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(54) Title: LIGHTWEIGHT SETTABLE COMPOSITIONS COMPRISING CEMENT KBLN DUST AND METHODS OF USING THEM

(57) Abstract: Settable compositions that comprise water, CKD, and microspheres, wherein the lightweight settable composition has a density less than about 13 pounds per gallon. Methods of cementing that comprise providing a lightweight settable composition having a density less than about 13 pounds per gallon, the lightweight settable composition comprising water, CKD, and microspheres, introducing the lightweight settable composition into a location to be cemented and allowing the lightweight settable composition to set therein.



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**LIGHTWEIGHT SETTABLE COMPOSITIONS COMPRISING
CEMENT KILN DUST AND METHODS OF USING THEM**

BACKGROUND

The present invention relates to cementing operations and, more particularly, to lightweight settable compositions comprising water, cement kiln dust ("CKD"), and microspheres, and associated methods of use.

Settable compositions may be used in a variety of above ground (*e.g.*, in the construction industry) and 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 and remedial cementing. For example, 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 subterranean formation 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. Settable compositions also are used in remedial cementing operations such as plugging highly permeable zones or fractures in well bores, plugging cracks and holes in pipe strings, and the like.

In some instances, settable compositions utilized in subterranean operations may be lightweight, for example, to prevent excessive hydrostatic pressure from being exerted on subterranean formations penetrated by the well bore, whereby the formations may be unintentionally fractured or the hole may collapse. One type of lightweight settable composition is a foamed cement composition, *e.g.*, a cement composition that comprises a surfactant and a gas. Additionally, lightweight additives (*e.g.*, microspheres) also may be added to settable compositions to reduce the density thereof.

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 typically 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
5 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 .

SUMMARY

10 The present invention relates to cementing operations and, more particularly, to lightweight settable compositions comprising water, CKD, and microspheres, and associated methods of use.

According to one aspect of the invention there is provided a lightweight settable composition that comprises water, CKD, and microspheres, wherein the lightweight
15 settable composition has a density of less than about 13 pounds per gallon.

According to another aspect of the invention there is provided a lightweight settable composition that comprises water, CKD, microspheres, vitrified shale, and hydrated lime, wherein the lightweight settable composition has a density of less than about 13 pounds per gallon.

20 According to another aspect of the invention there is provided a lightweight settable composition that comprises water, CKD, and microspheres comprising soda lime borosilicate glass, wherein the lightweight settable composition has a density of less than about 13 pounds per gallon.

According to another aspect of the invention there is provided a method of
25 cementing that comprises providing a lightweight settable composition having a density of less than about 13 pounds per gallon, the lightweight settable composition comprising water, CKD, and microspheres, introducing the lightweight settable composition into a location to be cemented, and allowing the lightweight settable composition to set therein.

According to another aspect of the invention there is provided method of
30 primary cementing that comprises providing a lightweight settable composition having a density of less than about 13 pounds per gallon, the lightweight settable composition

comprising water, CKD, and microspheres, introducing the lightweight settable composition into an annulus between a subterranean formation and a pipe string located in the subterranean formation, and allowing the lightweight settable composition to set in the annulus.

5 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

10 The present invention relates to cementing operations and, more particularly, to lightweight settable compositions comprising water, CKD, and microspheres, and associated methods of use. The lightweight settable compositions of the present invention may be used in a variety of subterranean applications, including primary cementing, and remedial cementing. The lightweight settable compositions of the present invention also may be used in surface applications, for example, construction cementing.

15 In one embodiment, a lightweight settable composition of the present invention comprises water, CKD, and microspheres. The lightweight 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. Lightweight settable compositions generally have a density of less than about 13 pounds per gallon ("ppg"). In
20 some embodiments, the lightweight settable compositions of the present invention may have a density in the range of from about 4 ppg to about 13 ppg. In the some embodiments, the lightweight settable composition may be foamed to further reduce the density thereof, for example, in the range of from about 4 ppg to about 11 ppg.

25 The water used in the lightweight 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 lightweight settable composition. In some embodiments, the water may be included in
30 an amount sufficient to form a pumpable slurry. In some embodiments, the water may be included in the lightweight settable compositions of the present invention in an amount in the

range of from about 20% to about 80% by weight of the lightweight settable composition. In some embodiments, the water may be included in an amount in the range of from about 30% to about 70% by weight of the lightweight settable composition.

