

Cement Slurry Composition

Technical Field

The present invention relates to a cement slurry composition, a method of preparing the cement slurry composition, a set or hardened cement obtained from the cement slurry composition and the use of the cement slurry composition in cementing or plugging oil and gas well, as well as in civil construction and architecture.

Background Art

Generic well cement slurries are commonly used in the oil and gas cementing industry. One of the most troublesome problems encountered during cement formation is annular gas migration, which may occur during drilling or well completion procedures. Annular gas migration occurs when formation gas invades into the annulus of the cement structure. During cement placement, the cement slurry develops a certain gel strength. That is, the slurry will develop a low shear strength value at the beginning, that fully transmits hydrostatic pressure. However, as the gel strength development continues, the cement will no longer transmit the total hydrostatic pressure. Due to the slurry's capability to sustain shear stress, hydrostatic pressure within the annulus is continually reduced by slurry gelation, resulting in the ability for gas to flow into areas with lower pressure, or to the surface. Gas migration through a cement matrix may occur due to loss of hydrostatic pressure because of natural and unavoidable phenomena that occur during cement hydration. This increases the risk of losing control or collapse of the cement structure.

One specific example of annular gas migration is gas-channelling, which is a phenomenon that occurs when a compressed (pressurised) gas migrates within the cemented annulus during well cementing or within a cemented in-fill during well abandonment. Gas migration occurs after the cement slurry has been injected into the annular space between the drilled formations and the well casing, or in the case of plugging, into the internal space of the casing. Initially, the pressurised gas is prevented from upward migration by the hydrostatic pressure exerted by the fresh cement mixture column sitting above it. During setting of the cement, as the mixture starts to gain rigidity and stiffens, the hydrostatic pressure starts to decrease. When this hydrostatic pressure drops below the opposing gas pressure, gas migration into the cemented column occurs. The pressurized gas then migrates through the cement in the course of its setting and/or between the cement and the drilled formations, creating a series of channels in the cement which may reach the surface of the well. Gas channelling is thus a serious drawback leading to weakening of the cement and poses safety problems on the surface.

In view of the limitations of current cement compositions, there is a need for development of a cement slurry composition that overcomes or at least ameliorates, one or more of the disadvantages described above.

Summary

In an aspect, there is provided a cement slurry composition comprising:

25 % to 60 % by volume of cenospheres;

15 % to 45 % by volume of a combination of a cementitious material and an additive;

5 20 % to 35 % by volume of water; and

3 % to 15 % by volume of air;

wherein the total volume of the composition adds to 100%, and

wherein the cementitious material comprises 30 % to 95 % of hydraulic cement by weight of total cementitious material (BWTC) and 5 % to 70 % of pozzolan BWTC, and

10 the additive is present at an amount of 0.1 % to 6 % BWTC,

whereby the total weight of the cementitious material adds to 100%.

Advantageously, the cement slurry composition may facilitate the formation of cement composite that is lightweight, high-strength and that has a short gel transition time (GTT) with right-angle set (RAS) behaviour.

15 The lightweight property may advantageously be due to the use of cenospheres in the composition. The set or hardened cement resulting from the cement slurry composition may advantageously be a low-density material having a density in the range of about 1,000 kg/m³ to about 1,900 kg/m³, which may bear lower stress on weaker formations during circulation for well cementing or well plugging. This may advantageously result in less formations being lost, while having the
20 advantage that the material may be able to secure exact placement on a location during well plugging for the purpose of abandonment, when a temporary base foundation such as a gel plug may be required.

The high-strength of the set or hardened cement resulting from the cement slurry composition may advantageously be due to optimised packing density with an ultra-fine filler such as
25 microsilica or nanosilica, well-distributed grading size of particles in the composition, use of pozzolans to promote secondary pozzolanic chemical reaction with cement, and the use of high quality additives such as water reducing polymer such as polycarboxylate ether (PCE) polymers. Advantageously, the hardened or set cement resulting from the cement slurry composition may exhibit superior strength properties for use in strengthening and supporting well casing strings for
30 the purposes of well cementing, especially in areas of weak formation, or to create a strong permanent plug to shut off a well for the purposes of well abandonment. The set or hardened cement may have a compressive strength of about 15 MPa to about 90 MPa. Besides strength, the hardened or set cement resulting from the cement slurry composition may be advantageously highly impermeable and durable due to its dense microstructure, and may make it an effective

barrier against fluid migration and aggressive fluids that may attack traditional cementing materials.

The short gel transition time (GTT) with right-angled set (RAS) characteristics may advantageously be due to the use of set altering additives such as calcium sulfoaluminate (CSA) cement, superplasticizer, shrinkage-reducing agent (SRA), set retarding agent (retarder) and/or gypsum. Through the use of both chemical and mineral additives to control and alter the setting behaviour of the cement composition, RAS or a short GTT may advantageously be achieved. Due to the RAS or a short GTT, the cement slurry composition may have gas inhibiting abilities that may prevent gas-channelling during cementing and plugging of oil and gas wells.

10 In another aspect, there is provided a method of preparing a cement slurry composition according to any one of the preceding claims, comprising the step of:

mixing 25 % to 60 % by volume of cenospheres with 15 % to 45 % by volume of a combination of a cementitious material and an additive, 20 % to 35 % by volume of water, and 3 % to 15 % by volume of air; such that the total volume adds to 100%, and

15 wherein the cementitious material comprises 30 % to 95 % of hydraulic cement by weight of total cementitious material (BWTC) and 5 % to 70 % of pozzolan BWTC, and

the additive is present at an amount of 0.1 % to 6 % BWTC,

whereby the total weight of the cementitious material adds to 100%.

In another aspect, there is provided a cement dry mix comprising:

20 14 % to 45 % by weight of cenospheres; and

55 % to 86 % by weight of a combination of a cementitious material and an additive;

wherein the total weight of the composition adds to 100%, and

wherein the cementitious material comprises 30% to 95% of hydraulic cement by weight of total cementitious material (BWTC) and 5% to 70% of pozzolan BWTC, and

25 the additive is present at an amount of 0.1% to 6% BWTC,

whereby the total weight of the cementitious material adds to 100%.

In another aspect, there is provided a set or hardened cement obtained from the cement slurry composition as defined above.

30 In another aspect, there is provided the use of a cement slurry composition as defined above in cementing or plugging oil and gas wells and in civil construction and architecture.

Definitions

The following words and terms used herein shall have the meaning indicated:

"Alkyl" as a group or part of a group refers to a straight or branched aliphatic hydrocarbon group, preferably a C₁–C₁₂ alkyl, more preferably a C₁–C₁₀ alkyl, most preferably C₁–C₆ unless otherwise noted. Examples of suitable straight and branched C₁–C₆ alkyl substituents include methyl, ethyl, n-propyl, 2-propyl, n-butyl, sec-butyl, t-butyl, hexyl, and the like. The group may be a terminal group or a bridging group.

The word "substantially" does not exclude "completely" e.g. a composition which is "substantially free" from Y may be completely free from Y. Where necessary, the word "substantially" may be omitted from the definition of the invention.

Unless specified otherwise, the terms "comprising" and "comprise", and grammatical variants thereof, are intended to represent "open" or "inclusive" language such that they include recited elements but also permit inclusion of additional, unrecited elements.

As used herein, the term "about", in the context of concentrations of components of the formulations, typically means +/- 5% of the stated value, more typically +/- 4% of the stated value, more typically +/- 3% of the stated value, more typically, +/- 2% of the stated value, even more typically +/- 1% of the stated value, and even more typically +/- 0.5% of the stated value.

Throughout this disclosure, certain embodiments may be disclosed in a range format. It should be understood that the description in range format is merely for convenience and brevity and should not be construed as an inflexible limitation on the scope of the disclosed ranges. Accordingly, the description of a range should be considered to have specifically disclosed all the possible sub-ranges as well as individual numerical values within that range. For example, description of a range such as from 1 to 6 should be considered to have specifically disclosed sub-ranges such as from 1 to 3, from 1 to 4, from 1 to 5, from 2 to 4, from 2 to 6, from 3 to 6 etc., as well as individual numbers within that range, for example, 1, 2, 3, 4, 5, and 6. This applies regardless of the breadth of the range.

Certain embodiments may also be described broadly and generically herein. Each of the narrower species and subgeneric groupings falling within the generic disclosure also form part of the disclosure. This includes the generic description of the embodiments with a proviso or negative limitation removing any subject matter from the genus, regardless of whether or not the excised material is specifically recited herein.

