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(54) **Title**: REDUCED CARBON FOOTPRINT SETTABLE COMPOSITIONS FOR USE IN SUBTERRANEAN FORMATIONS

(57) **Abstract**: An example method of cementing in a subterranean formation includes determining a settable composition for use in the subterranean formation; calculating a total carbon footprint of the settable composition; determining at least one additive for use in the settable composition, wherein the additive replaces at least a portion of the settable composition and reduces the total carbon footprint of the settable composition; preparing the settable composition comprising the additive; placing the settable composition comprising the additive in the subterranean formation; and allowing the settable composition comprising the additive to set in the subterranean formation. Additional embodiments of the present invention include determining an amount of reduction in the carbon footprint of the settable composition; and/or communicating the amount of reduction in the carbon footprint of the settable composition to a customer or end user.

REDUCED CARBON FOOTPRINT SETTABLE COMPOSITIONS FOR USE IN SUBTERRANEAN FORMATIONS

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application is a continuation-in-part of U.S. Application Serial No. 11/223,669 entitled "Settable Compositions Comprising Cement Kiln Dust and Additive(s)," filed September 9, 2005, the entire disclosure of which is hereby incorporated by reference.

BACKGROUND

[0002] The present invention relates to cementing operations and, more particularly, in certain embodiments, to settable compositions having reduced carbon footprints and associated methods of use.

[0003] Settable compositions may be used in a variety of subterranean applications. As used herein, the term "settable composition" refers to any composition that over time will set to form a hardened mass. One example of a settable composition comprises hydraulic cement and water. Subterranean applications that may involve settable compositions include, but are not limited to, primary cementing, remedial cementing, and drilling operations. Settable compositions also may be used in surface applications, for example, construction cementing.

[0004] Settable compositions may be used in primary cementing operations whereby pipe strings, such as casing and liners, are cemented in well bores. In performing primary cementing, a settable composition may be pumped into an annular space between the walls of a well bore and the pipe string disposed therein. The settable composition sets in the annular space, thereby forming an annular sheath of hardened cement (*e.g.*, a cement sheath) that supports and positions the pipe string in the well bore and bonds the exterior surface of the pipe string to the walls of the well bore.

[0005] Settable compositions also may be used in remedial cementing operations, such as sealing voids in a pipe string or a cement sheath. As used herein the term "void" refers to any type of space, including fractures, holes, cracks, channels, spaces, and the like. Such voids may include: holes or cracks in the pipe strings; holes, cracks, spaces, or channels in the cement sheath; and very small spaces (commonly referred to as "microannuli") between the cement sheath and the exterior surface of the well casing or

formation. Sealing such voids may prevent the undesired flow of fluids (*e.g.*, oil, gas, water, etc.) and/or fine solids into, or from, the well bore.

[0006] The sealing of such voids, whether or not made deliberately, has been attempted by introducing a substance into the void and permitting it to remain therein to seal the void. If the substance does not fit into the void, a bridge, patch, or sheath may be formed over the void to possibly produce a termination of the undesired fluid flow. Substances used heretofore in methods to terminate the undesired passage of fluids through such voids include settable compositions comprising water and hydraulic cement, wherein the methods employ hydraulic pressure to force the settable composition into the void. Once placed into the void, the settable composition may be permitted to harden.

[0007] Remedial cementing operations also may be used to seal portions of subterranean formations or portions of gravel packs. The portions of the subterranean formation may include permeable portions of a formation and fractures (natural or otherwise) in the formation and other portions of the formation that may allow the undesired flow of fluid into, or from, the well bore. The portions of the gravel pack include those portions of the gravel pack, wherein it is desired to prevent the undesired flow of fluids into, or from, the well bore. A "gravel pack" is a term commonly used to refer to a volume of particulate materials (such as sand) placed into a well bore to at least partially reduce the migration of unconsolidated formation particulates into the well bore. While screenless gravel packing operations are becoming more common, gravel packing operations commonly involve placing a gravel pack screen in the well bore neighboring a desired portion of the subterranean formation, and packing the surrounding annulus between the screen and the well bore with particulate materials that are sized to prevent and inhibit the passage of formation solids through the gravel pack with produced fluids. Among other things, this method may allow sealing of the portion of the gravel pack to prevent the undesired flow of fluids without requiring the gravel pack's removal.

[0008] Settable compositions also may be used during the drilling of the well bore in a subterranean formation. For example, in the drilling of a well bore, it may be desirable, in some instances, to change the direction of the well bore. In some instances, settable compositions may be used to facilitate this change of direction, for example, by drilling a pilot hole in a hardened mass of cement, commonly referred to as a "kickoff plug," placed in the well bore.

[0009] Certain formations may cause the drill bit to drill in a particular direction. For example, in a vertical well, this may result in an undesirable well bore deviation from vertical. In a directional well (which is drilled at an angle from vertical), after drilling an initial portion of the well bore vertically, the direction induced by the formation may make following the desired path difficult. In those and other instances, special directional drilling tools may be used, such as a whipstock, a bent sub-downhole motorized drill combination, and the like. Generally, the directional drilling tool or tools used may be orientated so that a pilot hole is produced at the desired angle to the previous well bore in a desired direction. When the pilot hole has been drilled for a short distance, the special tool or tools are removed, if required, and drilling along the new path may be resumed. To help ensure that the subsequent drilling follows the pilot hole, it may be necessary to drill the pilot hole in a kickoff plug, placed in the well bore. In those instances, prior to drilling the pilot hole, a settable composition may be introduced into the well bore and allowed to set to form a kickoff plug therein. The pilot hole then may be drilled in the kickoff plug, and the high strength of the kickoff plug helps ensure that the subsequent drilling proceeds in the direction of the pilot hole.

[0010] Settable compositions used heretofore commonly comprise Portland cement. Portland cement generally is a major component of the cost for the settable compositions. To reduce the cost of such settable compositions, other components may be included in the settable composition in addition to, or in place of, the Portland cement. Such components may include fly ash, slag cement, shale, metakaolin, micro-fine cement, and the like. "Fly ash," as that term is used herein, refers to the residue from the combustion of powdered or ground coal, wherein the fly ash carried by the flue gases may be recovered, for example, by electrostatic precipitation. "Slag," as that term is used herein, refers to a granulated, blast furnace by-product formed in the production of cast iron and generally comprises the oxidized impurities found in iron ore. Slag cement generally comprises slag and a base, for example, such as sodium hydroxide, sodium bicarbonate, sodium carbonate, or lime, to produce a settable composition that, when combined with water, may set to form a hardened mass.

[0011] During the manufacture of cement, a waste material commonly referred to as "CKD" is generated. "CKD," as that term is used herein, refers to a partially calcined kiln feed which is removed from the gas stream and collected in a dust collector

during the manufacture of cement. Usually, large quantities of CKD are collected in the production of cement that are commonly disposed of as waste. Disposal of the waste CKD can add undesirable costs to the manufacture of the cement, as well as the environmental concerns associated with its disposal. The chemical analysis of CKD from various cement manufactures varies depending on a number of factors, including the particular kiln feed, the efficiencies of the cement production operation, and the associated dust collection systems. CKD generally may comprise a variety of oxides, such as SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO, SO_3, Na_2O, and K_2O.

[0012] The manufacture of cement, such as Portland cement, is a very energy-intensive industry. Globally, cement manufactures account for as much as 2% of total energy consumption and as much as 5% of total industrial energy consumption. Much of this energy is producing by burning fossil fuels such as coal, contributing to the production of "greenhouse gases." One of the most discussed of these greenhouse gases is carbon dioxide (CO_2). The effect certain activities have on the climate in terms of the total amount of greenhouse gases produced is often described as a "carbon footprint." A relatively large producer of CO_2, with a relatively large carbon footprint, is the cement industry. It is estimated that the cement industry currently accounts for about 5% of the total global production of greenhouse gases.

SUMMARY

[0013] The present invention relates to cementing operations and, more particularly, in certain embodiments, to settable compositions having reduced carbon footprints and associated methods of use.

[0014] Certain embodiments of the present invention include calculating a total carbon footprint of a settable composition; determining an amount of reduction in the carbon footprint of the settable composition; and/or communicating the amount of reduction in the carbon footprint of the settable composition to a customer or end user.

[0015] In one embodiment, the present invention provides a method of cementing in a subterranean formation comprising: determining a settable composition for use in the subterranean formation; calculating a total carbon footprint of the settable composition; determining at least one additive for use in the settable composition, wherein the additive replaces at least a portion of the settable composition and reduces the total carbon footprint of the settable composition; preparing the settable composition comprising

the additive; placing the settable composition comprising the additive in the subterranean formation; and allowing the settable composition comprising the additive to set in the subterranean formation.

[0016] Another embodiment of the present invention provides a method of cementing in a subterranean formation comprising: determining a settable composition comprising a hydraulic cement and water for use in the subterranean formation, wherein the settable composition has a carbon footprint; replacing at least a portion of the hydraulic cement in the settable composition with at least one additive, wherein the carbon footprint of the settable composition is reduced by the additive; determining an amount of reduction in the carbon footprint of the settable composition; preparing the settable composition comprising the additive and having a reduced carbon footprint; placing the settable composition comprising the additive in the subterranean formation; and allowing the settable composition comprising the additive to set in the subterranean formation.

[0017] Another embodiment of the present invention provides a method of cementing in a subterranean formation comprising determining a settable composition for use in the subterranean formation, wherein the settable composition comprises Portland cement and water; calculating a total carbon footprint of the settable composition; replacing at least a portion of the Portland cement in the settable composition with cement kiln dust, wherein the total carbon footprint of the settable composition is reduced by the cement kiln dust; preparing the settable composition comprising the cement kiln dust; placing the settable composition comprising the cement kiln dust in the subterranean formation; and allowing the settable composition comprising the cement kiln dust to set in the subterranean formation.

[0018] The features and advantages of the present invention will be apparent to those skilled in the art. While numerous changes may be made by those skilled in the art, such changes are within the spirit of the invention.

