurry behavior at room temperature and pressure. These procedures were repeated for all samples.

[0064] Sample 7 was monitored for 72 hours over which time no strength was developed and the slurry was still pourable when removed from the UCA. The portion kept at room temperature and pressure was likewise still pourable after 72 hours.

[0065] Sample 8 was prepared using the same slurry design as Sample 7 except that sodium hydroxide was added as an activator. The sodium hydroxide was added in solid form directly to the mixing jar that contained the prepared sample. As can be seen from Table 6, Sample 8, reached 50 psi of compressive strength at 16 hours and 36 minutes. The strength continued to build, reaching a maximum of 1,300 psi, when the test was stopped at 72 hours. The cured cement was removed from the UCA and crushed with a mechanical press which gave a compressive strength of 969 psi. The portion kept at room temperature and pressure was crushed after 7 days resulting in a compressive strength of 143 psi.

[0066] Sample 9 was prepared using the same slurry design as Sample 8 except that sodium sulfate was added as an activator. The sodium sulfate was added in solid form directly to the mixing jar that contained the prepared slurry. Sample 9 reached 50 psi of compressive strength at 67 hours and 29 minutes. The strength continued to build, slowly, reaching a maximum of 78 psi, when the test was stopped at 72 hours. The cured cement was removed from the UCA and crushed with a mechanical press which gave a compressive strength of 68.9 psi. The portion kept at room temperature and pressure was still too soft to be crushed after 7 days.

[0067] Sample 10 was prepared using the same slurry design as Sample 8 except that equal amounts of sodium hydroxide and sodium sulfate were added as an activator. The sodium hydroxide and sodium sulfate were added in solid form directly to the mixing jar that contained the prepared slurry. Sample 10 reached 50 psi of compressive strength at 22 hours and 40 minutes. The strength continued to build, reaching a maximum of 900 psi, when the test was stopped at 72 hours. The cured cement was removed from the UCA and crushed with a mechanical press which gave a compressive strength of 786 psi. The portion kept at room temperature and pressure was crushed after 7 days resulting in a compressive strength of 47.9 psi.

[0068] The results of these tests are set forth in the table below. The abbreviation "% bwop" refers to the percent of the component by weight of the pumice. The abbreviation

"gal/sk" refers to gallons of the component per 46-pound sack of the pumice. The abbreviation "RTP" refers to room temperature and pressure.

Table 6
Compressive Strength Tests

Sample		**7**	**8**	**9**	**10**
Density	lb/gal	13.38	13.38	13.38	13.38
Water	% bwop	61.97	63.60	64.62	64.11
Pumice	% bwop	100	100	100	100
Hydrated Lime	% bwop	20	20	20	20
Dispersant	gal/sk	0.07	0.07	0.07	0.07
Set Retarder	% bwop	0.06	0.06	0.06	0.06
Sodium Hydroxide	% bwop	--	4	--	2
Sodium Sulfate	% bwop	--	--	4	2
UCA					
Temp/Press	F/Psi	100/3000	100/3000	100/3000	100/3000
Initial Set (50 psi)	hr:min	>78	16:36	67:29	22:40
Final Set (100 psi)	hr:min	--	21:08	--	32:44
24 Hr Comp. Strength	psi	--	138.74	--	59.60
48 Hr Comp. Strength	psi	--	711.35	--	331.48
72 Hr Comp. Strength	psi	--	1300	78	900
72 Hr Crush Strength (UCA)	psi	--	969	68.90	786
7-Day Crush Strength (RTP)	psi	--	143.20	0.00	47.90

[0069] Example 5 thus indicates that sodium hydroxide, sodium sulfate, and combinations of the two can activate the set-delayed cement compositions, but to varying degrees. The testing showed that both sodium hydroxide and combinations of sodium hydroxide with sodium sulfate activated the cement compositions to an acceptable level. When compared to the non-activated composition, sodium sulfate activated the cement compositions, but much less so than the sodium hydroxide or combination of sodium hydroxide and sodium sulfate.