Detailed Disclosure of Optional Embodiments

There is provided a cement slurry composition comprising:

about 25 % to about 60 % by volume of cenospheres;

about 15 % to about 45 % by volume of a combination of a cementitious material and an additive;

about 20 % to about 35% by volume of water; and

about 3 % to about 15 % by volume of air;

5 wherein the total volume of the composition adds to 100%, and

wherein the cementitious material comprises about 30% to about 95% of hydraulic cement by weight of total cementitious material (BWTC) and about 5% to about 70% of pozzolan BWTC, and

the additive is present at an amount of about 0.1% to about 6% BWTC,

10 whereby the total weight of the cementitious material adds to 100%.

Cenospheres may be hollow ceramic microspheres that may be a type of floating fly ash, and may be a by-product from the effluent of coal fired power plants. Cenospheres may be made largely of silica and alumina and may be filled with vacuum, air or inert gas. Cenospheres may be hard, rigid, lightweight, inert, waterproof, innocuous, insulative and buoyant. Cenospheres may have a high melting point, usually in the range of about 1600 °C to about 1800 °C. The high melting point may enable the cenospheres to be nonabsorbent, non-flammable, possess high chemical resistance and in combination with vacuum in the spheres, may provide both thermal and acoustic insulation.

20 The cenospheres may be present in the composition at an amount in the range of about 25 % to about 60 %, about 25% to about 30%, about 25% to about 40%, about 25% to about 50%, about 25% to about 55%, about 30% to about 40%, about 30% to about 50%, about 30% to about 55%, about 30% to about 60%, about 40% to about 50%, about 40% to about 55%, about 40% to about 55%, about 40% to about 60%, by volume of the composition.

25 The cenospheres may have a bulk density ranging from about 0.1 g/cm³ to about 0.7 g/cm³, about 0.1 g/cm³ to about 0.2 g/cm³, about 0.1 g/cm³ to about 0.3 g/cm³, about 0.1 g/cm³ to about 0.5 g/cm³, about 0.2 g/cm³ to about 0.3 g/cm³, about 0.2 g/cm³ to about 0.5 g/cm³, or about 0.3 g/cm³ to about 0.5 g/cm³.

30 The cenospheres may have a particle density ranging from about 0.2 g/cm³ to about 1.2 g/cm³, about 0.2 g/cm³ to about 0.4 g/cm³, about 0.2 g/cm³ to about 0.6 g/cm³, about 0.2 g/cm³ to about 0.9 g/cm³, about 0.4 g/cm³ to about 0.6 g/cm³, about 0.4 g/cm³ to about 0.9 g/cm³, about 0.4 g/cm³ to about 1.2 g/cm³, about 0.6 g/cm³ to about 0.9 g/cm³, about 0.6 g/cm³ to about 1.2 g/cm³ or about 0.9 g/cm³ to about 1.2 g/cm³.

35 The cenospheres may have a particle diameter ranging from about 20 μm to about 800 μm, about 20 μm to about 30 μm, about 20 μm to about 50 μm, about 20 μm to about 100 μm, about 20 μm to about 200μm, about 20 μm to about 400μm, about 20 μm to about 600μm, about 30 μm to

about 50 μm , about 30 μm to about 100 μm , about 30 μm to about 200 μm , about 30 μm to about 400 μm , about 30 μm to about 600 μm , about 30 μm to about 800 μm , about 50 μm to about 100 μm , about 50 μm to about 200 μm , about 50 μm to about 400 μm , about 50 μm to about 600 μm , about 50 μm to about 800 μm , about 100 μm to about 200 μm , about 100 μm to about 400 μm , about 100 μm to about 600 μm , about 100 μm to about 800 μm , about 200 μm to about 400 μm , about 200 μm to about 600 μm , about 200 μm to about 800 μm , about 400 μm to about 600 μm , about 400 μm to about 800 μm , about 600 μm to about 800 μm .

The cenospheres may have a crushing strength ranging from about 8 MPa to about 60 MPa about 8 MPa to about 10 MPa, about 8 MPa to about 20 MPa, about 8 MPa to about 50 MPa, about 10 MPa to about 20 MPa, about 10 MPa to about 50 MPa, about 10 MPa to about 60 MPa, about 20 MPa to about 50 MPa, about 20 MPa to about 60 MPa, or about 50 MPa to about 60 MPa.

The strength of the cenospheres may be higher if the particle diameter is smaller.

The cenospheres may comprise a compound selected from the group consisting of SiO_2 , Al_2O_3 , Fe_2O_3 , CaO , TiO_2 , MgO , K_2O , Na_2O , and any mixture thereof.

The cenosphere may have the following composition by weight:

SiO_2 : about 52% to about 65%, about 52% to about 54%, about 52% to about 57%, about 52% to about 60%, about 52% to about 61%, about 52% to about 57%, about 52% to about 60%, about 52% to about 61%, about 52% to about 65%, about 57% to about 60%, about 57% to about 61%, about 57% to about 65%, or about 61% to about 65%;

Al_2O_3 : about 24% to about 45%, about 24% to about 26%, about 24% to about 30%, about 24% to about 35%, about 24% to about 41%, about 26% to about 30%, about 26% to about 35%, about 26% to about 41%, about 26% to about 45%, about 30% to about 35%, about 30% to about 41%, about 30% to about 45%, about 35% to about 41%, about 35% to about 45% or about 41% to about 45%;

Fe_2O_3 : about 0.3% to about 12%, about 0.3% to about 1%, about 0.3% to about 0.5%, about 0.3% to about 1%, about 0.3% to about 2%, about 0.3% to about 5%, about 0.3% to about 10%, about 0.5% to about 1%, about 0.5% to about 2%, about 0.5% to about 5%, about 0.5% to about 10%, about 0.5% to about 12%, about 1% to about 2%, about 1% to about 5%, about 1% to about 10%, about 2% to about 5%, about 2% to about 10%, about 2% to about 12%, about 5% to about 10%, about 5% to about 12% or about 10% to about 12%;

CaO : about 0.1% to about 1.4%, about 0.1% to about 0.2%, about 0.1% to about 0.5%, about 0.1% to about 1.1%, about 0.2% to about 0.5%, about 0.2% to about 1.1%, about 0.2% to about 1.4%, about 0.5% to about 1.1%, about 0.5% to about 1.4%, or about 1.1% to about 1.4%;

TiO_2 : about 0.1% to about 1.3%; about 0.1% to about 0.23%, about 0.1% to about

0.5%, about 0.1% to about 1.05%, about 0.23% to about 0.5%, about 0.23% to about 1.05%, about 0.23% to about 1.3%, about 0.5% to about 1.05%, about 0.5% to about 1.3%, or about 1.05% to about 1.3%;

- 5 MgO: about 0.05% to about 4%, about 0.05% to about 0.1%, about 0.05% to about 0.5%, about 0.05% to about 1%, about 0.05% to about 2.5%, about 0.05% to about 3.5%, about 0.1% to about 0.5%, about 0.1% to about 1%, about 1.5% to about 2.5%, about 0.1% to about 3.5%, about 0.1% to about 4%, about 0.5% to about 1%, about 0.5% to about 2.5%, about 0.5% to about 3.5%, about 0.5% to about 4%, about 1% to about 2%, about 1% to about 2.5%, about 1% to about 3.5%, about 1% to about 4%, about 2% to about 2.5%, about 2.5% to about 3.5%, about 2.5% to about 4% or about 3.5% to about 4%;
- 10
- K₂O: about 0.005% to about 4%, about 0.005% to about 0.1%, about 0.005% to about 0.5%, about 0.005% to about 0.8%, about 0.005% to about 1.5%, about 0.005% to about 2%, about 0.005% to about 3.5%, about 0.1% to about 0.5%, about 0.1% to about 0.8%, about 0.1% to about 1.5%, about 0.1% to about 2%, about 0.1% to about 3.5%, about 0.1% to about 4%, about 0.5% to about 0.8%, about 0.5% to about 1.5%, about 0.5% to about 2%, about 0.5% to about 3.5%, about 0.5% to about 4%, about 0.8% to about 1.5%, about 0.8% to about 2%, about 0.8% to about 3.5%, about 0.5% to about 4%, about 1.5% to about 2%, about 1.5% to about 3.5%, about 1.5% to about 4%, about 2% to about 3.5%, about 2% to about 4% or about 3.5% to about 4%; and/or
- 15
- Na₂O: about 0.005% to about 1.2%, about 0.005% to about 0.01%, about 0.005% to about 0.1%, about 0.005% to about 0.3%, about 0.005% to about 0.5%, about 0.005% to about 1%, about 0.01% to about 0.1%, about 0.01% to about 0.3%, about 0.01% to about 0.5%, about 0.01% to about 1%, about 0.01% to about 1.2%, about 0.3% to about 0.5%, about 0.3% to about 0.8%, about 0.3% to about 1%, about 0.3% to about 1.2%, about 0.5% to about 0.8%, about 0.5% to about 1%, about 0.5% to about 1.2%, about 0.8% to about 1%, about 0.8% to about 1.2% or about 1% to about 1.2%.
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- 30 The cement slurry composition may comprise about 15% to about 45%, about 15% to about 25% about 25% to about 35%, about 25% to about 35%, about 25% to about 45% or about 35% to about 45% by volume of a combination of a cementitious material and an additive.