DESCRIPTION OF PREFERRED EMBODIMENTS

[0019] The present invention relates to cementing operations and, more particularly, in certain embodiments, to settable compositions having reduced carbon footprints and associated methods of use. The settable compositions of the present invention may be used in a variety of subterranean applications, including primary cementing, remedial cementing, and drilling operations. The settable compositions of the present

invention also may be used in surface applications, for example, construction cementing. The settable compositions of the present invention also may be used in order to reduce the carbon footprint of a cementing operation.

Example Settable Compositions of the Present Invention

[0020] In one embodiment, a settable composition of the present invention comprises water and CKD. In some embodiments, a settable composition of the present invention may be foamed, for example, comprising water, CKD, a gas, and a surfactant. A foamed settable composition may be used, for example, where it is desired for the settable composition to be lightweight. Others means to reduce the densities of the settable compositions may be used in accordance with embodiments of the present invention, including, for example, hollow microspheres, low-density elastic beads, or other density-reducing additives known in the art. Other optional additives may also be included in the settable compositions of the present invention as desired, including, but not limited to, hydraulic cement, fly ash, slag cement, shale, zeolite, metakaolin, combinations thereof, and the like. By replacing at least a portion of the hydraulic cement that would typically be used in the settable composition with an additive (*e.g.*, CKD, ground granulated blast furnace slag, etc.) the carbon footprint of the settable composition is reduced.

[0021] The settable compositions of the present invention should have a density suitable for a particular application as desired by those of ordinary skill in the art, with the benefit of this disclosure. In some embodiments, the settable compositions of the present invention may have a density in the range of from about 6 pounds per gallon ("ppg") to about 18 ppg. In certain lightweight embodiments, the settable compositions of the present invention may have a density in the range of from about 6 ppg to about 13 ppg.

[0022] The water used in the settable compositions of the present invention may include freshwater, saltwater (*e.g.*, water containing one or more salts dissolved therein), brine (*e.g.*, saturated saltwater produced from subterranean formations), seawater, or combinations thereof. Generally, the water may be from any source, provided that it does not contain an excess of compounds that may adversely affect other components in the settable composition. In some embodiments, the water may be included in an amount sufficient to form a pumpable slurry. In some embodiments, the water may be included in the settable compositions of the present invention in an amount in the range of from about 40% to about 200% by weight. As used herein, the term "by weight," when used herein to

refer to the percent of a component in the settable composition, means by weight included in the settable compositions of the present invention relative to the weight of the dry components in the settable composition. In some embodiments, the water may be included in an amount in the range of from about 40% to about 150% by weight.

[0023] The CKD should be included in the settable compositions in an amount sufficient to provide the desired compressive strength, density, and/or cost reduction. In some embodiments, the CKD may be present in the settable compositions of the present invention in an amount in the range of from about 0.01% to 100% by weight. In some embodiments, the CKD may be present in the settable compositions of the present invention in an amount in the range of from about 5% to 100% by weight. In some embodiments, the CKD may be present in the settable compositions of the present invention in an amount in the range of from about 5% to about 80% by weight. In some embodiments, the CKD may be present in the settable compositions of the present invention in an amount in the range of from about 10% to about 50% by weight.

[0024] In some embodiments, the CKD may be included as an additive in cement composition in an amount necessary to achieve a desired reduction of a carbon footprint. By way of example, if the manufacture of 1 lb of cement produced 1 lb of CKD as a waste material, then a 50/50 blend of cement/CKD would result in a 50% reduction in the carbon footprint of the cementitious material being used. By way of another example, if a 25/75 blend of cement/CKD was used, a 75% reduction in the carbon footprint of the cementitious material being used could be achieved. Any desired reduction of carbon footprint may be achieved by including any desired blend of cement/CKD. A person of ordinary skill in the art, with the benefit of this disclosure, would be able to determine a desired reduction of a carbon footprint of a cementitious material and incorporate within that material an appropriate amount of CKD to achieve the desired reduction. In some embodiments, the desired reduction of carbon footprint may be from about 1% to about 100%. In other embodiments, the desired reduction of carbon footprint may be from about 5% to 75%. In other embodiments, the desired reduction of carbon footprint may be from about 10% to about 50%.

[0025] The settable compositions of the present invention may optionally comprise a hydraulic cement. A variety of hydraulic cements may be utilized in accordance with the present invention, including, but not limited to, those comprising calcium,

aluminum, silicon, oxygen, iron, and/or sulfur, which set and harden by reaction with water. Suitable hydraulic cements include, but are not limited to, Portland cements, pozzolana cements, gypsum cements, high alumina content cements, slag cements, silica cements, and combinations thereof. In certain embodiments, the hydraulic cement may comprise a Portland cement. Suitable hydraulic cements include those classified as Classes A through H according to American Petroleum Institute, *API Specification for Materials and Testing for Well Cements*, API Specification 10, Fifth Ed., July 1, 1990. In certain embodiments, API Class A, C, G and H Portland cements may be preferred.

[0026] Where present, the hydraulic cement generally may be included in the settable compositions in an amount sufficient to provide the desired compressive strength, density, and/or cost. In some embodiments, the hydraulic cement may be present in the settable compositions of the present invention in an amount in the range of from 0% to about 99.9% by weight. In some embodiments, the hydraulic cement may be present in the settable compositions of the present invention in an amount in the range of from 0% to about 75% by weight. In some embodiments, the hydraulic cement may be present in the settable compositions of the present invention in an amount in the range of from about 0% to about 50% by weight. In some embodiments, the hydraulic cement may be present in the settable compositions of the present invention in an amount in the range of from about 0% to about 25% by weight.

[0027] In some embodiments, a pozzolana cement that may be suitable for use comprises fly ash. A variety of fly ashes may be suitable, including fly ash classified as Class C and Class F fly ash according to American Petroleum Institute, *API Specification for Materials and Testing for Well Cements*, API Specification 10, Fifth Ed., July 1, 1990. Class C fly ash comprises both silica and lime so that, when mixed with water, it sets to form a hardened mass. Class F fly ash generally does not contain sufficient lime, so an additional source of calcium ions is required for the Class F fly ash to form a settable composition with water. In some embodiments, lime may be mixed with Class F fly ash in an amount in the range of from about 0.1% to about 25% by weight of the fly ash. In some instances, the lime may be hydrated lime. Suitable examples of fly ash include, but are not limited to, "POZMIX® A" cement additive, commercially available from Halliburton Energy Services, Inc., Duncan, Oklahoma.

[0028] Where present, the fly ash generally may be included in the settable compositions in an amount sufficient to provide the desired compressive strength, density, and/or cost. In some embodiments, the fly ash may be present in the settable compositions of the present invention in an amount in the range of from about 1% to about 75% by weight. In some embodiments, the fly ash may be present in the settable compositions of the present invention in an amount in the range of from about 5% to about 50% by weight.

[0029] In some embodiments, a slag cement that may be suitable for use may comprise slag. Slag generally does not contain sufficient basic material, so slag cement further may comprise a base to produce a settable composition that may react with water to set to form a hardened mass. Examples of suitable sources of bases include, but are not limited to, sodium hydroxide, sodium bicarbonate, sodium carbonate, lime, and combinations thereof.

[0030] Where present, the slag cement generally may be included in the settable compositions in an amount sufficient to provide the desired compressive strength, density, and/or cost. In some embodiments, the slag cement may be present in the settable compositions of the present invention in an amount in the range of from about 1% to about 99.9% by weight. In some embodiments, the slag cement may be present in the settable compositions of the present invention in an amount in the range of from about 1% to about 50% by weight.

[0031] In certain embodiments, the settable compositions of the present invention further may comprise metakaolin. Generally, metakaolin is a white pozzolan that may be prepared by heating kaolin clay, for example, to temperatures in the range of from about 600° to about 800°C. In some embodiments, the metakaolin may be present in the settable compositions of the present invention in an amount in the range of from about 1% to about 95% by weight. In some embodiments, the metakaolin may be present in an amount in the range of from about 1% to about 50% by weight.

[0032] In certain embodiments, the settable compositions of the present invention further may comprise shale. Among other things, shale included in the settable compositions may react with excess lime to form a suitable cementing material, for example, calcium silicate hydrate. A variety of shales are suitable, including those comprising silicon, aluminum, calcium, and/or magnesium. An example of a suitable shale comprises vitrified shale. Suitable examples of vitrified shale include, but are not limited to, "PRESSUR-

SEAL® FINE LCM" material and "PRESSUR-SEAL® COARSE LCM" material, which are commercially available from TXI Energy Services, Inc., Houston, Texas. Generally, the shale may have any particle size distribution as desired for a particular application. In certain embodiments, the shale may have a particle size distribution in the range of from about 37 micrometers to about 4,750 micrometers.

[0033] Where present, the shale may be included in the settable compositions of the present invention in an amount sufficient to provide the desired compressive strength, density, and/or cost. In some embodiments, the shale may be present in an amount in the range of from about 1% to about 75% by weight. In some embodiments, the shale may be present in an amount in the range of from about 1% to about 35% by weight. One of ordinary skill in the art, with the benefit of this disclosure, will recognize the appropriate amount of the shale to include for a chosen application.

[0034] In certain embodiments, the settable compositions of the present invention further may comprise zeolite. Zeolites generally are porous alumino-silicate minerals that may be either a natural or synthetic material. Synthetic zeolites are based on the same type of structural cell as natural zeolites, and may comprise aluminosilicate hydrates. As used herein, the term "zeolite" refers to all natural and synthetic forms of zeolite.