[0070] It should be understood that the compositions and methods are described in terms of "comprising," "containing," or "including" various components or steps, the compositions and methods can also "consist essentially of" or "consist of" the various components and steps. Moreover, the indefinite articles "a" or "an," as used in the claims, are defined herein to mean one or more than one of the element that it introduces.

[0071] For the sake of brevity, only certain ranges are explicitly disclosed herein. However, ranges from any lower limit may be combined with any upper limit to recite a range not explicitly recited, as well as, ranges from any lower limit may be combined with any other lower limit to recite a range not explicitly recited, in the same way, ranges from any upper limit may be combined with any other upper limit to recite a range not explicitly recited. Additionally, whenever a numerical range with a lower limit and an upper limit is disclosed, any number and any included range falling within the range are specifically disclosed. In particular, every range of values (of the form, "from about a to about b," or, equivalently, "from approximately a to b," or, equivalently, "from approximately a-b") disclosed herein is to be understood to set forth every number and range encompassed within the broader range of values even if not explicitly recited. Thus, every point or individual value may serve as its own lower or upper limit combined with any other point or individual value or any other lower or upper limit, to recite a range not explicitly recited.

[0072] Therefore, the present embodiments are well adapted to attain the ends and advantages mentioned as well as those that are inherent therein. The particular embodiments disclosed above are illustrative only, as the present embodiments may be modified and practiced in different but equivalent manners apparent to those skilled in the art having the benefit of the teachings herein. Although individual embodiments are discussed, all combinations of each embodiment are contemplated and covered by the disclosure. Furthermore, no limitations are intended to the details of construction or design herein shown, other than as described in the claims below. Also, the terms in the claims have their plain, ordinary meaning unless otherwise explicitly and clearly defined by the patentee. It is therefore evident that the particular illustrative embodiments disclosed above may be altered or modified and all such variations are considered within the scope and spirit of the present disclosure. If there is any conflict in the usages of a word or term in this specification and one or more patent(s) or other documents that may be incorporated herein by reference, the definitions that are consistent with this specification should be adopted.

CLAIMS

What is claimed is:

1. A method of spraying a surface with a set-delayed cement composition, the method comprising:

providing a set-delayed cement composition comprising water, pumice, hydrated lime, and a set retarder;

spraying a surface with the set-delayed cement composition; and

allowing the set-delayed cement composition to set on the surface.

2. The method of claim 1 wherein the set retarder comprises at least one retarder selected from the group consisting of a phosphate, a phosphonate, a phosphonic acid, a phosphonic acid derivative, a lignosulfonate, a salt, an organic acid, a carboxymethylated hydroxyethylated cellulose, a synthetic co- or ter-polymer comprising sulfonate and carboxylic acid groups, a borate compound, and any mixture thereof.

3. The method of claim 1 wherein the set-delayed cement composition further comprises a cement set activator selected from the group consisting of a zeolite, amine, silicate, Group IA hydroxide, Group IIA hydroxide, monovalent salt, divalent salt, nanosilica, polyphosphate, and any combination thereof.

4. The method of claim 3, wherein the set-delayed cement composition comprising the cement set activator further comprises a thickening time in a range between about 30 seconds to about 10 minutes.

5. The method of claim 1 wherein the set-delayed cement composition further comprises a fiber.

6. The method of claim 1 wherein the set-delayed cement composition further comprises a dispersant selected from the group consisting of a sulfonated-formaldehyde-based dispersant, a polycarboxylated ether dispersant, and any combination thereof.

7. The method of claim 1 further comprising, prior to the spraying step, storing the set-delayed cement composition for a period of at least about 1 day.

8. The method of claim 1, wherein the surface is disposed about, on, or within a mine, a pond, a creek, a river, the ocean floor, a beach shore, a wall, a ceiling, a floor, an attic, or a basement.

9. The method of claim 1, wherein the set-delayed cement composition is disposed within a mine and wherein the set-delayed cement composition is pumped from a vessel outside of the mine into the mine.