- The cementitious material may comprise about 30% to about 95%, about 30% to about 50%, about 30% to about 75%, about 30% to about 90%, about 50% to about 75%, about 50% to about 90%, about 50% to about 95%, about 75% to about 90%, about 75% to about 95%, or about 90% to about 95% of hydraulic cement by weight of total cementitious material (BWTC).
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 The cementitious material may comprise about 5% to about 70%, about 5% to about 20%, about 5% to about 40%, about 20% to about 40%, about 20% to about 70% or about 40% to about 70% of pozzolan by weight of total cementitious material (BWTC).

The total weight of the cementitious material must add to 100% by weight of total cementitious material (BWTC). BWTC may exclude the weight% of additives.

The hydraulic cement may be Portland cement and/or a calcium sulfoaluminate (CSA) cement.

- 5 The Portland cement may be ASTM Type I, Type IA, Type II, Type IIA, Type II(MH), Type II(MH)A, Type V cement, API class A, B, G or H cement, or EN CEM I, II, III, IV or V cement. The Portland cement may be selected from the group consisting of ASTM Type I, Type II, or Type V cement, API class A, B, G, or H cement, EN CEM I, II, III, IV, or V cement and any mixture thereof.

The CSA cement may comprise the following phases:

- 10 ettringite or anhydrous calcium sulfoaluminate ($4\text{CaO} \cdot 3\text{Al}_2\text{O}_3 \cdot \text{CaSO}_4$);
belite or Dicalcium silicate ($2\text{CaO} \cdot \text{SiO}_2$); and/or
gypsum or calcium sulfate di-hydrate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$).

- 15 The CSA cement may be present in the composition at an amount of 0% to about 8%, 0% to about 2%, 0% to about 4%, 0% to about 6%, about 2% to about 4%, about 2% to about 6%, about 2% to about 8%, about 4% to about 6%, about 4% to about 8% or about 6% to about 8% by weight of the total cementitious material (BWTC).

CSA cement is a specialty cement that may be used for shrinkage-control and as a set accelerator. CSA cement may be used for the specific purpose of set control to achieve a short gel transition time (GTT) and right-angle set (RAS).

- 20 The pozzolan may be siliceous or siliceous and aluminous materials, which in themselves, may possess little or no cementitious value but which will, in finely divided form and in the presence of water, react chemically with calcium hydroxide at room temperature to form compounds possessing cementitious properties. The use of pozzolans may promote secondary pozzolanic chemical reaction with cement. The pozzolan may be natural or artificial.
- 25 The pozzolan may be selected from the group consisting of microsilica, nanosilica, pulverized fly ash, ground-granulated blast furnace slag (GGBS), metakaolin, and any mixture thereof.

- 30 The pozzolan may be microsilica, and the microsilica may be present in the composition at an amount of about 1% to about 12%, about 1% to about 2%, about 1% to about 5%, about 1% to about 10%, about 2% to about 5%, about 2% to about 10%, about 2% to about 12%, about 5% to about 10%, about 5% to about 12% or about 10% to about 12% by weight of total cementitious material (BWTC).

The microsilica may have a particle size greater than 80 nm but less than 1000 nm. The microsilica may have a particle size in the range of about 80 nm to about 1000 nm, about 80 nm to about 100 nm, about 80 nm to about 150 nm, about 80 nm to about 300 nm, about 80 nm to about 500 nm,

about 80 nm to about 750 nm, about 100 nm to about 150 nm, about 100 nm to about 300 nm, about 100 nm to about 500 nm, about 100 nm to about 750 nm, about 100 nm to about 1000 nm, about 150 nm to about 300 nm, about 150 nm to about 500 nm, about 150 nm to about 750 nm, about 150 nm to about 1000 nm, about 300 nm to about 500 nm, about 300 nm to about 750 nm, about 300 nm to about 1000 nm, about 500 nm to about 750 nm, or about 1000 nm to about 1000 nm.

The pozzolan may be nanosilica, and the nanosilica may be present in the composition at an amount of 0% to about 2%, 0% to about 0.5%, 0% to about 1%, 0% to about 1.5%, about 0.5% to about 1%, about 0.5% to about 1.5%, about 0.5% to about 2%, about 1% to about 1.5%, about 1% to about 2%, or about 1.5% to about 2% by weight of total cementitious material (BWTC).

The nanosilica may have a particle size greater than 5 nm but less than 80 nm. The nanosilica may have a particle size in the range of about 5 nm to about 80 nm, about 5 nm to about 10 nm, about 5 nm to about 30 nm, about 5 nm to about 50 nm, about 10 nm to about 30 nm, about 10 nm to about 50 nm, about 10 nm to about 80 nm, about 30 nm to about 50 nm, about 30 nm to about 80 nm or about 50 nm to about 80 nm.

The pozzolan may be pulverized fly ash and may be present in the composition at an amount of 0% to about 55%, 0% to about 5%, 0% to about 10%, 0% to about 20%, 0% to about 50%, about 5% to about 10%, about 5% to about 20%, about 5% to about 50%, about 5% to about 55%, about 10% to about 20%, about 10% to about 50%, about 10% to about 55%, about 20% to about 50%, about 20% to about 55% or about 50% to about 55% by weight of total cementitious material (BWTC). The pulverized fly ash may be of the standard ASTM C618 Class F, BS EN 450 or equivalent.

The pozzolan may be ground-granulated blast furnace slag (GGBS) and may be present in the composition at an amount of 0% to about 70%, 0% to about 5%, 0% to about 10%, 0% to about 20%, 0% to about 50%, 0% to about 65%, about 5% to about 10%, about 5% to about 20%, about 5% to about 50%, about 5% to about 65%, about 5% to about 70%, about 10% to about 20%, about 10% to about 50%, about 10% to about 65%, about 10% to about 70%, about 20% to about 50%, about 20% to about 65%, about 20% to about 70%, about 50% to about 65%, about 50% to about 70% or about 65% to about 70% by weight of total cementitious material (BWTC).

The pozzolan may be metakaolin, and may be present in the composition at an amount of 0% to about 15%, 0% to about 5%, 0% to about 10%, about 5% to about 10%, about 5% to about 15% or about 10% to about 15% by weight of total cementitious material (BWTC).

The additive may be present at an amount of about 0.1 % to about 6%, about 0.1% to about 0.2%, about 0.1 % to about 0.5%, about 0.1% to about 1%, about 0.1% to about 2%, about 0.2% to about 0.5%, about 0.2% to about 1%, about 0.2% to about 2%, about 0.2% to about 6%, about 0.5% to about 1%, about 0.5% to about 2%, about 0.5% to about 6%, about 1% to about 2%, about 1% to about 6% or about 2% to about 6% by weight of total cementitious material (BWTC).

The additive may be selected from the group consisting of superplasticizer (SP), shrinkage-reducing agent (SRA), gypsum, air entraining agent (AEA), set retarding agent (retarder), set accelerating agent, viscosity modifying agent (VMA), fluid loss agent, and any mixture thereof.

5 The additive may be superplasticizer (SP) and may be present in the composition at an amount of about 0.1% to about 4%, about 0.1% to about 0.3%, about 0.1% to about 1%, about 0.1% to about 2%, about 0.1% to about 4%, about 0.3% to about 1%, about 0.3% to about 2%, about 0.3% to about 3%, about 0.3% to about 4%, about 1% to about 2%, about 1% to about 3%, about 1% to about 4%, about 2% to about 3%, about 2% to about 4% or about 3% to about 4% by weight of total cementitious material (BWTC).