[0035] In certain embodiments, suitable zeolites for use in present invention may include "analcime" (which is hydrated sodium aluminum silicate), "bikitaite" (which is lithium aluminum silicate), "brewsterite" (which is hydrated strontium barium calcium aluminum silicate), "chabazite" (which is hydrated calcium aluminum silicate), "clinoptilolite" (which is hydrated sodium aluminum silicate), "faujasite" (which is hydrated sodium potassium calcium magnesium aluminum silicate), "ferrierite," "harmotome" (which is hydrated barium aluminum silicate), "heulandite" (which is hydrated sodium calcium aluminum silicate), "laumontite" (which is hydrated calcium aluminum silicate), "mesolite" (which is hydrated sodium calcium aluminum silicate), "natrolite" (which is hydrated sodium aluminum silicate), "paulingite" (which is hydrated potassium sodium calcium barium aluminum silicate), "phillipsite" (which is hydrated potassium sodium calcium aluminum silicate), "scolecite" (which is hydrated calcium aluminum silicate), "stellerite" (which is hydrated calcium aluminum silicate), "stilbite" (which is hydrated sodium calcium aluminum silicate), and "thomsonite" (which is hydrated sodium calcium aluminum silicate),

and combinations thereof. In certain embodiments, suitable zeolites for use in the present invention include chabazite and clinoptilolite. An example of a suitable source of zeolite is available from the C2C Zeolite Corporation of Calgary, Canada.

[0036] In some embodiments, the zeolite may be present in the settable compositions of the present invention in an amount in the range of from about 1% to about 65% by weight. In certain embodiments, the zeolite may be present in an amount in the range of from about 1% to about 40% by weight.

[0037] In certain embodiments, the settable compositions of the present invention further may comprise a set retarding additive. As used herein, the term "set retarding additive" refers to an additive that retards the setting of the settable compositions of the present invention. Examples of suitable set retarding additives include, but are not limited to, ammonium, alkali metals, alkaline earth metals, metal salts of sulfoalkylated lignins, hydroxycarboxy acids, copolymers that comprise acrylic acid or maleic acid, and combinations thereof. One example of a suitable sulfoalkylated lignin comprises a sulfomethylated lignin. Suitable set retarding additives are disclosed in more detail in United States Patent No. Re. 31,190, the entire disclosure of which is incorporated herein by reference. Suitable set retarding additives are commercially available from Halliburton Energy Services, Inc. under the tradenames "HR® 4," "HR® 5," HR® 7," "HR® 12," "HR® 15," HR® 25," "SCR™ 100," and "SCR™ 500." Generally, where used, the set retarding additive may be included in the settable compositions of the present invention in an amount sufficient to provide the desired set retardation. In some embodiments, the set retarding additive may be present in an amount in the range of from about 0.1% to about 5% by weight.

[0038] Optionally, other additional additives may be added to the settable compositions of the present invention as deemed appropriate by one skilled in the art, with the benefit of this disclosure. Examples of such additives include, but are not limited to, accelerators, weight reducing additives, heavyweight additives, lost circulation materials, filtration control additives, dispersants, and combinations thereof. Suitable examples of these additives include crystalline silica compounds, amorphous silica, salts, fibers, hydratable clays, microspheres, pozzolan lime, latex cement, thixotropic additives, combinations thereof and the like.

[0039] An example of a settable composition of the present invention may comprise water and CKD. As desired by one of ordinary skill in the art, with the benefit of this disclosure, such settable composition of the present invention further may comprise any of the above-listed additives, as well any of a variety of other additives suitable for use in subterranean applications.

[0040] Another example of a settable composition of the present invention may comprise water and CKD, and an additive comprising at least one of the following group: fly ash; shale; zeolite; slag cement; metakaolin; and combinations thereof. As desired by one of ordinary skill in the art, with the benefit of this disclosure, such settable composition of the present invention further may comprise any of the above-listed additives, as well any of a variety of other additives suitable for use in subterranean applications.

[0041] As mentioned previously, in certain embodiments, the settable compositions of the present invention may be foamed with a gas. In some embodiments, foamed settable compositions of the present invention may comprise water, CKD, a gas, and a surfactant. Other suitable additives, such as those discussed previously, also may be included in the foamed settable compositions of the present invention as desired by those of ordinary skill in the art, with the benefit of this disclosure. The gas used in the foamed settable compositions of the present invention may be any gas suitable for foaming a settable composition, including, but not limited to, air, nitrogen, or combinations thereof. Generally, the gas should be present in the foamed settable compositions of the present invention in an amount sufficient to form the desired foam. In certain embodiments, the gas may be present in the foamed settable compositions of the present invention in an amount in the range of from about 10% to about 80% by volume of the composition.

[0042] Where foamed, the settable compositions of the present invention further comprise a surfactant. In some embodiments, the surfactant comprises a foaming and stabilizing surfactant. As used herein, a "foaming and stabilizing surfactant composition" refers to a composition that comprises one or more surfactants and, among other things, may be used to facilitate the foaming of a settable composition and also may stabilize the resultant foamed settable composition formed therewith. Any suitable foaming and stabilizing surfactant composition may be used in the settable compositions of the present invention. Suitable foaming and stabilizing surfactant compositions may 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. In one certain embodiment, the foaming and stabilizing surfactant composition comprises a mixture of an ammonium salt of an alkyl ether sulfate, a cocoamidopropyl betaine surfactant, a cocoamidopropyl dimethylamine oxide surfactant, sodium chloride, and water. A suitable example of such a mixture is "ZONESEAL® 2000" foaming additive, commercially available from Halliburton Energy Services, Inc. Suitable foaming and stabilizing surfactant compositions are described in United States Patent Nos. 6,797,054, 6,547,871, 6,367,550, 6,063,738, and 5,897,699, the entire disclosures of which are incorporated herein by reference.

[0043] Generally, the surfactant may be present in the foamed settable compositions of the present invention in an amount sufficient to provide a suitable foam. In some embodiments, the surfactant may be present in an amount in the range of from about 0.8% and about 5% by volume of the water.

[0001] Embodiments of the settable compositions of the present invention may also comprise swellable particles. As used herein, a particle is characterized as swelling when it swells upon contact with oil and/or an aqueous fluid (e.g., water). Swellable particles suitable for use in embodiments of the present invention may generally swell by up to about 50% of their original size at the surface. Under downhole conditions, this swelling may be more, or less, depending on the conditions presented. For example, the swelling may be at least 10% at downhole conditions. In some embodiments, the swelling may be up to about 50% under downhole conditions. However, as those of ordinary skill in the art, with the benefit of this disclosure, will appreciate, the actual swelling when the swellable particles are included in a settable composition may depend on, for example, the concentration of the swellable particles included in the settable composition. In accordance with embodiments of the present invention, the swellable particles may be included in the settable composition, for example, to counteract the formation of cracks in the cement sheath and/or micro-annulus between the cement sheath and the pipe string or the formation. In general, the swellable

particles should be capable of swelling when contacted by aqueous fluids and/or oil to inhibit fluid flow through the crack and/or micro-annulus. Accordingly, the swellable particles may prevent and/or reduce the loss of zonal isolation in spite of the formation of cracks and/or micro-annulus, potentially resulting in an improved annular seal for the extended cement compositions.

[0002] An example of swellable particles that may be utilized in embodiments of the present invention comprises a swellable elastomer. Some specific examples of suitable swellable elastomers include, but are not limited to, natural rubber, acrylate butadiene rubber, polyacrylate rubber, isoprene rubber, choloroprene rubber, butyl rubber (IIR), brominated butyl rubber (BIIR), chlorinated butyl rubber (CIIR), chlorinated polyethylene (CM/CPE), neoprene rubber (CR), styrene butadiene copolymer rubber (SBR), sulphonated polyethylene (CSM), ethylene acrylate rubber (EAM/AEM), epichlorohydrin ethylene oxide copolymer (CO, ECO), ethylene-propylene rubber (EPM and EDPM), ethylene-propylene-diene terpolymer rubber (EPT), ethylene vinyl acetate copolymer, fluorosilicone rubbers (FVMQ), silicone rubbers (VMQ), poly 2,2,1-bicyclo heptene (polynorborneane), and alkylstyrene. One example of a suitable swellable elastomer comprises a block copolymer of a styrene butadiene rubber. Examples of suitable elastomers that swell when in contact with oil include, but are not limited to, nitrile rubber (NBR), hydrogenated nitrile rubber (HNBR, HNS), fluoro rubbers (FKM), perfluoro rubbers (FFKM), tetrafluorethylene/propylene (TFE/P), isobutylene maleic anhydride. Combinations of suitable swellable elastomers may also be used. Other swellable elastomers that behave in a similar fashion with respect to oil or aqueous fluids also may be suitable. Those of ordinary skill in the art, with the benefit of this disclosure, will be able to select an appropriate swellable elastomer for use in embodiments of the settable compositions of the present invention based on a variety of factors, including the application in which the composition will be used and the desired swelling characteristics.

[0003] An example of swellable particles that may be utilized in embodiments of the present invention comprises a water-swellable polymer. Some specific examples of suitable water-swellable polymers, include, but are not limited to starch-polyacrylate acid graft copolymer and salts thereof, polyethylene oxide polymer, carboxymethyl cellulose type polymers, polyacrylamide, poly(acrylic acid) and salts thereof, poly(acrylic acid-co-acrylamide) and salts thereof, graft-poly(ethylene oxide) of poly(acrylic acid) and salts

thereof, poly(2-hydroxyethyl methacrylate), and poly(2-hydroxypropyl methacrylate),. Combinations of suitable water-swellable polymers may also be used. In certain embodiments, the water-swellable polymers may be crosslinked and/or lightly crosslinked. Other water-swellable polymers that behave in a similar fashion with respect to aqueous fluids also may be suitable. Those of ordinary skill in the art, with the benefit of this disclosure, will be able to select appropriate water-swellable polymers for use in embodiments of the settable compositions of the present invention based on a variety of factors, including the application in which the composition will be used and the desired swelling characteristics.

[0004] Where used, the swellable particles generally may be included in the settable compositions in an amount sufficient to provide the desired mechanical properties. In some embodiments, the swellable particles may be present in the settable compositions in an amount up to about 25% by weight of the cementitious component. In some embodiments, the swellable particles may be present in the settable compositions in a range of about 5% to about 25% by weight of the cementitious component. In some embodiments, the swellable particles may be present in the settable compositions in a range of about 15% to about 20% by weight of the cementitious component.