The CKD should be included in the lightweight 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 lightweight settable compositions of the present invention in an amount in the range of from about 0.01% to about 80% by weight of the lightweight settable composition. In some embodiments, the CKD may be present in the lightweight settable compositions of the present invention in an amount in the range of from about 2.5% to about 80% by weight of settable materials. In some embodiments, the CKD may be present in the lightweight settable compositions of the present invention in an amount in the range of from about 2.5% to about 60% by weight of the lightweight settable composition. In some embodiments, the CKD may be present in the lightweight settable compositions of the present invention in an amount in the range of from about 5% to about 50% by weight of the lightweight settable composition.

The microspheres used in the lightweight settable compositions of the present invention may be any microsphere suitable for use in subterranean applications to, *inter alia*, reduce the density of the settable composition. Suitable microspheres generally have a density of less than about 8.345 ppg (1.0 gram per cubic centimeter (“g/cc”). A variety of microspheres may be utilized in accordance with the present invention, including hollow, solid, and/or porous microspheres. Generally, the microspheres should have a crush strength greater than about 100 psi. Suitable microspheres may comprise a variety of materials, including, but not limited to, microspheres that comprise glass, soda lime borosilicate glass, fly ash, ceramic, polystyrene, other polymeric materials, and mixtures thereof. In some embodiments of the lightweight settable compositions of the present invention, the microspheres are hollow, glass microspheres. In some embodiments, the microspheres may comprise a crosslinked polymeric material, such as polystyrene crosslinked with divinyl benzene (*e.g.*, plastic beads). The microspheres may be obtained from any suitable source. Examples of suitable fly ash microspheres are commercially available from Halliburton Energy Services, Inc., Duncan, Oklahoma, under the tradename SPHERELITE™ microspheres. Suitable hollow, soda lime borosilicate glass microspheres include 3M™ SCOTCHLITE™ glass bubbles.

Generally, suitable microspheres have a size of less than about 150 microns. In some embodiments, the microspheres have a size in the range of from about 5 microns to about 150 microns, alternatively from about 20 microns to about 105 microns, and alternatively from about 15 microns to about 80 microns.

5 The microspheres should be included in the lightweight settable compositions in an amount sufficient to provide the desired density, for example, less than about 13 ppg of the lightweight settable composition. In some embodiments, the microspheres may be present in the lightweight settable compositions of the present invention in an amount in the range of from about 1% to about 30% by weight of the lightweight settable composition. In
10 some embodiments, the microspheres may be present in the lightweight settable compositions of the present invention in an amount in the range of from about 3% to about 25% by weight of the lightweight settable composition. In other embodiments, the microspheres may be present in the lightweight settable compositions of the present invention in an amount in the range of from about 5% to about 20% by weight of the lightweight settable composition.

15 The lightweight 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
20 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. In some embodiments, the Portland cements that are suited for use in the present invention are classified as Classes A, C, H, and G cements according to American Petroleum Institute, *API Specification for Materials and Testing for Well Cements*, API
25 Specification 10, Fifth Ed., July 1, 1990.

Where present, the hydraulic cement generally may be included in the lightweight 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 lightweight settable compositions of the present invention in an amount up to about 75%
30 by weight of the lightweight settable composition. In some embodiments, the hydraulic cement may be present in the lightweight settable compositions of the present invention in an amount up to about 70% by weight of the lightweight settable composition. In some

embodiments, the hydraulic cement may be present in the lightweight settable compositions of the present invention in an amount in the range of from about 10% to about 70% by weight of the lightweight settable composition. In some embodiments, the hydraulic cement may be present in the lightweight settable compositions of the present invention in an amount in the
5 range of from about 20% to about 65% by weight of the lightweight settable composition.

In some embodiments, a pozzolana cement that may be suitable for use comprises fly ash. "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. A variety of fly ashes may be suitable,
10 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
15 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 15% 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.

20 Where present, the fly ash generally may be included in the lightweight 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 lightweight settable compositions of the present invention in an amount in the range of from about 5% to about 40% by weight of the lightweight settable composition. In some embodiments, the fly
25 ash may be present in the lightweight settable compositions of the present invention in an amount in the range of from about 7% to about 30% by weight of the lightweight settable composition.