10. The method of claim 1, wherein the set-delayed cement composition is foamed.

11. The method of claim 1, wherein the set-delayed cement composition comprises refractory materials.

12. The method of claim 1, wherein the set-delayed cement composition comprises a dye and/or beads.

13. A method of coating a surface with a set-delayed cement composition, the method comprising:

providing a set-delayed cement composition comprising water, pumice, hydrated lime, and a set retarder;

coating a surface with the set-delayed cement composition; and

allowing the set-delayed cement composition to set on the surface.

14. The method of claim 13 wherein the set retarder comprises at least one retarder selected from the group consisting of a phosphate, a phosphonate, a phosphonic acid, a phosphonic acid derivative, a lignosulfonate, a salt, an organic acid, a carboxymethylated hydroxyethylated cellulose, a synthetic co- or ter-polymer comprising sulfonate and carboxylic acid groups, a borate compound, and any mixture thereof.

15. The method of claim 13 wherein the set-delayed cement composition further comprises a cement set activator selected from the group consisting of a zeolite, amine, silicate, Group IA hydroxide, Group IIA hydroxide, monovalent salt, divalent salt, nanosilica, polyphosphate, and any combination thereof.

16. The method of claim 13 wherein the set-delayed cement composition comprising the cement set activator further comprises a thickening time in a range between about 30 seconds to about 10 minutes.

17. The method of claim 13 wherein the coating a surface with the set-delayed cement composition comprises painting the surface with the set-delayed cement composition or dipping the surface into a vessel containing the set-delayed cement composition.

18. A cementing system comprising:

a set-delayed cement composition comprising:

water,

pumice,

hydrated lime,

a set retarder, wherein the set-delayed cement composition is capable of remaining in a pumpable fluid state for at least about one day at 80° F;

a cementing unit comprising:

a vessel,

a conduit; and

a nozzle coupled to the conduit.

19. The cementing system of claim 18 wherein the cementing unit further comprises a pneumatic system comprising a gas compressor, a compressed gas, and a compressed gas conduit, wherein the compressed gas conduit is coupled to the nozzle, and wherein the compressed gas is capable of spraying the set-delayed cement composition.

20. The cementing system of claim 18, wherein the cementing unit further comprises a hydraulic system coupled to the nozzle, wherein the hydraulic system is capable of spraying the set-delayed cement composition.