[0044] In addition, the swellable particles that are utilized may have a wide variety of shapes and sizes of individual particles suitable for use in accordance with embodiments of the present invention. By way of example, the swellable particles may have a well-defined physical shape as well as an irregular geometry, including the physical shape of platelets, shavings, fibers, flakes, ribbons, rods, strips, spheroids, beads, pellets, tablets, or any other physical shape. In some embodiments, the swellable particles may have a particle size in the range of about 5 microns to about 1,500 microns. In some embodiments, the swellable particles may have a particle size in the range of about 20 microns to about 500 microns. However, particle sizes outside these defined ranges also may be suitable for particular applications.

Example Methods of the Present Invention

[0045] The settable compositions of the present invention may be used in a variety of subterranean applications, including, but not limited to, primary cementing, remedial cementing, and drilling operations. The settable compositions of the present invention also may be used in surface applications, for example, construction cementing.

[0046] An example of a method of the present invention comprises providing a settable composition of the present invention comprising water and CKD; placing the settable composition in a location to be cemented; and allowing the settable composition to set therein. In some embodiments, the location to be cemented may be above ground, for example, in construction cementing. In some embodiments, the location to be cemented may be in a subterranean formation, for example, in subterranean applications. In some embodiments, the settable compositions of the present invention may be foamed. As desired by one of ordinary skill in the art, with the benefit of this disclosure, the settable compositions of the present invention useful in this method further may comprise any of the above-listed additives, as well any of a variety of other additives suitable for use in subterranean applications.

[0047] Another example of a method of the present invention is a method of cementing a pipe string (*e.g.*, casing, expandable casing, liners, etc.) disposed in a well bore. An example of such a method may comprise providing a settable composition of the present invention comprising water and CKD; introducing the settable composition into the annulus between the pipe string and a wall of the well bore; and allowing the settable composition to set in the annulus to form a hardened mass. Generally, in most instances, the hardened mass should fix the pipe string in the well bore. In some embodiments, the settable compositions of the present invention may be foamed. As desired by one of ordinary skill in the art, with the benefit of this disclosure, the settable compositions of the present invention useful in this method further may comprise any of the above-listed additives, as well any of a variety of other additives suitable for use in subterranean application.

[0048] Another example of a method of the present invention is method of sealing a portion of a gravel pack or a portion of a subterranean formation. An example of such a method may comprise providing a settable composition of the present invention comprising water and CKD; introducing the settable composition into the portion of the gravel pack or the portion of the subterranean formation; and allowing the settable composition to form a hardened mass in the portion. The portions of the subterranean formation may include permeable portions of the formation and fractures (natural or otherwise) in the formation and other portions of the formation that may allow the undesired flow of fluid into, or from, the well bore. The portions of the gravel pack include those portions of the gravel pack, wherein it is desired to prevent the undesired flow of fluids into,

or from, the well bore. Among other things, this method may allow the sealing of the portion of the gravel pack to prevent the undesired flow of fluids without requiring the gravel pack's removal. In some embodiments, the settable compositions of the present invention may be foamed. As desired by one of ordinary skill in the art, with the benefit of this disclosure, the settable compositions of the present invention useful in this method further may comprise any of the above-listed additives, as well any of a variety of other additives suitable for use in subterranean applications.

[0049] Another example of a method of the present invention is a method of sealing voids located in a pipe string (*e.g.*, casing, expandable casings, liners, etc.) or in a cement sheath. Generally, the pipe string will be disposed in a well bore, and the cement sheath may be located in the annulus between the pipe string disposed in the well bore and a wall of the well bore. An example of such a method may comprise providing a settable composition comprising water and CKD; introducing the settable composition into the void; and allowing the settable composition to set to form a hardened mass in the void. In some embodiments, the settable compositions of the present invention may be foamed. As desired by one of ordinary skill in the art, with the benefit of this disclosure, the settable compositions of the present invention useful in this method further may comprise any of the above-listed additives, as well any of a variety of other additives suitable for use in subterranean applications.

[0050] When sealing a void in a pipe string, the methods of the present invention, in some embodiments, further may comprise locating the void in the pipe string; and isolating the void by defining a space within the pipe string in communication with the void; wherein the settable composition may be introduced into the void from the space. The void may be isolated using any suitable technique and/or apparatus, including bridge plugs, packers, and the like. The void in the pipe string may be located using any suitable technique.

[0051] When sealing a void in the cement sheath, the methods of the present invention, in some embodiments, further may comprise locating the void in the cement sheath; producing a perforation in the pipe string that intersects the void; and isolating the void by defining a space within the pipe string in communication with the void via the perforation, wherein the settable composition is introduced into the void via the perforation. The void in the pipe string may be located using any suitable technique. The perforation

may be created in the pipe string using any suitable technique, for example, perforating guns. The void may be isolated using any suitable technique and/or apparatus, including bridge plugs, packers, and the like.

[0052] Another example of a method of the present invention is a method of changing the direction of drilling a well bore. An example of such a method may comprise providing a settable composition comprising CKD; introducing the settable composition into the well bore at a location in the well bore wherein the direction of drilling is to be changed; allowing the settable composition to set to form a kickoff plug in the well bore; drilling a hole in the kickoff plug; and drilling of the well bore through the hole in the kickoff plug. In some embodiments, the settable compositions of the present invention may be foamed. As desired by one of ordinary skill in the art, with the benefit of this disclosure, the settable compositions of the present invention useful in this method further may comprise any of the above-listed additives, as well any of a variety of other additives suitable for use in subterranean applications.

[0053] Generally, the drilling operation should continue in the direction of the hole drilled through the kickoff plug. The well bore and hole in the kickoff plug may be drilled using any suitable technique, including rotary drilling, cable tool drilling, and the like. In some embodiments, one or more oriented directional drilling tools may be placed adjacent to the kickoff plug. Suitable directional drilling tools include, but are not limited to, whip-stocks, bent sub-downhole motorized drill combinations, and the like. The direction drilling tools then may be used to drill the hole in the kickoff plug so that the hole is positioned in the desired direction. Optionally, the directional drilling tool may be removed from the well bore subsequent to drilling the hole in the kickoff plug.

Example Methods of Reducing Carbon Footprints

[0054] In accordance with embodiments of the present invention, the settable compositions of the present invention may be used to achieve a reduction in the carbon footprint of a cementing operation. By way of example, replacement of at least a portion of the hydraulic cement typically used in the settable composition with an additive (*e.g.*, CKD, ground granulated blast furnace slag, etc.) will reduce the carbon footprint of the cementing operation.

[0055] An example of a method of the present invention comprises a method of cementing in a subterranean formation. The method may comprise determining a settable

composition for use in the subterranean formation. The method also may comprise calculating a total carbon footprint of the settable composition. The method also may comprise determining at least one additive for use in the settable composition, wherein the additive replaces at least a portion of the settable composition and reduces the total carbon footprint of the settable composition. The method also may comprise communicating the amount of reduction in the total carbon footprint of the settable composition to a customer or end user. The method also may comprise preparing the settable composition comprising the additive. The method also may comprise placing the settable composition comprising the additive in the subterranean formation. The method also may comprise allowing the settable composition comprising the additive to set in the subterranean formation.

[0056] When determining a settable composition for use in the subterranean formation, a person of ordinary skill in the art would be able to determine what type of cementing operation is to be performed and also, with the benefit of this disclosure, determine an appropriate settable composition for use in the cementing operation. In some embodiments, the settable composition may comprise a hydraulic cement and water. As described above, additional additives also may be included in the settable composition as desired by those of ordinary skill in the art.

[0057] In some embodiments, once a settable composition is determined, the total carbon footprint of the settable composition may be calculated. The total carbon footprint of the settable composition may be calculated or estimated by any suitable method. In certain embodiments, the total carbon footprint may be calculated by determining the amount of CO_2 produced when creating one pound of the settable composition. In other embodiments, the total carbon footprint may be calculated based upon the embodied carbon (*i.e.* the carbon input into the production of the cementitious materials). Any method of determining the carbon footprint is acceptable for use in embodiments of the present invention.

[0058] When determining at least one additive for use in the settable composition, an appropriate additive may be selected which would reduce the total carbon footprint of the cement composition. By way of example, the additive may be used to replace at least a portion of the hydraulic cement in the settable composition. In accordance with embodiments of the present invention, any additive known in the art which may reduce the total carbon footprint of the cement composition may be suitable. Examples of such

additives may include CKD and ground granulated blast furnace slag. The additive may be included in the cement composition in any amount. In some embodiments, the additive may be included in the cement composition in an amount to achieve a desired reduction in carbon footprint. By way of example, the additive may be included in the cement composition in an amount sufficient to achieve at least about a 1% reduction in carbon footprint, , alternatively, at least about a 5% recution in carbon footprint, alternatively, at least about a 10% reduction in carbon footprint, alternatively, at least about a 25% reduction in carbon footprint, and alternatively, at least about a 50% reduction in carbon footprint.

[0059] The reduction of the carbon footprint in the cementing operation may also be determined, in accordance with embodiments of the present invention. By way of example, the reduction of the carbon footprint may be the difference in the embodied carbon between the replaced hydraulic cement and the replacement additive. As described above, CKD is a by-product from the manufacture of cement. In one embodiment, the reduction in carbon footprint from using CKD as a replacement additive may therefore be determined as follows. For example, the amount of hydraulic cement may be determined for use in the settable composition. As CKD is a by-product from cement manufacture, the percentage of CKD generated during the production of the hydraulic cement may be readily determined. The hydraulic cement may then be replaced with CKD in an amount up to the percentage of CKD generated in the production of the hydraulic cement. The carbon footprint of the cementing operation thus would be reduced by the percentage of CKD. For example, if the manufacture of one pound of cement produced 1 pound of CKD, then a 50/50 blend of cement and CKD would result in a 50% reduction in the carbon footprint for the cementing operation. Once determined, the reduction in the carbon footprint may be communicated to a customer or an end user. For example, the reduction in the carbon footprint may be communicated to a customer of an oilfield services company.