10 The superplasticizer (SP) may be based on a high molecular weight polymer resin. This SP may reduce the water/cement ratio which means that the mechanical strength and wear and weathering resistance of the cement composition when set or hardened may be increased and shrinkage which causes cracking may be reduced. The SP may be a chemical derivative of a compound selected from the group consisting of polycarboxylate ether (PCE) polymers, PCE comb-copolymers,
15 sulphonated naphthalene formaldehyde (SNF), and sulphonated melamine formaldehyde (SMF). The SP may be added to the composition in the form of an aqueous solution (or water-based liquid) or as a dry-spray powder.

The SP may influence the set behaviour of the composition by acting as a water-reducer.

20 As a water-reducer, any chemical derivatives of a compound selected from the group consisting of polycarboxylate ether (PCE) comb-copolymers, sulphonated naphthalene formaldehyde (SNF), and sulphonated melamine formaldehyde (SMF) may not be used together in the same composition.

The additive may be a shrinkage-reducing agent (SRA), and may be present in the composition at an amount of about 0.05% to about 5%, about 0.05% to about 0.1%, about 0.05% to about 1%,
25 about 0.05% to about 3%, about 0.1% to about 1%, about 0.1% to about 3%, about 0.1% to about 5%, about 1% to about 3%, about 1% to about 5% or about 3% to about 5% by weight of total cementitious material (BWTC). The SRA may be added to the composition in the form of a liquid, water-based liquid or solid dry powder.

The SRA may comprise glycol ether, polyoxyalkylene alkyl ether, or any mixture thereof.

30 The SRA may influence set behaviour of the composition by acting as a shrinkage reducing agent with a retarding influence on the set behaviour.

Although CSA cement may contain natural gypsum, an additional amount of gypsum may be added to the composition for control and adjusting the set behaviour of the cement composite.

35 The additive may be gypsum, and may be present in the composition at an amount of 0% to about 3%, 0% to about 1%, 0% to about 2%, about 1% to about 2%, about 1% to about 3% or about 2% to about 3% by weight of total cementitious material (BWTC).

Gypsum may be used for the specific purpose of set control to achieve a short gel transition time (GTT) and right-angle set (RAS).

The additive may be an air entraining agent (AEA). In some examples, the AEA may be selected from the group consisting of rosin resin, alkyl sulfonate, aliphatic alcohol sulfonate, protein salt, petroleum sulfonate and any mixture thereof. The AEA may be added to the composition to entrain minute air bubbles in the composition to further reduce the unit weight of the slurry composition. The AEA may be present in the composition at an amount of 0% to about 1%, 0% to about 0.25%, 0% to about 0.5%, 0% to about 0.75%, about 0.25% to about 0.5%, about 0.25% to about 0.75%, about 0.25% to about 1%, about 0.5% to about 0.75%, about 0.5% to about 1% or about 0.75% to about 1% by weight of total cementitious material (BWTC). The AEA may be added to the composition in the form of a water-based liquid or solid dry powder.

The additive may be a viscosity modifying agent (VMA). In some examples, the VMA may be a fine, inorganic material such as colloidal silica or polymers selected from the group consisting of polyethylene oxide, cellulose ether, alginate, natural and synthetic gum, polyacrylamide, polyvinyl alcohol, hydrophobically modified ethoxylated urethane (HEUR) and any mixture thereof. The VMA may be added to the composition to further modify the rheology of the slurry composition consistency. The VMA may be present in the composition at an amount of 0% to about 5%, 0% to about 1%, 0% to about 2%, 0% to about 3%, 0% to about 4%, about 1% to about 2%, about 1% to about 3%, about 1% to about 4%, about 1% to about 5%, about 2% to about 3%, about 2% to about 4%, about 2% to about 5%, about 3% to about 4%, about 3% to about 5% or about 4% to about 5% by weight of total cementitious material (BWTC). The VMA may be added to the composition in the form of a liquid or solid dry powder.

The additive may be a set retarding agent (retarder). The retarder may be selected from the group consisting of phosphonate, borate, Pb salt, Zn salt, Cu salt, As salt, Sb salt, Ligno sulphonate, hydroxyl carboxylic acid or any mixture thereof. The retarder may be added to the composition to delay the setting times of the slurry composition. The retarder may be present in the composition at an amount of 0% to about 3%, 0% to about 1%, 0% to about 2%, about 1% to about 2%, about 1% to about 3%, or about 2% to about 3% by weight of total cementitious material (BWTC). The retarder may be added to the composition in the form of a water-based liquid or solid dry powder.

The additive may be a set accelerating agent. The set accelerating agent may be a calcium salt of an anion selected from the group consisting of chloride, nitrate, nitrite, formate and any mixture thereof. The set accelerating agent may be added to the composition to shorten the setting time of the slurry composition. The set accelerating agent may be present in the composition at an amount of 0% to about 1%, 0% to about 0.25%, 0% to about 0.5%, 0% to about 0.75%, about 0.25% to about 0.5%, about 0.25% to about 0.75%, about 0.25% to about 1%, about 0.5% to about 0.75%, about 0.5% to about 1% or about 0.75% to about 1% by weight of total cementitious material (BWTC). The set accelerating agent may be added to the composition in the form of a water-based liquid or solid dry powder.

The additive may be a fluid loss agent (FLA). The FLA may be selected from the group consisting of cellulose derivatives such as hydroxyethyl cellulose (HEC) and carboxymethyl hydroxyethyl cellulose (CMHEC), polyacrylamide and any mixture thereof, and may be added to the composition to improve stability of the slurry composition. The FLA may be present in the composition at an amount of 0% to about 1%, 0% to about 0.25%, 0% to about 0.5%, 0% to about 0.75%, about 0.25% to about 0.5%, about 0.25% to about 0.75%, about 0.25% to about 1%, about 0.5% to about 0.75%, about 0.5% to about 1% or about 0.75% to about 1% by weight of total cementitious material (BWTC). The FLA may be added to the composition in the form of a liquid or solid dry powder.

- 10 Other additives may be present in trace amounts.

For additives that are provided in the form of a water-based liquid, they comprise the active ingredient of the additive in solid form dissolved or suspended in water. In the examples above, only the weight of the active ingredient in solid form contributes to the % by weight of total cementitious material (BWTC) of the additive to be added to the composition. The % by weight or % by volume of the water present in the water-based liquid is counted as part of the total water added to the composition.

The cement slurry composition may comprise about 20 % to about 35%, about 20 % to about 25%, about 20% to about 30%, about 25% to about 30%, about 25% to about 35% or about 30% to about 35% by volume of water. The water may be potable water.

- 20 The cement slurry composition may comprise about 3% to about 15%, 3% to about 5%, about 3% to about 9%, about 3% to about 12%, about 5% to about 9%, about 5% to about 12%, about 5% to about 15%, about 9% to about 12%, about 9% to about 15% or about 9% to about 15% by volume of air. The cement slurry composition may comprise about 3 % to about 6 % by volume of air. The air may be naturally entrapped air.

- 25 The cement slurry composition may comprise an air entraining agent. The cement slurry composition may comprise about 5 % to about 15 % by volume of entrained air when an air entraining agent is used.

The air may be deliberately included in the cement slurry composition to entrain minute air bubbles to further reduce the unit weight of the slurry composition.

- 30 The total volume of the composition must add to 100% by volume.

There is provided a cement slurry composition comprising:

about 25 % to about 60 % by volume of cenospheres;

about 40 % to about 70 % by volume of a combination of water, a cementitious material and an additive;

- 35 about 3 % to about 15 % by volume of air;

wherein the total volume of the composition adds to 100%, and

wherein the cementitious material comprises about 30% to about 95% of hydraulic cement by weight of total cementitious material (BWTC) and about 5% to about 70% of pozzolan BWTC, and

- 5 the additive is present at an amount of about 0.1% to about 6 % BWTC,
 whereby the total weight of the cementitious material adds to 100%.

The cement slurry composition may comprise about 40 % to about 70%, about 40% to about 50%, about 40% to about 60%, about 50% to about 60%, about 50% to about 70% or about 60% to about 70% by volume of a combination of water, a cementitious material and an additive.

- 10 The cement slurry composition may comprise a hydraulic cement, microsilica, cenospheres, water, superplasticizer and a shrinkage-reducing agent in the amounts as specified above.