In some embodiments, a slag cement that may be suitable for use may comprise slag. "Slag," as that term is used herein, refers to a granulated, blast furnace by-
30 product formed in the production of cast iron and generally comprises the oxidized impurities found in iron ore. 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.

Where present, the slag cement generally may be included in the lightweight
5 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 lightweight settable compositions of the present invention in an amount up to about 60% by weight of the lightweight settable composition. In some embodiments, the slag cement may be present in the lightweight settable compositions of the present invention in an amount in
10 the range of from about 5% to about 40% by weight of the lightweight settable composition.

In certain embodiments, the lightweight settable compositions of the present invention further may comprise metakaolin. Generally, metakaolin may be prepared by heating kaolin clay, for example, to temperatures in the range of from about 600° C to about 800°C. In some embodiments, the metakaolin may be present in the lightweight settable
15 compositions of the present invention in an amount in the range of from about 2.5% to about 40% by weight of the lightweight settable composition. In some embodiments, the metakaolin may be present in an amount in the range of from about 5% to about 30% by weight of the lightweight settable composition.

In certain embodiments, the lightweight settable compositions of the present
20 invention further may comprise vitrified shale. Among other things, vitrified shale included in the lightweight settable compositions may react with excess lime to form a suitable cementing material, for example, calcium silicate hydrate. A variety of vitrified shales are suitable, including those comprising silicon, aluminum, calcium, and/or magnesium. Suitable examples of vitrified shale include, but are not limited to, PRESSUR-SEAL® FINE LCM
25 material and PRESSUR-SEAL® COARSE LCM material, which are commercially available from TXI Energy Services, Inc., Houston, Texas. Generally, the vitrified shale may have any particle size distribution as desired for a particular application. In certain embodiments, the vitrified shale may have a particle size distribution in the range of from about 37 micrometers to about 4,750 micrometers.

30 Where present, the vitrified shale may be included in the lightweight settable compositions of the present invention in an amount sufficient to provide the desired compressive strength, density, and/or cost. In some embodiments, the vitrified shale and

necessary amount of lime for setting may be present in an amount up to about 50% by weight of the lightweight settable composition. In some embodiments, the vitrified shale may be present in an amount in the range of from about 5% to about 30% by weight of the lightweight settable composition. One of ordinary skill in the art, with the benefit of this disclosure, will recognize the appropriate amount of the vitrified shale to include for a chosen application.

In certain embodiments, the lightweight settable compositions of the present invention further may comprise zeolite. Zeolites generally are porous aluminosilicate 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. An example of a suitable source of zeolite is available from the C2C Zeolite Corporation of Calgary, Canada. In some embodiments, the zeolite may be present in the lightweight settable compositions of the present invention in an amount in the range of from about 2.5% to about 2.5% by weight of the lightweight settable composition.

In certain embodiments, the lightweight settable compositions of the present invention further may comprise a set retarding additive. 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 sulfoalkylate 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 lightweight 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 0.02% to about 2.5% by weight of the lightweight settable composition.

Optionally, other additional additives may be added to the lightweight 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, lost circulation materials, filtration control additives, dispersants, and combinations thereof. Suitable examples of these additives include crystalline silica compounds, amorphous silica, salts, fibers, calcined clays, combinations thereof and the like.

In certain embodiments, the lightweight settable compositions of the present invention may be foamed with a gas. These foamed embodiments may comprise water, CKD, microspheres, a gas, and a surfactant. Other suitable additives, such as those discussed previously, also may be included in the foamed lightweight 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 lightweight 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 lightweight 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 lightweight settable compositions of the present invention in an amount in the range of from about 10% to about 80% by volume of the composition.

Generally, the surfactant may be present in the foamed lightweight 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 0.5% and about 5% by volume of the water ("bvow").

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

An example of a method of the present invention comprises providing a lightweight settable composition of the present invention having a density of less than about 13 ppg, the lightweight settable composition comprising water, CKD, and microspheres, placing the lightweight settable composition in a location to be cemented, and allowing the lightweight 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. As desired by one of ordinary skill in the art, with the benefit of this disclosure, the lightweight 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.

Another example of a method of the present invention is a method of primary cementing. An example of such a method may comprise providing a lightweight settable composition of the present invention having a density of less than about 13 ppg, the lightweight settable composition comprising water, CKD, and microspheres; introducing the lightweight settable composition into an annulus between a subterranean formation and a pipe string located in the subterranean formation; and allowing the lightweight settable composition to set in the annulus. Generally, in most instances, the lightweight settable composition should set into hardened mass that fixes the pipe string to the subterranean formation. As desired by one of ordinary skill in the art, with the benefit of this disclosure, the lightweight 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.