[0060] Another example of a method of the present invention provides a method of cementing in a subterranean formation. The method may comprise determining a settable composition comprising a hydraulic cement and water for use in the subterranean formation, wherein the settable composition has a carbon footprint. The method also may comprise replacing at least a portion of the hydraulic cement in the settable composition with at least one additive, wherein the carbon footprint of the settable composition is reduced by the additive. The method also may comprise determining the reduction in the carbon

footprint of the settable composition. The method also may comprise preparing the settable composition comprising the additive and having a reduced carbon footprint. The method also may comprise communicating the amount of reduction in the carbon footprint of the settable composition to a customer or end user. The method also may comprise placing the settable composition comprising the additive in the subterranean formation. The method also may comprise allowing the settable composition comprising the additive to set in the subterranean formation.

[0061] Another example of a method of the present invention provides a method of cementing in a subterranean formation. The method may comprise determining a settable composition for use in the subterranean formation, wherein the settable composition comprises Portland cement and water. The method also may comprise calculating a total carbon footprint of the settable composition. The method also may comprise replacing at least a portion of the Portland cement in the settable composition with cement kiln dust, wherein the total carbon footprint of the settable composition is reduced by the cement kiln dust. The method also may comprise communicating the amount of reduction in the carbon footprint of the settable composition to a customer or end user. The method also may comprise preparing the settable composition comprising the cement kiln dust. The method also may comprise placing the settable composition comprising the cement kiln dust in the subterranean formation. The method also may comprise allowing the settable composition comprising the cement kiln dust to set in the subterranean formation.

[0062] To facilitate a better understanding of the present invention, 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 scope of the invention.

EXAMPLE 1

[0063] A series of sample settable compositions were prepared at room temperature and subjected to 48-hour compressive strength tests at 140°F in accordance with API Specification 10. The sample compositions comprised water, Class A CKD, and Class A Portland cement.

[0064] The results of the compressive strength tests are set forth in the table below.

TABLE 1

Unfoamed Compressive Strength Tests: Class A Cement and Class A CKD

Sample	Density (ppg)	Portland Cement Class A (% by wt)	CKD Class A (% by wt)	48-Hour Compressive Strength at 140°F (psi)
No. 1	14	0	100	228
No. 2	15.15	25	75	701
No. 3	14.84	50	50	1,189
No. 4	15.62	75	25	3,360
No. 5	15.6	100	0	2,350

EXAMPLE 2

[0065] Sample Compositions No. 6 and 7 were prepared at room temperature and subjected to thickening time and fluid loss tests at 140°F and 240°F, respectively, in accordance with API Specification 10.

[0066] Sample Composition No. 6 comprised water, Class A Portland Cement (50% by weight), Class A CKD (50% by weight), "HALAD® 23" fluid loss control additive (0.75% by weight), and "HR®-5" set retarder (0.25% by weight). Accordingly, Sample Composition No. 6 had a Portland cement-to-CKD weight ratio of about 50:50. This Sample had a density of 14.84 ppg. "HALAD® 23" additive is a cellulose-based fluid loss control additive that is commercially available from Halliburton Energy Services, Inc., Duncan, Oklahoma. "HR®-5" retarder is a lignosulfonate set retarder that is commercially available from Halliburton Energy Services, Inc., Duncan, Oklahoma.

[0067] Sample Composition No. 7 comprised water, Class A Portland Cement (50% by weight), Class A CKD (50% by weight), "HALAD® 413" fluid loss control additive (0.75% by weight), and "HR®-12" set retarder (0.3% by weight). Accordingly, Sample Composition No. 7 had a Portland cement-to-CKD weight ratio of 50:50. This Sample had a density of 14.84 ppg. "HALAD® 413" additive is a grafted copolymer fluid loss control additive that is commercially available from Halliburton Energy Services, Inc., Duncan, Oklahoma. "HR®-12" retarder is a mixture of a lignosulfonate and hydroxycarboxy acid set retarder that is commercially available from Halliburton Energy Services, Inc., Duncan, Oklahoma.

[0068] The results of the fluid loss and thickening time tests are set forth in the table below.

TABLE 2

Unfoamed Thickening Time and Fluid Loss Tests: Class A Cement and Class A CKD

Sample	Cement-to-CKD Weight Ratio	Test Temperature (°F)	Thickening Time to 70 BC (hr:min)	API Fluid Loss in 30 min (ml)
No. 6	50:50	140	6:06	147
No. 7	50:50	240	2:20	220

EXAMPLE 3

[0069] A series of sample settable compositions were prepared at room temperature and subjected to 48-hour compressive strength tests at 140°F in accordance with API Specification 10. The sample compositions comprised water, Class H CKD, and Class H Portland cement.

[0070] The results of the compressive strength tests are set forth in the table below.

TABLE 3

Unfoamed Compressive Strength Tests: Class H Cement and Class H CKD

Sample	Density (ppg)	Portland Cement Class H (% by wt)	CKD Class H (% by wt)	48-Hour Compressive Strength at 140°F (psi)
No. 8	15.23	0	100	74.9
No. 9	15.4	25	75	544
No. 10	16	50	50	1,745
No. 11	16.4	75	25	3,250
No. 12	16.4	100	0	1,931

EXAMPLE 4

[0071] Sample Compositions No. 13 and 14 were prepared at room temperature and subjected to thickening time and fluid loss tests at 140°F and 240°F, respectively, in accordance with API Specification 10.

[0072] Sample Composition No. 13 comprised water, Class H Portland Cement (50% by weight), Class H CKD (50% by weight), "HALAD® 23" fluid loss control additive (0.75% by weight), and 0.25% by weight "HR®-5" set retarder (0.25% by weight). Accordingly, Sample Composition No. 13 had a Portland cement-to-CKD weight ratio of about 50:50. This Sample had a density of 16 ppg.

[0073] Sample Composition No. 14 comprised water, Class H Portland Cement (50% by weight), Class H CKD (50% by weight), "HALAD® 413" fluid loss control additive (0.75% by weight), and "HR®-12" set retarder (0.3% by weight). Accordingly, Sample Composition No. 14 had a Portland cement-to-CKD weight ratio of about 50:50. This Sample had a density of 16 ppg.

[0074] The results of the fluid loss and thickening time tests are set forth in the table below.

TABLE 4

Unfoamed Thickening Time and Fluid Loss Tests: Class H Cement and Class H CKD

Sample	Cement-to-CKD Weight Ratio	Test Temperature (°F)	Thickening Time to 70 BC (hr:min)	API Fluid Loss in 30 min (ml)
No. 13	50:50	140	5:04	58
No. 14	50:50	240	1:09	220

EXAMPLE 5

[0075] A series of sample settable compositions were prepared at room temperature and subjected to 48-hour compressive strength tests at 140°F in accordance with API Specification 10. The sample compositions comprised water, Class G CKD, and Class G Portland cement.

[0076] The results of the compressive strength tests are set forth in the table below.

TABLE 5

Unfoamed Compressive Strength Tests: Class G Cement and Class G CKD

Sample	Density (ppg)	Portland Cement Class G (% by wt)	CKD Class G (% by wt)	48-Hour Compressive Strength at 140°F (psi)
No. 15	14.46	0	100	371
No. 16	14.47	25	75	601
No. 17	14.49	50	50	1,100
No. 18	14.46	75	25	3,160
No. 19	14.46	100	0	3,880

EXAMPLE 6

[0077] Sample Compositions No. 20 and 21 were prepared at room temperature and subjected to thickening time and fluid loss tests at 140°F and 240°F, respectively, in accordance with API Specification 10.

[0078] Sample Composition No. 20 comprised water, Class G Portland Cement (50% by weight), Class G CKD (50% by weight), "HALAD® 23" fluid loss control additive (0.75% by weight), and "HR®-5" set retarder (0.25% by weight). Accordingly, Sample Composition No. 20 had a Portland cement-to-CKD weight ratio of about 50:50. This Sample had a density of 15.23 ppg.

[0079] Sample Composition No. 21 comprised water, Class G Portland Cement (50% by weight), Class G CKD (50% by weight), "HALAD® 413" fluid loss control additive (0.75% by weight), and "HR®-12" set retarder (0.3% by weight). Accordingly, Sample Composition No. 21 had a Portland cement-to-CKD weight ratio of about 50:50. This Sample had a density of 15.23 ppg.

[0080] The results of the fluid loss and thickening time tests are set forth in the table below.

TABLE 6

Unfoamed Thickening Time and Fluid Loss Tests: Class G Cement and Class G CKD

Sample	Cement-to-CKD Weight Ratio	Test Temperature (°F)	Thickening Time to 70 BC (hr:min)	API Fluid Loss in 30 min (ml)
No. 20	50:50	140	3:19	132
No. 21	50:50	240	1:24	152

[0081] Accordingly, Examples 1-6 indicate that settable compositions comprising Portland cement and CKD may have suitable thickening times, compressive strengths, and/or fluid loss properties for a particular application.

EXAMPLE 7

[0082] A series of foamed sample compositions were prepared in accordance with the following procedure. For each sample, a base sample composition was prepared that comprised water, Class A Portland cement, and Class A CKD. The amounts of CKD and Portland cement were varied as shown in the table below. "ZONESEAL® 2000" foaming additive was then added to each base sample composition in an amount of 2% bvow. Next, each base sample composition was foamed down to about 12 ppg. After preparation, the resulting foamed sample compositions were subjected to 72-hour compressive strength tests at 140°F in accordance with API Specification 10.

[0083] The results of the compressive strength tests are set forth in the table below.