There is also provided a cement slurry composition comprising:

- about 12 % to about 40 % by weight of cenospheres;
 about 35 % to about 74 % by weight of a combination of a cementitious material and an
 15 additive;
 about 14 % to about 22% by weight of water;
 wherein the total weight of the composition adds to 100%, and
 wherein the cementitious material may comprise about 30% to about 95% of hydraulic
 cement by weight of total cementitious material (BWTC) and about 5% to about 70% of
 20 pozzolan BWTC, and
 the additive may be present at an amount of about 0.1% to about 6% BWTC,
 whereby the total weight of the cementitious material adds to 100%.

- The cement slurry composition may also comprise air, which, in combination with the weight%
 of the cenospheres, weight% of the combination of the cementitious material and the additive,
 25 and the weight% of the water, may add to 100% of the total weight of the composition.

The cement slurry composition may comprise the cenospheres in a range about 12 % to about 40 %, about 12% to about 20%, about 12% to about 30%, about 20% to about 30%, about 20% to about 40% or about 30% to about 40% by weight of the total weight of the composition.

- The cement slurry composition may comprise the combination of the cementitious material and
 30 the additive in a range of about 35% to about 50%, about 35% to about 74% or about 50% to
 about 74% by weight of the total weight of the composition.

The cement slurry composition may comprise the cementitious material in a range of about 35% to about 70%, about 35% to about 45%, about 35% to about 55%, about 45% to about 55%, about 45% to about 70%, or about 55% to about 70% by weight of the total weight of the composition.

5 The cement slurry composition may comprise water in a range of about 14 % to about 22%, about 14% to about 17%, about 14% to about 18%, about 17% to about 18%, about 17% to about 22% or about 18% to about 22% by weight of the total weight of the composition.

10 The cement slurry composition may have a short gel transition time (GTT) in the range of about 10 minutes to about 50 minutes, about 10 minutes to about 15 minutes, about 10 minutes to about 20 minutes, about 10 minutes to about 30 minutes, about 10 minutes to about 40 minutes, about 15 minutes to about 20 minutes, about 15 minutes to about 20 minutes, about 15 minutes to about 30 minutes, about 15 minutes to about 40 minutes, about 15 minutes to about 50 minutes, about 20 minutes to about 30 minutes, about 20 minutes to about 40 minutes, about 20 minutes to about 50 minutes, about 30 minutes to about 40 minutes, about 30 minutes to about 50 minutes or about 40 minutes to about 50 minutes.

15 The definition of 'gel transition time (GTT)' may be the time at which the cement slurry is no longer a liquid that is capable of transmitting hydrostatic pressure, but is also not yet solid, and able to bond and isolate the formation. When solidified, the solid cement mass may have a certain adhesion strength to the surrounding geological formation, which is known as the bond strength. This may create an effective seal to isolate the lower channel of flow from the upper channel.
20 During the transition time, the solid content in the cement slurry may become self-supported as a result of hydration (gelled structure), and the pressure in the remaining pores filled with water-like fluid become underbalanced, as formation pore pressure develops.

In this regard, the following parameters may need to be considered:

- 25 - Time period for a slurry to reach a gel strength value of 48 Pa (100lbf/100sq.ft), referred to as "zero gel time".
- Time period for a slurry to increase its gel strength from 48 Pa (100lb/100sq.ft) to 240 Pa (500lbf/100sq.ft), referred to as "transition time".

30 The gel strength value of 48 Pa may indicate the loss in hydrostatic pressure transmission. Consequently, for the zero gel time, it may be better if the period is longer. The gel strength value of 240 Pa may signify that the gas can no longer migrate in a slurry at such a high gel strength value. For transition time, it may be better if the period is shorter, as this time period for the gel strength to increase from 48 Pa to 240 Pa may be considered as critical for gas migration.

35 Static gel strength (SGS) may be measured using an analyser (Model # 15-400, CTE corp., USA) at a speed of 0.1825°/min (0.0005 rpm) using a stepper motor drive to measure torque on the paddle to derive the gel strength. Accordingly, GTT may be derived from a time difference from SGS 48 Pa to 240 Pa.

The cement slurry composition may have a right-angle set time in the range of about 10 minutes to about 70 minutes, about 10 minutes to about 15 minutes, about 10 minutes to about 30 minutes,

about 10 minutes to about 45 minutes, about 10 minutes to about 60 minutes, about 15 minutes to about 30 minutes, about 15 minutes to about 45 minutes, about 15 minutes to about 60 minutes, about 15 minutes to about 70 minutes, about 30 minutes to about 45 minutes, about 30 minutes to about 60 minutes, about 30 minutes to about 70 minutes, about 45 minutes to about 60 minutes, about 45 minutes to about 70 minutes or about 60 minutes to about 70 minutes.

“Right-angle set (RAS)” may refer to well-dispersed cement slurries which show no progressive gelation tendency, yet set very rapidly because of rapid hydration kinetics. Such systems may maintain full hydrostatic load on the gas zone up to the commencement of set, and develop a very low-permeability matrix with sufficient speed to prevent significant gas intrusion. The slurry may maintain a low consistency until setting, when the slurry viscosity may rapidly increase from the point of departure or increase from 30 B_c to 100 B_c in a short time. The term may refer to the characteristic 90-degree bend in a plot of cement consistency versus time.

Consistency and thickening time of the cement slurry may be measured using a fully automatic consistometer (Model # M22-400-Auto, CTE corp., USA) in accordance with procedures outlined in API RP 10B-2. The slurry cup may be rotated at 150 rpm $\pm$ 15 rpm and the torque, exerted on the paddle attachment, may be measured in B_c. The time taken to reach 30 B_c is commonly considered as the time available for pumping and placing a cement slurry in the wellbore. According to API RP 10B-2, thickening time may be defined as “time elapsed from the initial application of pressure and temperature to the time at which the slurry reaches a consistency deemed sufficient to make it unpumpable (eg. 100 B_c).” Accordingly, the right-angle set (RAS) property may be derived from the time difference to reach 100 B_c from 30 B_c.

Compressive strength may be calculated based on 50mm cubes of cement casted and tested in a uniaxial hydraulic compression test machine. Density may be measured using a OFI Testing Equipment mud balance.

The cement slurry composition may have a short GTT between 10 to 50 minutes and have a RAS time between 10 to 70 minutes.

The cement slurry composition may have a density in the range of about 1,000 kg/m³ to about 1,900kg/m³, about 1,000 kg/m³ to about 1,200kg/m³, about 1,000 kg/m³ to about 1,500kg/m³, about 1,000 kg/m³ to about 1,700kg/m³, about 1,200 kg/m³ to about 1,500kg/m³, about 1,200 kg/m³ to about 1,700kg/m³, about 1,200 kg/m³ to about 1,900kg/m³, about 1,500 kg/m³ to about 1,700kg/m³, about 1,500 kg/m³ to about 1,900kg/m³, or about 1,700 kg/m³ to about 1,900kg/m³.

There is also provided a method of preparing a cement slurry composition comprising the step of:

mixing about 25 % to about 60 % by volume of cenospheres with about 15 % to about 45% by volume of a combination of a cementitious material and an additive, about 20 % to about 35 % by volume of water and about 3 % to about 15 % by volume of air; such that the total volume adds to 100%, and

wherein the cementitious material may comprise about 30% to about 95% of hydraulic cement by weight of total cementitious material (BWTC) and about 5% to about 70% of pozzolan BWTC,

the additive may be present at an amount of about 0.1 % to about 6% BWTC, and

whereby the total weight of the cementitious material adds to 100%.

The cement slurry composition may be prepared by mixing the ingredients together. The mixing may be conducted in any suitable apparatus which may achieve adequate blending and dispersion of the ingredients in the shortest time, for example, a high shear cement mixer.

There is also provided a cement dry mix comprising:

about 14 % to about 45 % by weight of cenospheres; and

about 55 % to about 86 % by weight of a combination of a cementitious material and an additive;

wherein the total weight of the composition adds to 100%, and

wherein the cementitious material comprises about 30% to about 95% of hydraulic cement by weight of total cementitious material (BWTC) and about 5% to about 70% of pozzolan BWTC, and

the additive is present at an amount of about 0.1% to about 6% BWTC,

whereby the total weight of the cementitious material adds to 100%.