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

A series of sample settable compositions were prepared at room temperature and subjected to 96-hour compressive strength tests at 120°F in accordance with API Specification 10. The sample compositions comprised microspheres (3M™ SCOTCHLITE™ glass bubbles), and Class C Portland cement or Class A CKD in the amounts indicated in the table below. Sample No. 1 additionally comprised water (200% bwoc), SILICALITE™ cement additive (17.8% bwoc), CAL-SEAL® calcined gypsum plaster (8.9% bwoc), and MICRO MATRIX® cement (17.8% bwoc). Sample No. 2 additionally comprised water (257.14% bwoc), SILICALITE™ cement additive (28.6% bwoc), CAL-SEAL® calcined gypsum plaster (17.1% bwoc), and MICRO MATRIX® cement (28.6% bwoc). In these examples, “bwoc” refers to by weight of cement, wherein the cement is the Portland cement and/or CKD included in the sample composition. SILICALITE™ cement additive is an amorphous silica powder commercially available from Halliburton Energy Services, Inc. CAL-SEAL CAL-SEAL® calcined gypsum plaster is commercially available from U.S.

Gypsum Company. MICRO MATRIX[®] cement is a fine hydraulic cement, commercially available from Halliburton Energy Services, Inc.

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

TABLE 1

Compressive Strength Tests

5

Sample	Density (ppg)	Portland Cement Class C (% bwoc)	CKD Class A (% bwoc)	SCOTCH-LITE [™] Glass Bubbles K25 ¹ (% bwoc)	SCOTCH-LITE [™] Glass Bubbles S32 ² (% bwoc)	96-Hour Compressive Strength at 120°F (psi)
No. 1	7.6	100	0	20	35.5	822
No. 2	7.67	0	100	22.9	40	509

¹ 3M[™] SCOTCHLITE[™] glass bubbles K25 have a density of about 2.086 ppg (0.25 g/cc).

² 3M[™] SCOTCHLITE[™] Glass Bubbles S32 have a density of about 2.671 ppg (0.32 g/cc).

EXAMPLE 2

10

A series of sample settable compositions were prepared at room temperature and subjected to 24-hour compressive strength tests at 100°F in accordance with API Specification 10. The sample compositions comprised microspheres (3M[™] SCOTCHLITE[™] glass bubbles), Class C Portland cement, and Class A CKD in the amounts indicated in Table 2 below. Each of the sample compositions also comprised water (180% bwoc),
 15 SILICALITE[™] cement additive (8% bwoc), CAL-SEAL[®] calcined gypsum plaster (4% bwoc), and MICRO MATRIX[®] cement (12% bwoc).

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

TABLE 2

Compressive Strength Tests

Sample	Density (ppg)	Portland Cement Class C (% bwoc)	CKD Class A (% bwoc)	SCOTCH-LITE [™] Glass Bubbles K25 (% bwoc)	SCOTCH-LITE [™] Glass Bubbles S32 (% bwoc)	24-Hour Compressive Strength at 100°F (psi)
No. 3	7.53	100	0	18	32	137
No. 4	7.50	70	30	18	32	136.5
No. 5	7.49	60	40	18	32	102

20

EXAMPLE 3

A series of sample settable compositions were prepared at room temperature and subjected to 24-hour compressive strength tests at 100°F and 140°F in accordance with API Specification 10. The sample compositions comprised microspheres (3M™ SCOTCHLITE™ glass bubbles), Class G CKD, and Class G Portland cement in the amounts indicated in the table below. Each of the sample compositions also comprised water (86.47% bwoc), SILICALITE™ cement additive (4% bwoc), CAL-SEAL® calcined gypsum plaster (2% bwoc), and MICRO MATRIX® cement (6% bwoc).