TABLE 7

**Foamed Compressive Strength Test:
Class A Cement and Class A CKD**

Sample	Base Density (ppg)	Foam Density (ppg)	Portland Cement Class A (% by wt)	CKD Class A (% by wt)	72-Hour Compressive Strength at 140°F (psi)
No. 22	14.34	12	0	100	167.6
No. 23	14.15	12	25	75	701
No. 24	15.03	12	50	50	1,253
No. 25	15.62	12	75	25	1,322
No. 26	15.65	12	100	0	1,814

EXAMPLE 8

[0084] A series of foamed sample compositions were prepared in accordance with the following procedure. For each sample, a base sample composition was prepared that comprised water, Class H Portland cement, and Class H CKD. The amounts of CKD and Portland cement were varied as shown in the table below. "ZONESEAL® 2000" foaming additive was then added to each base sample composition in an amount of 2% bvow. Next, each base sample composition was foamed down to about 12 ppg. After preparation, the resulting foamed sample compositions were subjected to 72-hour compressive strength tests at 140°F in accordance with API Specification 10.

[0085] The results of the compressive strength tests are set forth in the table below.

TABLE 8

**Foamed Compressive Strength Tests:
Class H Cement and Class H CKD**

Sample	Base Density (ppg)	Foam Density (ppg)	Portland Cement Class H (% by wt)	CKD Class H (% by wt)	72-Hour Compressive Strength at 140°F (psi)
No. 27	15.07	12	0	100	27.2
No. 28	15.4	12	25	75	285
No. 29	16	12	50	50	845
No. 30	16.4	12	75	25	1,458
No. 31	16.57	12	100	0	1,509

EXAMPLE 9

[0086] A series of foamed sample compositions were prepared in accordance with the following procedure. For each sample, a base sample composition was prepared that comprised water, Class G Portland cement, and Class G CKD. The amounts of CKD and Portland cement were varied as shown in the table below. "ZONESEAL® 2000" foaming additive was then added to each base sample composition in an amount of 2% bvow. Next, each base sample composition was foamed down to about 12 ppg. After preparation, the resulting foamed sample compositions were subjected to 72-hour compressive strength tests at 140°F in accordance with API Specification 10.

[0087] The results of the compressive strength tests are set forth in the table below.

TABLE 9

Foamed Compressive Strength Tests: Class G Cement and Class G CKD

Sample	Base Density (ppg)	Foam Density (ppg)	Portland Cement Class G (% by wt)	CKD Class G (% by wt)	72-Hour Compressive Strength at 140°F (psi)
No. 32	14.32	12	0	100	181
No. 33	14.61	12	25	75	462
No. 34	15	12	50	50	729
No. 35	15.43	12	75	25	1,196
No. 36	15.91	12	100	0	1,598

[0088] Accordingly, Examples 7-9 indicate that foamed settable compositions comprising Portland cement and CKD may have suitable compressive strengths for a particular application.

EXAMPLE 10

[0089] A series of sample settable compositions were prepared at room temperature and subjected to 24-hour compressive strength tests at 140°F in accordance with API Specification 10. Sufficient water was included in each sample to provide a density of about 14.2 ppg.

[0090] The results of the compressive strength tests are set forth in the table below.

TABLE 10

Unfoamed Compressive Strength Tests
Class A Cement, Class A CKD, Shale, Fly Ash, and Lime

Sample	Portland Cement Class A (% by wt)	CKD Class A (% by wt)	Vitrified Shale[1] (% by wt)	POZMIZ® A Additive (% by wt)	Hydrated Lime (% by wt)	24-Hour Compressive Strength at 140°F (psi)
No. 37	26	0	0	61	13	1,024
No. 38	19.5	6.5	0	61	13	766
No. 39	20.7	5.3	0	61	13	825
No. 40	23.3	2.7	0	61	13	796
No. 41	19.4	3.3	3.3	61	13	717
No. 42	20.7	2.65	2.65	61	13	708
No. 43	23.3	1.35	1.35	61	13	404

[1] The vitrified shale used was "PRESSUR-SEAL® FINE LCM" material.

EXAMPLE 11

[0091] A series of sample compositions were prepared and subjected to thickening time tests at 140°F in accordance with API Specification 10.

[0092] Sample Composition No. 44 comprised water, Class A Portland Cement (26% by weight), "POZMIX® A" cement additive (61% by weight), hydrated lime (13% by weight), "HALAD® 23" fluid loss control additive (0.6% by weight), and "HR®-5" set retarder (0.1% by weight). This Sample had a density of 14.2 ppg.

[0093] Sample Composition No. 45 comprised water, Class A Portland Cement (19.5% by weight), Class A CKD (6.5% by weight), "POZMIX® A" cement additive (61% by weight), hydrated lime (13% by weight), "HALAD® 23" fluid loss control additive (0.6% by weight), and "HR®-5" set retarder (0.1% by weight). This Sample had a density of 14.2 ppg. The vitrified shale was "PRESSUR-SEAL® FINE LCM" material.

[0094] Sample Composition No. 46 comprised water, Class A Portland Cement (19.5% by weight), Class A CKD (3.25% by weight), vitrified shale (3.25% by weight), "POZMIX® A" cement additive (61% by weight), hydrated lime (13% by weight), "HALAD® 23" fluid loss control additive (0.6% by weight), and "HR®-5" set retarder (0.1% by weight). This Sample had a density of 14.2 ppg. The vitrified shale was "PRESSUR-SEAL® FINE LCM" material.

[0095] The results of the fluid loss and thickening time tests are set forth in the table below.

TABLE 11

Unfoamed Thickening Time Tests:
Class A Cement, Class A CKD, Shale, Fly ash, and Lime

Sample	Portland Cement Class A (% by wt)	CKD Class A (% by wt)	Vitrified Shale[1] (% by wt)	POZMIX® A Additive (% by wt)	Hydrated Lime (% by wt)	Thickening Time to 70 BC at 140°F (hr:min)
No. 44	26	0	0	61	13	2:57
No. 45	19.5	6.5	0	61	13	2:20
No. 46	19.5	2.25	2.25	61	13	3:12

[1] The vitrified shale used was "PRESSUR-SEAL® FINE LCM" material.

EXAMPLE 12

[0096] A series of sample settable compositions were prepared at room temperature and subjected to 24-hour compressive strength tests at 140°F in accordance with API Specification 10. Sufficient water was included in each sample to provide a density of about 14.2 ppg.

[0097] The results of the compressive strength tests are set forth in the table below.

TABLE 12

Unfoamed Compressive Strength Tests:
Class H Cement, Class H CKD, Shale, Fly ash, and Lime

Sample	Portland Cement Class H (% by wt)	CKD Class H (% by wt)	Vitrified Shale[1] (% by wt)	POZMIX® A Additive (% by wt)	Hydrated Lime (% by wt)	24-Hour Compressive Strength at 140°F (psi)
No. 47	26	0	0	61	13	704
No. 48	19.5	6.5	0	61	13	576
No. 49	20.7	5.3	0	61	13	592
No. 50	23.3	2.7	0	61	13	627
No. 51	19.4	3.3	3.3	61	13	626
No. 52	20.7	2.65	2.65	61	13	619
No. 53	23.3	1.35	1.35	61	13	594

[1] The vitrified shale used was "PRESSUR-SEAL® FINE LCM" material.

EXAMPLE 13

[0098] Sample Composition No. 54 was prepared and subjected to a fluid loss test at 140°F in accordance with API Specification 10. Sample Composition No. 54 comprised water, Class H Portland Cement (19.5% by weight), Class H CKD (3.3% by weight), vitrified shale (3.3% by weight), "POZMIX® A" cement additive (61% by weight), hydrated lime (13% by weight), "HALAD® 23" fluid loss control additive (0.6% by weight), and "HR®-5" set retarder (0.1% by weight). This Sample had a density of 14.2 ppg. Accordingly, Sample Composition No. 54 had a Portland cement-to-CKD weight ratio of 75:25. The vitrified shale was "PRESSUR-SEAL® FINE LCM" material.

[0099] The result of this fluid loss test is set forth in the table below.

TABLE 13

Unfoamed Fluid Loss Test:
Class H Cement, Class H CKD, Shale, Fly ash, and Lime

Sample	Portland Cement Class H (% by wt)	CKD Class H (% by wt)	Vitrified Shale[1] (% by wt)	POZMIX® A Additive (% by wt)	Hydrated Lime (% by wt)	Fluid Loss in 30 min API at 140°F (ml)
No. 54	19.5	3.3	3.3	61	13	117

[1] The vitrified shale used was "PRESSUR-SEAL® FINE LCM" material.

EXAMPLE 14

[00100] A series of sample settable compositions were prepared at room temperature and subjected to 24-hour compressive strength tests at 140°F in accordance with API Specification 10. Sufficient water was included in each sample to provide a density of about 14.2 ppg.

[0100] The results of the compressive strength tests are set forth in the table below.

TABLE 14

**Unfoamed Compressive Strength Tests:
Class G Cement, Class G CKD, Shale, Fly ash, and Lime**

Sample	Portland Cement Class G (% by wt)	CKD Class G (% by wt)	Vitrified Shale[1] (% by wt)	POZMIX® A Additive (% by wt)	Hydrated Lime (% by wt)	24-Hour Compressive Strength at 140°F (psi)
No. 55	26	0	0	61	13	491
No. 56	19.5	6.5	0	61	13	526
No. 57	20.7	5.3	0	61	13	474
No. 58	23.3	2.7	0	61	13	462
No. 59	19.4	3.3	3.3	61	13	523
No. 60	20.7	2.65	2.65	61	13	563

[1] The vitrified shale used was "PRESSUR-SEAL® FINE LCM" material.

[0101] Accordingly, Examples 10-14 indicate that settable compositions comprising Portland cement, CKD, fly ash, hydrated lime, and optionally vitrified shale may have suitable compressive strengths, thickening times, and/or fluid loss properties for a particular application.

EXAMPLE 15

[0102] A series of foamed sample compositions were prepared in accordance with the following procedure. For each sample, a base sample composition was prepared that comprised water, Class A Portland cement, Class A CKD, vitrified shale, "POZMIX® A" cement additive (61% by weight), and hydrated lime (13% by weight). This Sample had a density of 14.2 ppg. The vitrified shale used was "PRESSUR-SEAL® FINE LCM" material. The amounts of CKD, Portland cement, and vitrified shale were varied as shown in the table below. "ZONESEAL® 2000" foaming additive was then added to each base sample composition in an amount of 2% bvow. Next, each base sample composition was foamed down to about 12 ppg. After preparation, the resulting foamed sample compositions were subjected to 10-day compressive strength tests at 140°F in accordance with API Specification 10.