The cenospheres may be present in the dry mix at an amount in the range of about 14% to about 45%, about 14% to about 20%, about 14% to about 30%, about 20% to about 30%, about 20% to about 45% or about 30% to about 45% of the total weight of the composition.

The combination of the cementitious material and the additive may be present in the dry mix in an amount in the range of about 55% to about 86%, about 55% to about 65%, about 55% to about 75%, about 65% to about 75%, about 65% to about 86% or about 75% to about 86% of the total weight of the composition.

The cementitious material may be present in the dry mix at an amount in the range of about 60% to about 80% by weight, about 60% to about 65%, about 60% to about 70%, about 60% to about 75%, about 65% to about 70%, about 65% to about 75%, about 65% to about 80%, about 70% to about 75%, about 70% to about 80% or about 75% to about 70% of the total weight of the composition.

The dry mix may be stored in dry condition away from direct sunlight and protected from humidity until it is ready for use.

The cement slurry composition may be first prepared as a dry mix in the absence of water in a dry blending facility. Water may be added to the dry blend just prior to use, to form the cement slurry composition. Depending on the mixing efficiency of the mixer, the mixing time from water addition till completion of mixing may be in the range of about 4 minutes to about 12 minutes,

about 4 minutes to about 6 minutes, about 4 minutes to about 8 minutes, about 4 minutes to about 10 minutes, about 6 minutes to about 8 minutes, about 6 minutes to about 8 minutes, about 6 minutes to about 10 minutes, about 6 minutes to about 12 minutes, about 8 minutes to about 10 minutes, about 8 minutes to about 12 minutes, or about 10 minutes about 12 minutes.

- 5 The cement dry mix as defined above may form the cement slurry composition as defined above when mixed with water in the volumes as defined above.

Preparation of the cement dry mix may comprise pre-blending the cenospheres, cementitious material and additives together using a forced shearing mixer such as a benchtop N50 5-Quart Hobart mixer, paddle pan-mixer, shaft-mixer or planetary mixer. During the blending process, if
10 the mixer has multiple options for rotation speed, the lowest speed may be used. The rotation speed of the primary (main) mixer's arm / paddles about its central shaft during pre-blending may be in the range of 30 to 70, 30 to 40, 30 to 50, 30 to 60, 40 to 50, 40 to 60, 40 to 70, 50 to 60, 50 to 70 or 60 to 70 revolutions per minute (rpm).

15 Firstly, the cenospheres may be introduced into the mixer, followed by microsilica and/or nanosilica. If gypsum is being used, it may be added at this stage (Stage 1). Next, the remaining cementitious material (hydraulic cement and pozzolan) may be added into the mixer (Stage 2). Next, additives in solid dry powder form may be added into the mixer (Stage 3). The additive powders may be separately introduced into the mixer and may not be permitted to intermix with each other prior to introduction into the mixer. Finally, the
20 polymer liquid additive(s) may be added separately and consecutively into the mixer via a spray system, whereby the liquid polymer additives may be sprayed onto the contents of the mixer (Stage 4).

The liquid polymer additive may be selected from the group consisting of a shrinkage-reducing agent (SRA), viscosity modifying agent (VMA), fluid loss agent (FLA) and any
25 mixture thereof.

The spray system may comprise a spray bottle, or for commercial scale production, a pressurised piped spraying system such as a high-pressure nozzle.

The blending time after addition of each component may be in the range of about 0.5 minutes to about 6 minutes, about 0.5 minutes to about 1 minute, about 0.5 minutes to about 2 minutes,
30 about 0.5 minutes to about 4 minutes, about 1 minute to about 2 minutes, about 1 minute to about 4 minutes, about 1 minute to about 6 minutes, about 2 minutes to about 4 minutes, about 2 minutes to about 6 minutes or about 2 minutes to about 6 minutes.

For wet mixing, besides using the mixer types as defined above, a high-shear mixer with a higher rotation speed of up to 800 rpm may also be used. Water may be added to the cement
35 composite dry mix and mixed for a duration in the range of about 2 minutes to about 4 minutes, about 2 minutes to about 3 minutes or about 3 minutes to about 4 minutes. After this, the water-based liquid additives which had not been added during the dry-blending stage may be added and the mixture may be mixed for a further duration in the range of about 3

minutes to about 5 minutes, about 3 minutes to about 4 minutes or about 4 minutes to about 5 minutes.

Additives such as SP, AEA, retarder and set accelerating agent may be provided in the form of a water-based liquid or solid dry powder. If these additives are added to the composition in the form of a water-based liquid, then they may be added to the composition after water has been added to the composition during wet mixing. If, however, these additives are added to the composition in the form of a solid dry powder, then they may be added to the composition during the preparation of the dry mix, specifically at Stage 3, as defined above.

The mixing may be performed at ambient temperature in the range of about 10°C to about 40°C, about 10°C to about 20°C, about 10°C to about 30°C, about 20°C to about 30°C, about 20°C to about 30°C or about 30°C to about 40°C and at atmospheric pressure.

The cement slurry composition may be moulded or extruded into any shape, cast into thin or thick slabs, batts, panels, pavers, bricks and tiles, trowel applied as insulative renders, plasters or thin protective and decorative coat for many types of structures.

There is also provided a set or hardened cement obtained from the cement slurry composition as defined above.

The set or hardened cement may be formed by allowing the cement slurry composition to hydrate in the presence of water, which may result in the formation of calcium silicate hydrate, calcium hydroxide, calcium aluminate hydrate and/or ettringite. During setting or hardening of cement, the hydration products may form after a certain length of time known as the setting time, causing the cement to set or harden. The set or hardened cement may form from the cement slurry composition after a period of about 6 hours to about 24 hours, about 6 hours to about 12 hours, about 6 hours to about 18 hours, or about 12 hours to about 18 hours, about 12 hours to about 24 hours, about 18 hours to about 24 hours after the formation of the cement slurry composition.

The set or hardened cement may have a density in the range of about 1,000 kg/m³ to about 1,900kg/m³, about 1,000 kg/m³ to about 1,200kg/m³, about 1,000 kg/m³ to about 1,500kg/m³, about 1,000 kg/m³ to about 1,700kg/m³, about 1,200 kg/m³ to about 1,500kg/m³, about 1,200 kg/m³ to about 1,700kg/m³, about 1,200 kg/m³ to about 1,900kg/m³, about 1,500 kg/m³ to about 1,700kg/m³, about 1,500 kg/m³ to about 1,900kg/m³, or about 1,700 kg/m³ to about 1,900kg/m³.

The density of the cement slurry composition may be similar to the density of the set or hardened cement.

The set or hardened cement may have a compressive strength in the range of about 15 MPa to about 90 MPa, about 15 MPa to about 20 MPa, about 15 MPa to about 25 MPa, about 15 MPa to about 50 MPa, about 15 MPa to about 70 MPa, about 20 MPa to about 25 MPa, about 20 MPa to about 50 MPa, about 20 MPa to about 70 MPa, about 20 MPa to about 90 MPa, about 25 MPa to about 50 MPa, about 25 MPa to about 70 MPa, about 25 MPa to about 90 MPa, about 50 MPa to about 70 MPa, about 50 MPa to about 90 MPa or about 70 MPa to about 90 MPa.

There is also provided the use of a cement slurry composition as defined above in cementing or plugging oil and gas wells and in civil construction and architecture.

Cementing and plugging may be two applications that may have different objectives, whereby cementing may be related to securing and strengthening of steel casings either to the formations or to each other in a string of casings with different diameters set into each other, whereas plugging may be related to abandonment of wells such that the left-in-place steel casings may be sealed permanently. The similarity between the two applications may lie in the fact that both cementing and plugging may require a tight-fitting material to provide an effective barrier to prevent leakage of oil and gas into unintended areas.

10 **Examples**

Non-limiting examples of the invention will be further described in greater detail by reference to specific Examples, which should not be construed as in any way limiting the scope of the invention.

Methods And Materials

15 Density was measured using a OFI Testing Equipment mud balance.

Static gel strength (SGS) was measured using an analyser (Model # 15-400, CTE corp., USA) at a speed of 0.1825°/min (0.0005 rpm) using a stepper motor drive to measure torque on the paddle to derive the gel strength. Accordingly, GTT was derived from a time difference from SGS 48 Pa to 240 Pa.