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

10

TABLE 3

Compressive Strength Tests

Sample	Density (ppg)	Cement Class G (% bwoc)	CKD Class G (% bwoc)	SCOTCH-LITE™ Bead K25 (% bwoc)	24-Hour Compressive Strength at 100°F (psi)	24-Hour Compressive Strength at 140°F (psi)
No. 6	7.50	100	0	20	150	250
No. 7	7.50	70	30	20	85	238
No. 8	7.50	0	100	20	19	115

EXAMPLE 4

A series of sample settable compositions were prepared at room temperature and subjected to 96-hour compressive strength tests at 140°F and 160°F in accordance with API Specification 10. The sample compositions comprised microspheres (3M™ SCOTCHLITE™ glass bubbles) and Class H CKD. Each of the sample compositions also comprised water, hydrated lime, vitrified shale (PRESSUR-SEAL® FINE LCM material), and CFR™-3 cement dispersant. CFR™-3 cement dispersant is commercially available from Halliburton Energy Services, Inc.

20

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

TABLE 4
Compressive Strength Tests

Sample	Density (ppg)	CKD Class H (% bwoc)	Water (% bwoc)	Hydrated Lime (% bwoc)	Pressure Seal (% bwoc)	CFR-3 (% bwoc)	SCOTCH-LITE™ S32 Glass Bubbles (% bwoc)	96-Hour Compressive Strength at 140°F (psi)	96-Hour Compressive Strength at 160°F (psi)
No. 9	7.96	100	228.6	19	100	0	76.2	502	543
No. 10	8.01	100	228.6	9.5	0	0.28	38.1	305	323
No. 11	8.85	100	80	0	0	0.75	25	407	483

Accordingly, Examples 1-4 indicate that settable compositions comprising hydraulic cement, CKD, and microspheres may have suitable compressive strengths for a particular application.

Therefore, the present invention is well adapted to attain the ends and advantages
5 mentioned as well as those that are inherent therein. While numerous changes may be made by those skilled in the art, such changes are encompassed within the spirit of this invention as defined by the appended claims. The terms in the claims have their plain, ordinary meaning unless otherwise explicitly and clearly defined by the patentee.

CLAIMS:

1. A lightweight settable composition comprising water, cement kiln dust, and microspheres, wherein the lightweight settable composition has a density less than about 13 pounds per gallon.
- 5 2. The lightweight settable composition of claim 1 wherein the cement kiln dust is present in the lightweight settable composition in an amount in the range of from about 0.01% to about 80% by weight of the lightweight settable composition.
3. The lightweight settable composition of claim 1 wherein the microspheres are present in the lightweight settable composition in an amount in the range of
10 from about 1% to 30% by weight of the lightweight settable composition.
4. The lightweight settable composition of claim 1 wherein the microspheres have a size less than about 150 microns.
5. The lightweight settable composition of claim 1 wherein the microspheres comprise at least one microsphere selected from the group consisting of hollow
15 microspheres, solid microspheres, porous microspheres, and combinations thereof.
6. The lightweight settable composition of claim 1 wherein the microspheres comprise a material selected from the group consisting of glass, fly ash, ceramic, polystyrene, other polymeric materials, and combinations thereof.
7. The lightweight settable composition of claim 1 wherein the
20 microspheres comprise sodium lime borosilicate glass.
8. The lightweight settable composition of claim 1 wherein the microspheres comprise polystyrene crosslinked with divinyl benzene.
9. The lightweight settable composition of claim 1 wherein the microspheres have a crush strength of greater than about 100 psi.
- 25 10. The lightweight settable composition of claim 1 wherein the microspheres have a density of less than about 8.345 pounds per gallon.
11. The lightweight settable composition of claim 1 wherein the lightweight settable composition further comprises a hydraulic cement.

12. The lightweight settable composition of claim 1 wherein the lightweight settable composition further comprises an additive selected from the group consisting of fly ash, vitrified shale, zeolite, hydrated lime, slag cement, metakaolin, and combinations thereof.

5 13. The lightweight settable composition of claim 1 wherein the lightweight settable composition further comprises an additive selected from the group consisting of a set retarding additive, an accelerator, a lost circulation material, a filtration control additive, a dispersant, a gas, a foam stabilizing surfactant, and combinations thereof.

10 14. The lightweight settable composition of claim 1:
wherein the cement kiln dust is present in the lightweight settable composition in an amount in the range of from about 2.5% to about 60% by weight of the lightweight settable composition;
wherein the microspheres are present in the lightweight settable composition in an amount in the range of from about 1% to 30% by weight of the lightweight
15 settable composition; and
wherein the lightweight settable composition further comprises Portland cement in an amount in the range of from about 20% to about 65% by weight of the lightweight settable composition.