[0103] The results of the compressive strength tests are set forth in the table below.

TABLE 15

Foamed Compressive Strength Tests:
Class A Cement, Class A CKD, Shale, Fly ash, and Lime

Sample	Portland Cement Class A (% by wt)	CKD Class A (% by wt)	Vitrified Shale[1] (% by wt)	POZMIX® A Additive (% by wt)	Hydrated Lime (% by wt)	10-Day Compressive Strength at 140°F (psi)
No. 61	26	0	0	61	13	1,153
No. 62	19.5	6.5	0	61	13	1,151
No. 63	20.7	5.3	0	61	13	1,093
No. 64	23.3	2.7	0	61	13	950
No. 65	19.4	3.3	3.3	61	13	1,161
No. 66	20.7	2.65	2.65	61	13	1,009
No. 67	23.3	1.35	1.35	61	13	1,231

[1] The vitrified shale used was "PRESSUR-SEAL® FINE LCM" material.

EXAMPLE 16

[0104] A series of foamed sample compositions were prepared in accordance with the following procedure. For each sample, a base sample composition was prepared that comprised water, Class A Portland cement, Class A CKD, vitrified shale, "POZMIX® A" cement additive (61% by weight), and hydrated lime (13% by weight). This Sample had a density of 14.2 ppg. The vitrified shale used was "PRESSUR-SEAL® FINE LCM" material. The amounts of CKD, Portland cement, and vitrified shale were varied as shown in the table below. "ZONESEAL® 2000" foaming additive was then added to each base sample composition in an amount of 2% bvow. Next, each base sample composition was foamed down to about 12 ppg. After preparation, the resulting foamed sample compositions were subjected to 72-hour compressive strength tests at 140°F in accordance with API Specification 10.

[0105] The results of the compressive strength tests are set forth in the table below.

TABLE 16

Foamed Compressive Strength Tests:
Class A Cement, Class A CKD, Shale, Fly Ash, and Lime

Sample	Portland Cement Class A (% by wt)	CKD Class A (% by wt)	Vitrified Shale[1] (% by wt)	POZMIX® A Additive (% by wt)	Hydrated Lime (% by wt)	72-Hour Compressive Strength at 140°F (psi)
No. 68	26	0	0	61	13	1,057
No. 69	19.5	6.5	0	61	13	969
No. 70	20.7	5.3	0	61	13	984
No. 71	19.4	3.3	3.3	61	13	921
No. 72	20.7	2.65	2.65	61	13	811
No. 73	23.3	1.35	1.35	61	13	969

[1] The vitrified shale used was "PRESSUR-SEAL® FINE LCM" material.

EXAMPLE 17

[0106] Foamed Sample Composition No. 74 was prepared in accordance with the following procedure. A base sample composition was prepared that comprised water, Class G Portland cement (19.5% by weight), Class G CKD (6.5% by weight), "POZMIX® A" cement additive (61% by weight), and hydrated lime (13% by weight). This base sample had a density of 14.2 ppg. "ZONESEAL® 2000" foaming additive was then added to each base sample composition in an amount of 2% bvow. Next, the base sample was foamed down to about 12 ppg. After preparation, the resulting Foamed Sample Composition was subjected to a 72-hour compressive strength test at 140°F in accordance with API Specification 10.

[0107] The result of the compressive strength test is set forth in the table below.

TABLE 17

Foamed Compressive Strength Tests:
Class G Cement, Class G CKD, Fly Ash, and Lime

Sample	Portland Cement Class G (by wt)	CKD Class G (by wt)	POZMIX® A Additive (by wt)	Hydrated Lime (by wt)	72-Hour Compressive Strength at 140°F (psi)
No. 74	19.5	6.5	61	13	777

[0108] Accordingly, Examples 15-17 indicate that foamed settable compositions comprising Portland cement, CKD, fly ash, hydrated lime, and optionally vitrified shale may have suitable compressive strengths for a particular application.

EXAMPLE 18

[0109] A series of sample settable compositions were prepared at room temperature and subjected to 24-hour compressive strength tests at 180°F in accordance with API Specification 10. The sample compositions comprised water, Class A CKD, Class A Portland cement, zeolite, vitrified shale, and hydrated lime. The vitrified shale used was "PRESSUR-SEAL® FINE LCM" material. The amount of each component was varied as shown in the table below.

[0110] The results of the compressive strength tests are set forth in the table below.

TABLE 18

Unfoamed Compressive Strength Tests: Class A Cement, Class A CKD, Zeolite, Shale, and Lime

Sample	Density (ppg)	Portland Cement Class A (% by wt)	CKD Class A (% by wt)	Zeolite (% by wt)	Vitrified Shale[1] (% by wt)	Hydrated Lime (% by wt)	24-Hour Compressive Strength at 180°F (psi)
No. 75	13.3	50	25	25	0	0	1,915
No. 76	12.75	50	25	12.5	12.5	0	2,190
No. 77	11.6	0	75	10	25	0	31.6
No. 78	12.8	25	50	23.5	0	0	875
No. 79	12.5	25	50	12.5	12.5	0	923
No. 80	11.5	0	70	10	15	5	116.4

[1] The vitrified shale used was "PRESSUR-SEAL® FINE LCM" material.

EXAMPLE 19

[0111] Foamed Sample Composition No. 81 was prepared in accordance with the following procedure. A base sample composition was prepared that comprised water, Class A Portland cement, Class A CKD, and zeolite. This base sample had a density of 14.2 ppg. "ZONESEAL® 2000" foaming additive was then added in an amount of 2% bvow. Next, the base sample was foamed down to about 12 ppg. After preparation, the resulting Foamed Sample Composition was subjected to a 72-hour compressive strength test at 140°F in accordance with API Specification 10.

[0112] The result of the compressive strength test is set forth in the table below.

TABLE 19

Foamed Compressive Strength Tests:
Class A Cement, Class A CKD, and Zeolite

Sample	Base Density (ppg)	Foam Density (ppg)	Portland Cement Class A (% by wt)	CKD Class A (% by wt)	Zeolite (% by wt)	72-Hour Compressive Strength at 140°F (psi)
No. 81	13.35	12	50	25	25	972

EXAMPLE 20

[0113] Sample Composition No. 82 was prepared at room temperature and subjected to a 24-hour compressive strength test at 180°F in accordance with API Specification 10. Sample Composition No. 82 comprised water, Portland Class H Cement, Class H CKD, Zeolite, and vitrified shale. The vitrified shale used was "PRESSUR-SEAL® FINE LCM" material.

[0114] The result of the compressive strength test is set forth in the table below.

TABLE 20

**Unfoamed Compressive Strength Tests:
Class H Cement, Class H CKD, Zeolite and Shale**

Sample	Density (ppg)	Portland Cement Class H (% by wt)	CKD Class H (% by wt)	Zeolite (% by wt)	Vitrified Shale[1] (% by wt)	24-Hour Compressive Strength at 180°F (psi)
No. 82	15.2	50	25	12.5	12.5	2,280

[1] The vitrified shale used was "PRESSUR-SEAL® FINE LCM" material.

EXAMPLE 21

[0115] Sample Composition No. 83 was prepared at room temperature and subjected to thickening time and fluid loss tests at 140°F in accordance with API Specification 10. Sample Composition No. 83 comprised Class A Portland Cement (50% by weight), Class A CKD (25% by weight), zeolite (12.5% by weight), vitrified shale (12.5% by weight), "HALAD® 23" fluid loss control additive (.75% by weight), and "HR®-5" set retarder (0.5% by weight). This Sample had a density of 12.75 ppg. The vitrified shale used was "PRESSUR-SEAL® FINE LCM" material.

[0116] The results of the fluid loss and thickening time tests are set forth in the table below.

TABLE 21

**Unfoamed Thickening Time and Fluid Loss Tests:
Class A Cement, Class A CKD, Zeolite and Shale**

Sample	Portland Cement Class A (% by wt)	CKD Class A (% by wt)	Zeolite (% by wt)	Vitrified Shale[1] (% by wt)	Thickening Time to 70 BC at 140°F (hr:min)	Fluid Loss in 30 min at 140°F (ml)
No. 83	50	25	12.5	12.5	8:54	196

[1] The vitrified shale used was "PRESSUR-SEAL® FINE LCM" material.

[0117] Accordingly, Examples 18-21 indicate that foamed and unfoamed settable compositions comprising Portland cement, CKD, zeolite, and optionally vitrified shale may have suitable compressive strengths for a particular application.

EXAMPLE 22

[0118] A series of sample settable compositions were prepared at room temperature and subjected to 24-hour compressive strength tests at 190°F in accordance with

API Specification 10. The sample compositions comprised water, slag cement, Class H CKD, Class H Portland cement, sodium carbonate, and hydrated lime. The slag cement contained sodium carbonate in an amount of 6% by weight. The amount of each component was varied as shown in the table below.

[0119] The results of the compressive strength tests are set forth in the table below.

TABLE 22

Unfoamed Compressive Strength Tests:
Class H Cement, Class H CKD, Slag Cement, and Lime

Sample	Density (ppg)	Portland Cement Class H (% by wt)	CKD Class H (% by wt)	Slag Cement (% by wt)	Hydrated Lime (% by wt)	24-Hour Compressive Strength at 190°F (psi)
No. 84	13.2	0	50	45	5	123.6
No. 85	13.6	0	50	50	0	170.3
No. 86	14	30	50	20	0	183.2
No. 87	15	30	20	50	0	563

EXAMPLE 23

[0120] A series of foamed sample settable compositions were prepared at room temperature and subjected to 72-hour compressive strength tests at 140°F in accordance with API Specification 10. For each sample, a base sample composition comprised water, slag cement, Class H CKD, Class H Portland cement, and hydrated lime. The amount of each component was varied as shown in the table below. The slag cement contained sodium carbonate in an amount of 6% by weight. "ZONESEAL® 2000" foaming additive was then added to each base sample composition in an amount of 2% bvow. Next, each base sample composition was foamed down to about 11 ppg. After preparation, the resulting Foamed Sample Composition was subjected to a 72-hour compressive strength test at 140°F in accordance with API Specification 10.