20 Consistency and thickening time of the cement slurry was measured using a fully automatic consistometer (Model # M22-400-Auto, CTE corp., USA) in accordance with procedures outlined in API RP 10B-2. The slurry cup was rotated at 150 rpm $\pm$ 15 rpm and the torque, exerted on the paddle attachment, was measured in B_c. The time taken to reach 30 B_c is commonly considered as the time available for pumping and placing a cement slurry in the wellbore. According to API
25 RP 10B-2, thickening time may be defined as “time elapsed from the initial application of pressure and temperature to the time at which the slurry reaches a consistency deemed sufficient to make it unpumpable (eg. 100 B_c).” Accordingly, the right-angle set (RAS) property was derived from the time difference to reach 100 B_c from 30 B_c.

30 Compressive strength was measured based on 50mm cubes of cement casted and tested in a uniaxial hydraulic compression test machine.

Example 1: General Method For Preparation of The Composition

To prepare the cement slurry composition, a cement composite dry mix was first prepared by pre-blending the cenospheres, cementitious material and additives together using a forced shearing mixer at ambient temperature between 10°C to 40°C and at atmospheric pressure.

During the dry blending process, where the mixer has multiple options for rotation speed, the lowest speed was always used. The rotation speed of the primary (main) mixer's arm / paddles about its central shaft used for pre-blending was within the range of 30-70 revolutions per minute (rpm).

- 5 The cenospheres were introduced first into the mixer, followed by microsilica and/or nanosilica. If gypsum was being used, was also added at this stage (Stage 1). The premix was dry-blended in the mixer for about 0.5 to 1 minute. Next, the remaining cementitious material (hydraulic cement and pozzolan) were added into the mixer and blended for 0.5 to 1 minute (Stage 2). Next, additives in powder form were added into the mixer and blended for 0.5 to 10 1 minute (Stage 3). The additive powders were separately introduced into the mixer and were not permitted to intermix with each other prior to introduction into the mixer. The blending time did not include the time of adding the materials into the mixer. Finally, the liquid polymer additive(s) such as the shrinkage-reducing agent (SRA), viscosity modifying agent (VMA) and fluid loss agent (FLA), if used, were added separately and consecutively into the 15 mixer via a spray system, whereby the liquid polymer additive(s) were sprayed onto the contents of the mixer using a spray bottle (Stage 4).

Depending on the amount of liquid additive and spray rate, the time taken for mixing was between 1 to 4 minutes. The final mixture was mixed for another 1 minute. The cement composite dry mix was then ready. The dry mix was stored in dry condition away from direct 20 sunlight and protected from humidity until it was ready for wet mixing.

For wet mixing, besides using similar mixer types as stated above, a high-shear mixer with higher rotation speed of up to 800 rpm may also be used. Water was added to the cement composite dry mix and mixed for 2 to 4 minutes. After this, the water-based liquid additive which had not been added during the dry-blending stage was added and the mixture was 25 mixed for a further 4 minutes. The cement slurry was ready for use after this.

Example 2: Composition and Properties of the Cenospheres

Table 1 below describes the typical chemical composition of the cenospheres used in the present invention.

Table 1. Typical chemical composition of cenospheres

Chemical name	Typical value (by weight)
SiO ₂	53 - 61%
Al ₂ O ₃	26 - 41%
Fe ₂ O ₃	0.5 – 10%
CaO	0.2 - 1.1%
TiO ₂	0.23 - 1.05%
MgO	0.1 – 3.5%
K ₂ O	0.01 – 3.5%

Na ₂ O	0.01 – 1.0%
loss on ignition	0.01 – 2.0%

Table 2 below describes the physical properties of the cenospheres used in the present invention.

Table 2. Physical Properties of cenospheres

particle density g/cm³	0.4 - 0.9
density g/cm³	0.2 – 0.5
crush strength MPa	10 - 50
Size microns	30 - 600
thermal conductivity W/mK	0.08 – 1.10
oil absorption g/cm³	0.5 – 1.0
hardness Moh's scale	6
pH Value	6-8
melting point	1300 - 1600 °C
colour	gray
appearance	free flowing powder

5 Example 3: Composition A

Table 3 below describes the components and properties of an example of a cement composition prepared according to the present invention to give a one cubic metre volume of a cement slurry composition.

The ingredients for Composition A were blended in the following sequence:

- 10 Cenospheres under the tradename of QK300 supplied by Spheretek Ltd. (Hebei, China) was added into a mixer, followed by microsilica Elkem Microsilica® 940U supplied by Elkem (Oslo, Norway) and gypsum powder supplied by Laira (Selangor, Malaysia). After mixing for 0.5 minutes, cement API Class G supplied by CAG Asia Ltd. (Kuala Lumpur, Malaysia), fly ash Invicrete 83 supplied by Invicon Fly Ash Pvt. Ltd. (Andhra Pradesh, India), and CSA cement
- 15 from Denka Co. Ltd (Tokyo, Japan). were added and mixed for 0.5 minutes. After that, glycol ether Eclipse Floor supplied by W.R. Grace Ltd. (Warrington, England) was sprayed into the mixer and mixed for 1 more minute. Finally, water was added to the mixture and mixed for 2 minutes before polycarboxylate ether (PCE) ADVA181 supplied by W.R. Grace (S) Pte. Ltd. (Singapore) was added and mixed for a further 6 minutes to yield the final cement slurry.

Table 3. Component and properties of composition A

	Mass (kg) per cubic metre	Percent by weight of total cementitious content (BWTC)	Percent by volume of composite
Water	250	32.5% BWTC	25%
Cement API Class G	460	59% BWTC	30%
Microsilica	38	5% BWTC	
Fly ash	270	34% BWTC	
CSA	15	2% BWTC	
Gypsum	8	1.0% BWTC	
PCE	4	0.5% BWTC	
Glycol ether	20	2.6% BWTC	
Cenospheres	325		40%
Density = 1,400 kg/m ³ (11.7 ppg)			
GTT = 22.0 min			
RAS = 31.0 min			
Compressive strength, 3-day = 25 MPa (3625 psi)			
Compressive strength, 28-day = 50 MPa (7250 psi)			

Example 4: Composition B

Table 4 below describes the components and properties of an example of a cement composition prepared according to the present invention to give a one cubic metre volume of a cement slurry composition.

The ingredients for Composition B were blended in the following sequence:

Cenospheres under the tradename of QK300 supplied by Spheretek Ltd. (Hebei, China) was added into a mixer, followed by microsilica Elkem Microsilica® 940U supplied by Elkem (Oslo, Norway) and gypsum powder supplied by Laira (Selangor, Malaysia). After mixing for 0.5 minutes, cement ASTM Type II supplied by Asia Cement Corporation (Taipei, Taiwan), fly ash Invicrete 83 supplied by Invicon Fly Ash Pvt. Ltd. (Andhra Pradesh, India), and CSA cement from Denka Co. Ltd. (Tokyo, Japan) were added and mixed for 0.5 minutes. Powdered sulphonated naphthalene formaldehyde (SNF) Selflow110P supplied by MegaChem Ltd. (Singapore) and powdered retarder Targon-32 supplied by BK Giuliani GmbH (Ladenburg, Baden-Württemberg, Germany) were then added and mixed for 1 minute. Finally, glycol ether Eclipse Floor supplied by W.R. Grace Ltd. (Warrington, England) was sprayed into the mixer and mixed for 1 more minute. Finally, water was added to the mixture and mixed for 8 minutes to yield the final cement slurry.

Table 4. Component and properties of composition B

	Mass (kg) per cubic metre	Percent by weight of total cementitious content (BWTC)	Percent by volume of composite
Water	285	28.5% BWTC	28%
Cement ASTM Type II	840	78% BWTC	37%
Microsilica	32	3% BWTC	
Fly ash	166	16% BWTC	
CSA	36	3% BWTC	
Gypsum	16	1.5% BWTC	
SNF	24	2.2% BWTC	
Retarder	3	0.3% BWTC	
Glycol ether	10	0.9% BWTC	
Cenospheres	260		30%
Density = 1,680 kg/m ³ (14.0 ppg)			
GTT = 29.5 min			
RAS = 25.5 min			
Compressive strength, 3-day = 40 MPa (5800 psi)			
Compressive strength, 28-day = 80 MPa (11600 psi)			

Example 5: Composition C

Table 5 below describes the components and properties of an example of a cement composition prepared according to the present invention to give a one cubic metre volume of a cement slurry composition.