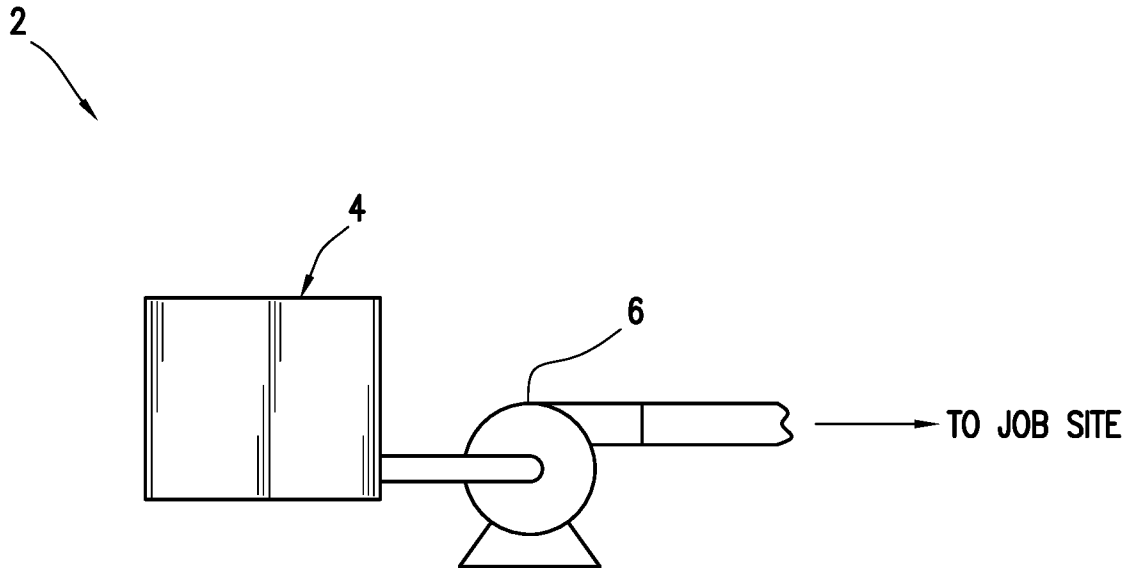


FIG. 1

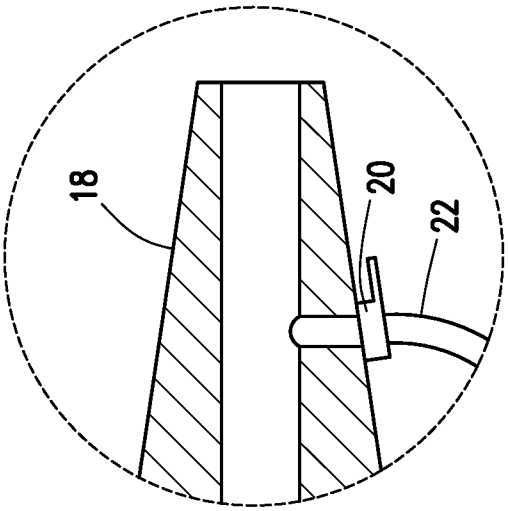


FIG. 2A

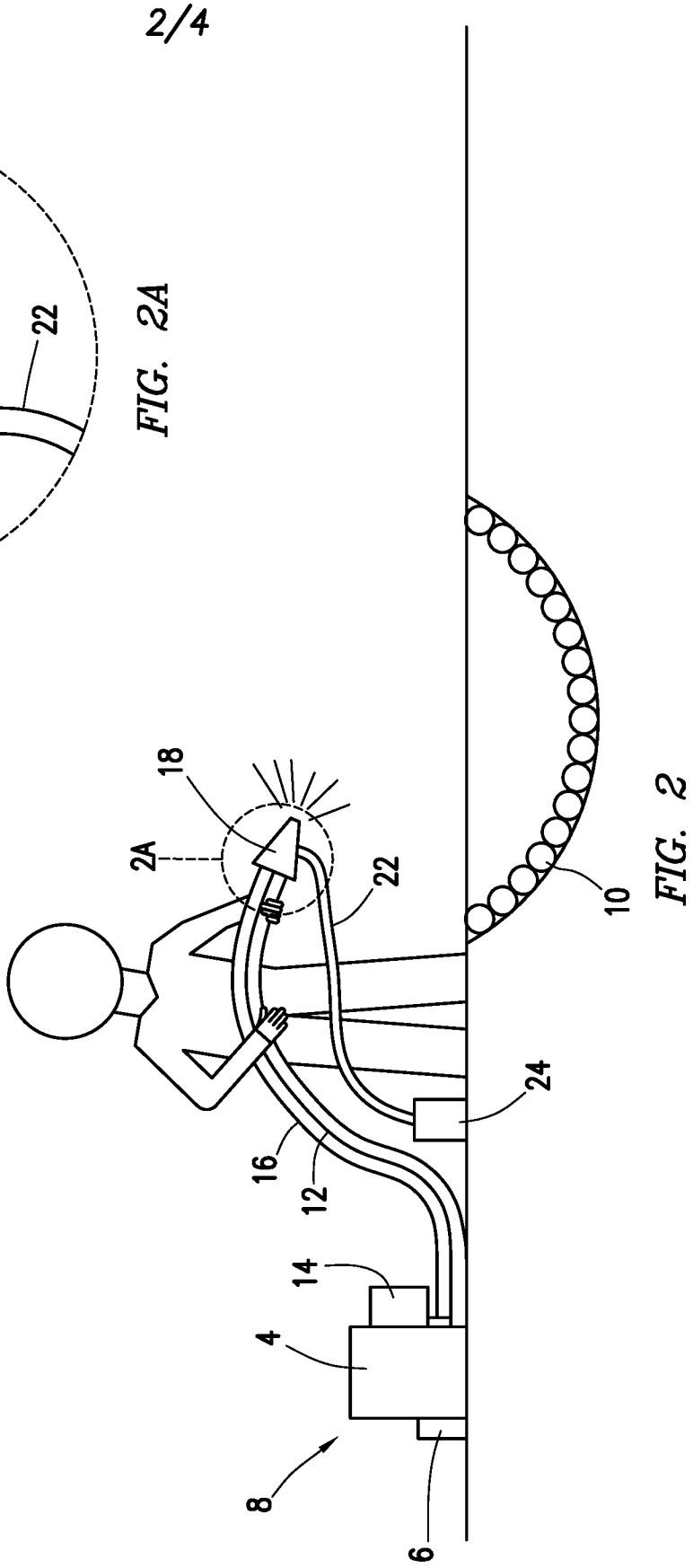


FIG. 2