20 15. A lightweight settable composition comprising water, CKD, microspheres, vitrified shale, and hydrated lime, wherein the lightweight settable composition has a density less than about 13 pounds per gallon.

16. The lightweight settable composition of claim 15 wherein the microspheres comprise at least one microsphere selected from the group consisting of hollow microspheres, solid microspheres, porous microspheres, and combinations thereof.

25 17. The lightweight settable composition of claim 15 wherein the microspheres comprise a material selected from the group consisting of glass, fly ash, ceramic, polystyrene, other polymeric materials, and combinations thereof.

18. A lightweight settable composition comprising water, CKD, and microspheres comprising soda lime borosilicate glass, wherein the lightweight settable
30 composition has a density less than about 13 pounds per gallon.

19. The lightweight settable composition of claim 18 wherein the

microspheres comprise at least one microsphere selected from the group consisting of hollow microspheres, solid microspheres, porous microspheres, and combinations thereof.

20. The lightweight settable composition of claim 18 wherein the microspheres comprise a material selected from the group consisting of glass, fly ash,
5 ceramic, polystyrene, other polymeric materials, and combinations thereof.

21. A method of cementing comprising:
providing a lightweight settable composition having a density less than
about 13 pounds per gallon, the lightweight settable composition comprising water, cement
kiln dust, and microspheres;
10 introducing the lightweight settable composition into a location to be
cemented; and
allowing the lightweight settable composition to set therein.

22. The method of claim 21 wherein the location to be cemented is in a
subterranean formation.

15 23. The method of claim 21 wherein the cement kiln dust is present in the
lightweight settable composition in an amount in the range of from about 0.01% to about
80% by weight of the lightweight settable composition.

24. The method of claim 21 wherein the microspheres are present in the
lightweight settable composition in an amount in the range of from about 1% to 30% by
20 weight of the lightweight settable composition.

25. The method of claim 21 wherein the microspheres have a size less than
about 150 microns.

26. The method of claim 21 wherein the microspheres comprise at least
one microsphere selected from the group consisting of hollow microspheres, solid
25 microspheres, porous microspheres, and combinations thereof.

27. The method of claim 21 wherein the microspheres comprise a material
selected from the group consisting of glass, fly ash, ceramic, polystyrene, other polymeric
materials, and combinations thereof.

28. The method of claim 21 wherein the microspheres comprise sodium
30 lime borosilicate glass.

29. The method of claim 21 wherein the microspheres comprise polystyrene crosslinked with divinyl benzene.

30. The method of claim 21 wherein the microspheres have a crush strength of greater than about 100 psi.

5 31. The method of claim 21 wherein the microspheres have a density of less than about 8.345 pounds per gallon.

32. The method of claim 21 wherein the lightweight settable composition further comprises a hydraulic cement.

10 33. The method of claim 21 wherein the lightweight settable composition further comprises an additive selected from the group consisting of fly ash, vitrified shale, zeolite, hydrated lime, slag cement, metakaolin, and combinations thereof.

15 34. The method of claim 21 wherein the lightweight settable composition further comprises an additive selected from the group consisting of a set retarding additive, an accelerator, a lost circulation material, a filtration control additive, a dispersant, a gas, a foam stabilizing surfactant, and combinations thereof.

35. The method of claim 21:
wherein the cement kiln dust is present in the lightweight settable composition in an amount in the range of from about 2.5% to about 60% by weight of the lightweight settable composition;
20 wherein the microspheres are present in the lightweight settable composition in an amount in the range of from about 1% to 30% by weight of the lightweight settable composition; and

wherein the lightweight settable composition further comprises Portland cement in an amount in the range of from about 20% to about 65% by weight of the
25 lightweight settable composition.

36. A method of primary cementing comprising:
providing a lightweight settable composition having a density less than about 13 pounds per gallon, the lightweight settable composition comprising water, cement kiln dust, and microspheres;
30 introducing the lightweight settable composition into an annulus

between a subterranean formation and a pipe string located in the subterranean formation;
and

allowing the lightweight settable composition to set in the annulus.

37. The method of claim 36 wherein the microspheres have a size less than
5 about 150 microns.

38. The method of claim 36 wherein the microspheres comprise at least
one microsphere selected from the group consisting of hollow microspheres, solid
microspheres, porous microspheres, and combinations thereof.