The ingredients for Composition C were blended in the following sequence:

Cenospheres under the tradename of CIL-30 supplied by Cenosphere India Pvt. Ltd. (Kolkata, India) was added into a mixer, followed by microsilica Elkem Microsilica® 940U supplied by Elkem (Oslo, Norway) and gypsum powder supplied by Laira (Selangor, Malaysia). After mixing for 0.5 minutes, cement ASTM Type V (HSR) supplied by Lafarge Cement Sdn. Bhd. (Johor, Malaysia), and CSA cement from Denka Co. Ltd. (Tokyo, Japan) were added and mixed for 0.5 minutes. Powdered sulphonated melamine formaldehyde (SMF) Melment F10 supplied by BASF (Ludwigshafen, Germany) and powdered retarder Targon-32 supplied by BK Giulini GmbH (Ladenburg, Baden-Württemberg, Germany) were then added and mixed for 1 minute. Finally, glycol ether Eclipse Floor supplied by W.R. Grace Ltd. (Warrington, England) was sprayed into the mixer and mixed for 1 more minute. Finally, water was added to the mixture and mixed for 5 minutes before AEA Darex AE4 supplied by W.R. Grace Ltd. (Warrington, England) was added and mixed for a further 3 minutes to yield the final cement slurry.

Table 5. Component and properties of composition C

	Mass (kg) per cubic metre	Percent by weight of total cementitious content (BTWC)	Percent by volume of composite
Water	220	40% BWTC	22%
Cement ASTM Type V	519	91% BWTC	19%
Microsilica	33	6% BWTC	
CSA	19	3% BWTC	
AEA	1	0.2% BWTC	
Gypsum	8	1.4% BWTC	
SMF	5	0.9% BWTC	
Retarder	3	0.5% BWTC	
Glycol ether	3	0.5% BWTC	
Cenospheres	420		49%
Density = 1,200 kg/m ³ (10.0 ppg)			
GTT = 31.5 min			
RAS = 17.0 min			
Compressive strength, 3-day = 7 MPa (1015 psi)			
Compressive strength, 28-day = 20 MPa (2900 psi)			

Industrial Applicability

The cement slurry composition according to the current invention may be used in either cementing or plugging oil and gas wells. The cement slurry composition may also be used in civil engineering applications where high strength-to-weight ratio, sound and thermal insulation properties are desired. For example, to form construction products such as architectural building components, infrastructure, bridges and buildings and highway noise abatement panels or other sound deadening and thermally insulating construction materials, concrete furniture or art objects. It may also be used as a replacement for fibreglass and other reinforced plastic composite products or as an ambient temperature hardened replacement for baked clay pottery and other ceramic products.

It will be apparent that various other modifications and adaptations of the invention will be apparent to the person skilled in the art after reading the foregoing disclosure without departing from the spirit and scope of the invention and it is intended that all such modifications and adaptations come within the scope of the appended claims.

Claims

1. A cement slurry composition comprising:
 - 25% to 60% by volume of cenospheres;
 - 15% to 45% by volume of a combination of a cementitious material and an additive;
- 5 20% to 35% by volume of water: and
 - 3% to 15% by volume of air;

wherein the total volume of the composition adds to 100%, and

wherein the cementitious material comprises 30% to 95% of hydraulic cement by weight of total cementitious material (BWTC) and 5% to 70% of pozzolan BWTC,
- 10 the additive is present at an amount of 0.1% to 6% BWTC,

whereby the total weight of the cementitious material adds to 100%.
2. The cement slurry composition according to claim 1, wherein the cenospheres have a bulk density ranging from 0.1 g/cm³ to 0.7 g/cm³, a particle density ranging from 0.2 g/cm³ to 1.2 g/cm³, a particle diameter ranging from 20 μm to 800 μm and/or a crushing strength ranging

15 from 8 MPa to 60 MPa.
3. The cement slurry composition according to claim 1 or 2, wherein the cenospheres comprise a compound selected from the group consisting of SiO₂, Al₂O₃, Fe₂O₃, CaO, TiO₂, MgO, K₂O, Na₂O, and any mixture thereof.
4. The cement slurry composition according to any one of the preceding claims, wherein the

20 hydraulic cement is Portland cement and/or a calcium sulfonate (CSA) cement, or a cement selected from the group consisting of ASTM Types I, II, and V cements, API Classes A, B, G or H cements, EN CEM I, II, III, IV or V cements, CSA cement and any mixture thereof.
5. The cement slurry composition according to any one of the preceding claims, wherein the

25 pozzolan is natural or artificial, or is selected from the group consisting of microsilica, nanosilica, pulverized fly ash, ground-granulated blast furnace slag (GGBS), metakaolin, and any mixture thereof.
6. The cement slurry composition according to claim 5, wherein the pozzolan is microsilica, and is present in the composition at an amount of 1% to 12% by weight of total cementitious material (BWTC).
- 30 7. The cement slurry composition according to claim 5, wherein the pozzolan is nanosilica, and is present in the composition at an amount of 0% to 2% by weight of total cementitious

material (BWTC), or the pozzolan is pulverized fly ash, and is present in the composition at an amount of 0% to 55% BWTC, or the pozzolan is ground-granulated blast furnace slag (GGBS) and is present in the composition at an amount of 0% to 70% BWTC, or the pozzolan is metakaolin, and is present in the composition at an amount of 0% to 15% BWTC.

- 5 8. The cement slurry composition according to any one of the preceding claims, wherein the additive is selected from the group consisting of a superplasticizer (SP), shrinkage-reducing agent (SRA), gypsum, air entraining agent (AEA), set retarding agent (retarder), set accelerating agent, viscosity modifying agent (VMA), fluid loss agent (FLA), and any mixture thereof.
- 10 9. The cement slurry composition according to claim 8, wherein the additive is superplasticizer (SP) and is present in the composition at an amount of 0.1% to 4% by weight of total cementitious material (BWTC), wherein the SP is added to the composition in the form of an aqueous solution or a water-based liquid, or as a dry-spray powder.
- 15 10. The cement slurry composition according to claim 8, wherein the additive is a shrinkage-reducing agent (SRA), and is present in the composition at an amount of 0.05% to 5% by weight of total cementitious material (BWTC), wherein SRA is added to the composition in the form of a liquid or solid dry powder.
- 20 11. The cement slurry composition according to claim 8, wherein the additive is gypsum, and is present in the composition at an amount of 0% to 3% by weight of total cementitious material (BWTC).
- 25 12. The cement slurry composition according to claim 8, wherein the additive is air entraining agent (AEA) and is present in the composition at an amount of 0 % to 1% by weight of total cementitious material (BWTC); or the additive is set retarding agent (retarder) and is present in the composition at an amount of 0% to 3% BWTC; or the additive is set accelerating agent and is present in the composition at an amount of 0% to 1% BWTC; or the additive is viscosity modifying agent (VMA) and is present in the composition at an amount of 0% to 5% BWTC; or the additive is fluid loss agent (FLA) and is present in the composition at an amount of 0% to 1% BWTC.
- 30 13. A method of preparing a cement slurry composition according to any one of the preceding claims, comprising the step of:

mixing 25 % to 60 % by volume of cenospheres with 15% to 45% by volume of a combination of a cementitious material and an additive; 20% to 35% by volume of water and 3% to 15% by volume of air; such that the total volume adds to 100%, and

wherein the cementitious material comprises 30% to 95% of hydraulic cement by weight of total cementitious material (BWTC) and 5% to 70% of pozzolan BWTC,

the additive is present at an amount of 0.1% to 6% BWTC, and
- 35

whereby the total weight of the cementitious material adds to 100%.

14. A cement dry mix comprising:

14% to 45% by weight of cenospheres; and

55% to 86% by weight of a combination of a cementitious material and an additive;

5 wherein the total weight of the composition adds to 100%, and

wherein the cementitious material comprises 30% to 95% of hydraulic cement by weight of total cementitious material (BWTC) and 5% to 70% of pozzolan BWTC, and

the additive is present at an amount of 0.1% to 6% BWTC,

whereby the total weight of the cementitious material adds to 100%.

10 15. A set or hardened cement obtained from the cement slurry composition according to any one of claims 1 to 12.

16. The set or hardened cement of claim 15, wherein the composition has a density in the range of 1,000 kg/m³ to 1,900kg/m³, or has a compressive strength in the range of 15 MPa to 90 MPa.

15 17. The use of a cement slurry composition according to any one of claims 1 to 12 in cementing or plugging oil and gas wells and in civil construction and architecture.