[0121] The result of the compressive strength tests are set forth in the table below.

TABLE 23

Foamed Compressive Strength Tests:
Class H Cement, Class H CKD, Slag Cement, and Lime

Sample	Base Density (ppg)	Foam Density (ppg)	Portland Cement Class H (% by wt)	CKD Class H (% by wt)	Slag Cement (% by wt)	Hydrated Lime (% by wt)	72-Hour Compressive Strength at 140°F (psi)
No. 88	13.63	11	0	50	45	5	148.9
No. 89	13.68	11	0	50	50	0	161.1
No. 90	14.07	11	30	50	20	0	125

[0122] Accordingly, Examples 22-23 indicate that foamed and unfoamed settable compositions comprising CKD, slag cement, optionally hydraulic cement, and optionally hydrated lime may have suitable compressive strengths for a particular application.

EXAMPLE 24

[0123] A series of sample settable compositions were prepared at room temperature and subjected to 24-hour compressive strength tests at 180°F in accordance with API Specification 10. The sample compositions comprised water, Portland Cement, CKD, metakaolin, and vitrified shale. The amount of each component was varied as shown in the table below. The vitrified shale used was "PRESSUR-SEAL® FINE LCM" material. Class A Portland Cement was used for this series of tests, except that Class H Portland Cement was used in Sample No. 93. Class A CKD was used for this series of tests, except that Class H CKD was used in Sample No. 93.

[0124] The results of the compressive strength tests are set forth in the table below.

TABLE 24

Compressive Strength Tests:
Cement CKD, Metakaolin, and Shale

Sample	Density (ppg)	Portland Cement (% by wt)	CKD (% by wt)	Metakaolin (% by wt)	Vitrified Shale[1] (% by wt)	24-Hour Compressive Strength at 180°F (psi)
No. 91	12.75	50	25	12.5	12.5	1,560
No. 92	13.5	50	25	25	0	1,082
No. 93	13	25	50	12.5	12.5	1,410

[1] The vitrified shale used was "PRESSUR-SEAL® FINE LCM" material.

EXAMPLE 25

[0125] A series of foamed sample settable compositions were prepared at room temperature and subjected to 72-hour compressive strength tests at 180°F in accordance with API Specification 10. For each sample, a base sample composition was prepared that comprised water, Portland Cement, CKD, metakaolin, and vitrified shale. The amount of each component was varied as shown in the table below. The vitrified shale used was "PRESSUR-SEAL® FINE LCM" material. Class A Portland Cement was used for this series

of tests, except that Class H Portland Cement was used in Sample No. 96. Class A CKD was used for this series of tests, except that Class H CKD was used in Sample No. 96. "ZONESEAL® 2000" foaming additive was then added to each base sample composition in an amount of 2% bvow. Next, each base sample composition was foamed down to the density shown in the table below.

[0126] The results of the compressive strength tests are set forth in the table below.

TABLE 25

Foamed Compressive Strength Tests: Cement, CKD, Metakaolin, and Shale

Sample	Base Density (ppg)	Foam Density (ppg)	Portland Cement (% by wt)	CKD (% by wt)	Metakaolin (% by wt)	Vitrified Shale[1] (% by wt)	72-Hour Compressive Strength at 180°F (psi)
No. 94	12.75	9.85	50	25	12.5	12.5	651
No. 95	13.5	9.84	50	25	25	0	512
No. 96	13	9.57	25	50	12.5	12.5	559

[1] The vitrified shale used was "PRESSUR-SEAL® FINE LCM" material.

[0127] Accordingly, Examples 24-25 indicate that foamed and unfoamed settable compositions comprising hydraulic cement, CKD, metakaolin, and optionally vitrified shale may have suitable compressive strengths for a particular application.

[0128] Therefore, the present invention is 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 invention may be modified and practiced in different but equivalent manners apparent to those skilled in the art having the benefit of the teachings herein. Furthermore, no limitations are intended to the details of construction or design herein shown, other than as described in the claims below. 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 invention. 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 as referring to the power set (the set of all subsets) of the respective range of values, and set forth every range encompassed within the broader range of values. Also, the terms in the claims have their plain, ordinary meaning unless otherwise explicitly and clearly defined by the patentee.

What is claimed is:

1. A method of cementing in a subterranean formation comprising:

determining a settable composition for use in the subterranean formation;

calculating a total carbon footprint of the settable composition;

determining at least one additive for use in the settable composition, wherein the additive replaces at least a portion of the settable composition and reduces the total carbon footprint of the settable composition;

preparing the settable composition comprising the additive;

placing the settable composition comprising the additive in the subterranean formation; and

allowing the settable composition comprising the additive to set in the subterranean formation.

2. The method of claim 1 wherein the additive comprises cement kiln dust.

3. The method of claim 1 wherein the additive comprises ground granulated blast furnace slag.

4. The method of claim 1 wherein the additive replaces at least a portion of hydraulic cement in the settable composition.

5. The method of claim 1 wherein the additive replaces at least a portion of Portland cement in the settable composition.

6. The method of claim 1 wherein the additive is present in the settable composition in an amount sufficient to achieve at least about a 1% reduction in the total carbon footprint of the settable composition.

7. The method of claim 1 wherein the additive is present in the settable composition in an amount sufficient to achieve at least about a 25% reduction in the total carbon footprint of the settable composition.

8. The method of claim 1 wherein the settable composition comprises a hydraulic cement and water.

9. The method of claim 1 wherein the placing the settable composition comprising the additive in the subterranean formation comprises placing the settable composition in an annulus between the subterranean formation and a pipe string.

10. The method of claim 1 further comprising determining an amount of reduction in the carbon footprint of the settable composition.

11. The method of claim 10 further comprising communicating the amount of reduction in the carbon footprint of the settable composition to a customer or end user.

12. A method of cementing in a subterranean formation comprising:

determining a settable composition comprising a hydraulic cement and water for use in the subterranean formation, wherein the settable composition has a carbon footprint;

replacing at least a portion of the hydraulic cement in the settable composition with at least one additive, wherein the carbon footprint of the settable composition is reduced by the additive;

determining an amount of reduction in the carbon footprint of the settable composition;

preparing the settable composition comprising the additive and having a reduced carbon footprint;

placing the settable composition comprising the additive in the subterranean formation; and

allowing the settable composition comprising the additive to set in the subterranean formation.

13. The method of claim 12 wherein the additive comprises cement kiln dust.

14. The method of claim 12 wherein the additive comprises ground granulated blast furnace slag.

15. The method of claim 12 wherein the hydraulic cement comprises Portland cement and the additive replaces at least a portion of the Portland cement in the settable composition.

16. The method of claim 12 wherein the additive is present in the settable composition in an amount sufficient to achieve at least about a 1% reduction in the carbon footprint of the settable composition.

17. The method of claim 12 wherein the additive is present in the settable composition in an amount sufficient to achieve at least about a 25% reduction in the carbon footprint of the settable composition.

18. The method of claim 12 further comprising communicating the amount of reduction in the carbon footprint of the settable composition to a customer or end user.

19. A method of cementing in a subterranean formation comprising:

determining a settable composition for use in the subterranean formation, wherein the settable composition comprises Portland cement and water;

calculating a total carbon footprint of the settable composition;

replacing at least a portion of the Portland cement in the settable composition with cement kiln dust, wherein the total carbon footprint of the settable composition is reduced by the cement kiln dust;

preparing the settable composition comprising the cement kiln dust;

placing the settable composition comprising the cement kiln dust in the subterranean formation; and

allowing the settable composition comprising the cement kiln dust to set in the subterranean formation.

20. The method of claim 19 wherein the cement kiln dust is present in the settable composition in an amount sufficient to achieve at least about a 1% reduction in the total carbon footprint of the settable composition.

21. The method of claim 19 wherein the cement kiln dust is present in the settable composition in an amount sufficient to achieve at least about a 25% reduction in the total carbon footprint of the settable composition.

22. The method of claim 19 wherein the settable composition has a density in the range of about 6 pounds per gallon to about 13 pounds per gallon.

23. The method of claim 19 wherein the settable composition further comprises a swellable particle.

24. The method of claim 19 further comprising determining an amount of reduction in the carbon footprint of the settable composition.

25. The method of claim 19 further comprising communicating the amount of reduction in the carbon footprint of the settable composition to a customer or end user.

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2009/002598

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09K8/467 C04B18/14 C04B18/16 C04B7/36

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)
C09K C04B

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

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2008/156491 A1 (RODDY CRAIG W [US] ET AL) 3 July 2008 (2008-07-03) paragraph [0011] paragraph [0013] - paragraph [0015]	1-25
X	US 7 077 203 B1 (RODDY CRAIG W [US] ET AL) 18 July 2006 (2006-07-18) paragraph [0010] tables 22, 23	1-25
A	US 2004/129181 A1 (LALANDE JEAN-MARIE [CA] ET AL) 8 July 2004 (2004-07-08) paragraph [0015] - paragraph [0036]	1-25

☐ *Further documents are listed in the continuation of Box C.*

☒ *See patent family annex.*

* Special categories of cited documents :

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Date of the actual completion of the international search	Date of mailing of the international search report
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/GB2009/002598

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2008156491 A1	03-07-2008	WO 2009103944 A1	27-08-2009
US 7077203 B1	18-07-2006	CA 2621832 A1	15-03-2007
		CN 101305069 A	12-11-2008
		EP 1928974 A1	11-06-2008
		WO 2007028951 A1	15-03-2007
		US 2007056728 A1	15-03-2007
US 2004129181 A1	08-07-2004	NONE	