39. The method of claim 36 wherein the microspheres comprise a material
10 selected from the group consisting of glass, fly ash, ceramic, polystyrene, other polymeric
materials, and combinations thereof.

40. The method of claim 36 wherein the microspheres comprise sodium
lime borosilicate glass.

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2006/003694

A. CLASSIFICATION OF SUBJECT MATTER INV. C04B28/02				
According to International Patent Classification (IPC) or to both national classification and IPC				
B. FIELDS SEARCHED				
Minimum documentation searched (classification system followed by classification symbols) C04B				
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 5 352 288 A (MALLOW WILLIAM A [US]) 4 October 1994 (1994-10-04)	1-14		
Y	column 2, line 55 - column 4, line 54 column 5; examples 1-3 column 6; example 4 columns 8-9; example 14	15-40		
Y	----- US 6 689 208 B1 (BROTHERS LANCE E [US]) 10 February 2004 (2004-02-10) columns 1-4	15-17		
Y	----- US 2002/073897 A1 (TRATO JAMES H [US]) 20 June 2002 (2002-06-20) paragraphs [0009] - [0012] paragraphs [0025] - [0034], [0048]	15-40		
-/--				
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C.				
<input checked="" type="checkbox"/> See patent family annex.				
* Special categories of cited documents :				
<table style="width: 100%; border: none;"> <tr> <td style="width: 50%; vertical-align: top; padding: 5px;"> *A* document defining the general state of the art which is not considered to be of particular relevance *E* earlier document but published on or after the international filing date *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) *O* document referring to an oral disclosure, use, exhibition or other means *P* document published prior to the international filing date but later than the priority date claimed </td> <td style="width: 50%; vertical-align: top; padding: 5px;"> *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. *&* document member of the same patent family </td> </tr> </table>			*A* document defining the general state of the art which is not considered to be of particular relevance *E* earlier document but published on or after the international filing date *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) *O* document referring to an oral disclosure, use, exhibition or other means *P* document published prior to the international filing date but later than the priority date claimed	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. *&* document member of the same patent family
A document defining the general state of the art which is not considered to be of particular relevance *E* earlier document but published on or after the international filing date *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) *O* document referring to an oral disclosure, use, exhibition or other means *P* document published prior to the international filing date but later than the priority date claimed	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. *&* document member of the same patent family			
Date of the actual completion of the international search	Date of mailing of the international search report			
8 December 2006	19/12/2006			
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer Lura, Pietro			

INTERNATIONAL SEARCH REPORT

International application No

PCT/GB2006/003694

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2005/098317 A1 (REDDY B R [US] ET AL REDDY B RAGHAVA [US] ET AL) 12 May 2005 (2005-05-12) paragraphs [0009] - [0012] paragraphs [0019], [0028] - [0033] -----	18-40
X,P	US 7 077 203 B1 (RODDY CRAIG W [US] ET AL) 18 July 2006 (2006-07-18) column 3 - column 9 columns 14-15; example 8; table 8 column 19; example 15; table 15 columns 20-21; examples 16,17; tables 16,17 -----	1-6, 11-17, 21-27, 32-39
A	EP 1 348 831 A (HALLIBURTON ENERGY SERV INC [US]) 1 October 2003 (2003-10-01) paragraph [0012] -----	17
A	US 2004/187740 A1 (TIMMONS SCOTT F [US]) 30 September 2004 (2004-09-30) the whole document -----	1-40

INTERNATIONAL SEARCH REPORT

Information on patent family members

international application No PCT/GB2006/003694

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5352288	A	CA 2125351 A1	08-12-1994
US 6689208	B1	AU 2003269168 A1 CA 2527736 A1 WO 2004109056 A1 MX PA05013095 A US 2004244650 A1	04-01-2005 16-12-2004 16-12-2004 09-03-2006 09-12-2004
US 2002073897	A1	US 2004256102 A1	23-12-2004
US 2005098317	A1	WO 2005047212 A1 US 2006169176 A1	26-05-2005 03-08-2006
US 7077203	B1	NONE	
EP 1348831	A	CA 2407365 A1 NO 20025316 A US 2003177955 A1 US 2003177954 A1	21-09-2003 22-09-2003 25-09-2003 25-09-2003
US 2004187740	A1	WO 2004087600 A2	14-10-2004