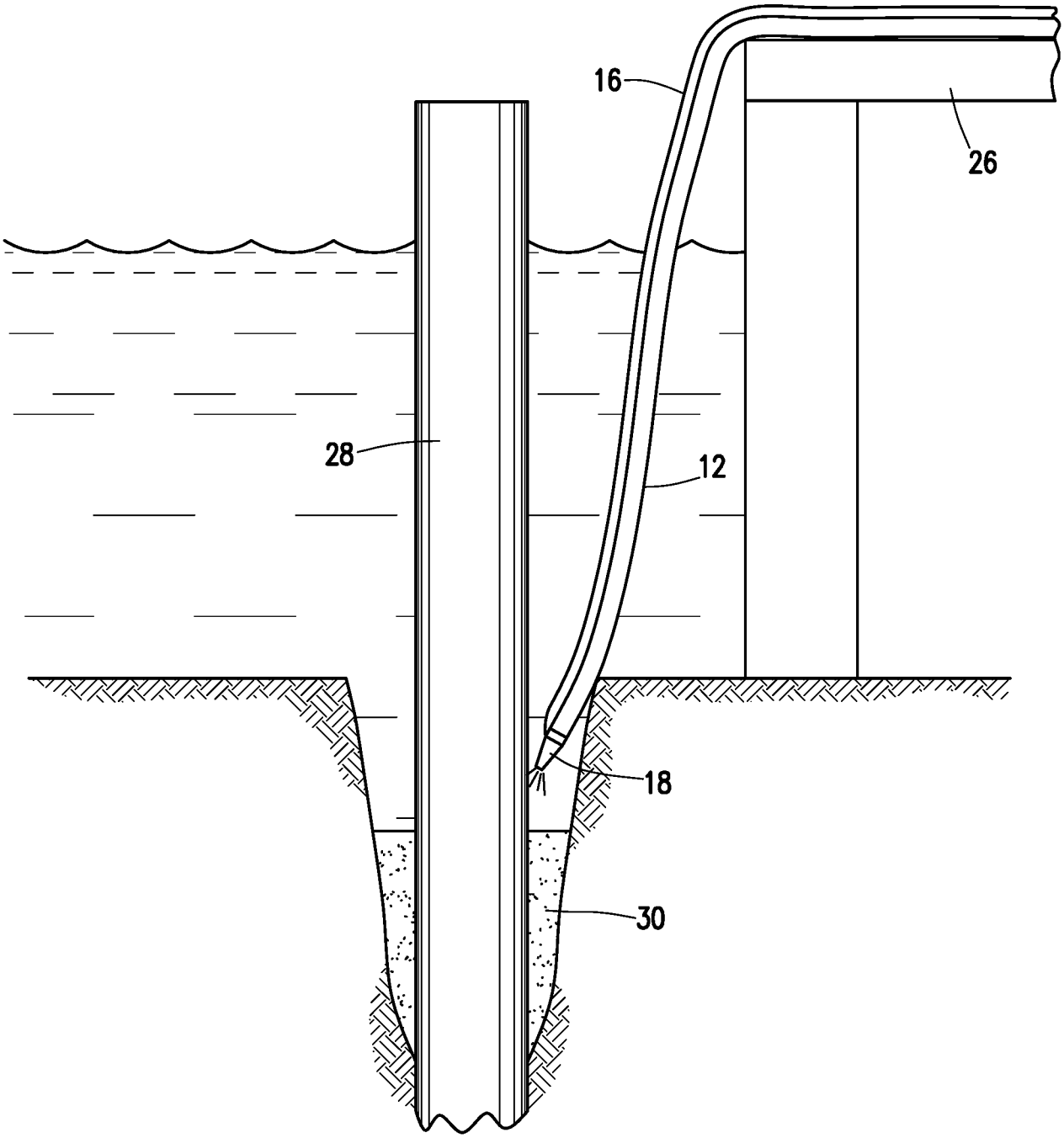


FIG. 3

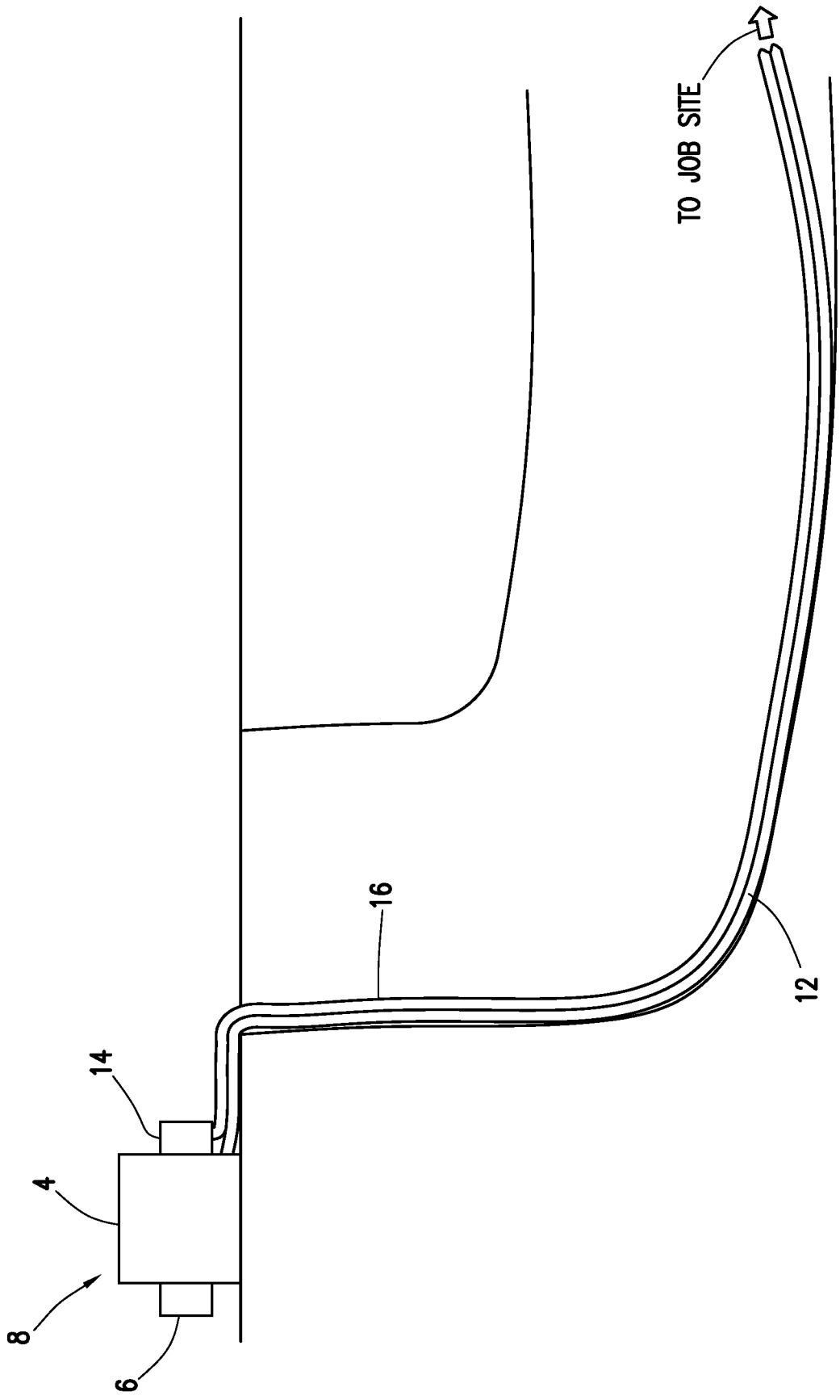


FIG. 4

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2016/014690

A. CLASSIFICATION OF SUBJECT MATTER

C04B 14/16(2006.01)i, C04B 28/10(2006.01)i, C04B 24/00(2006.01)i, C04B 24/16(2006.01)i, C04B 16/06(2006.01)i, C04B 41/45(2006.01)i

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)
C04B 14/16; B05D 1/02; B32B 13/00; B05B 1/28; E01C 7/14; E21B 33/13; E21B 33/14; C04B 14/00; C04B 28/10; C04B 24/00; C04B 24/16; C04B 16/06; C04B 41/45

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean utility models and applications for utility models
Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKOMPASS(KIPO internal) & keywords: spray, dipping, coat, surface, set-delayed cement, water, pumice, hydrated lime, set retarder, phosphate, set activator, thickening time, mine, pump

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 8851173 B2 (BROTHERS, LANCE E. et al.) 07 October 2014 See column 2, lines 33-53; column 5, lines 1-17; column 6, lines 4-9; column 6, line 61-column 7, line 17; example 4; claims 1, 5-9, 11, 12.	1-20
Y	US 2002-0009622 A1 (GOODSON, DAVID M.) 24 January 2002 See paragraphs [0005], [0009], [0010]; claims 1-16.	1-20
Y	US 4961536 A (CORREARD, JEAN-YVES) 09 October 1990 See column 3, lines 23-62; figures 1, 2.	1-20
Y	US 5407299 A (SUTTON, JOHN S.) 18 April 1995 See column 3, line 52-column 4, line 4; figures 1, 2.	1-20
A	US 2007-0054059 A1 (NAKASHIMA, YASUHIRO et al.) 08 March 2007 See paragraphs [0001], [0052], [0074], [0088], [0089]; claims 1-4, 19, 20.	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
"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
08 August 2016 (08.08.2016)	**08 August 2016 (08.08.2016)**

Name and mailing address of the ISA/KR
International Application Division
Korean Intellectual Property Office
189 Cheongsa-ro, Seo-gu, Daejeon, 35208, Republic of Korea
Facsimile No. +82-42-481-8578

Authorized officer
CHO, KI YUN
Telephone No. +82-42-481-5655

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/US2016/014690

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 8851173 B2	07/10/2014	AU 2013-230962 A1	11/09/2014
		AU 2013-230962 B2	09/07/2015
		AU 2015-205948 A1	20/08/2015
		AU 2015-227456 A1	15/10/2015
		CA 2866602 A1	12/09/2013
		EP 2822914 A1	14/01/2015
		MX 2014010765 A	09/03/2015
		PL 410494 A1	09/11/2015
		RU 2014140788 A	27/04/2016
		US 2013-0233550 A1	12/09/2013
		US 2014-0373756 A1	25/12/2014
		US 2014-0374098 A1	25/12/2014
		US 9260343 B2	16/02/2016
		WO 2013-134456 A1	12/09/2013
US 2002-0009622 A1	24/01/2002	US 6458423 B1	01/10/2002
		US 6783799 B1	31/08/2004
US 4961536 A	09/10/1990	EP 0341145 A1	08/11/1989
		EP 0341145 B1	01/07/1992
		FR 2630930 A1	10/11/1989
		JP 01-317563 A	22/12/1989
US 5407299 A	18/04/1995	None	
US 2007-0054059 A1	08/03/2007	CN 100345792 C	31/10/2007
		CN 1701045 A	23/11/2005
		EP 1657226 A1	17/05/2006
		EP 1657226 A4	25/05/2011
		EP 1657226 B1	17/12/2014
		JP 4746429 B2	10/08/2011
		KR 10-0916736 B1	14/09/2009
		KR 10-2006-0037229 A	03/05/2006
		NO 20055926 A	02/03/2006
		TW I348462 B	11/09/2011
		US 7618490 B2	17/11/2009
		WO 2005-019131 A1	03/03/2005