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(19) **United States**(12) **Patent Application Publication** (10) **Pub. No.: US 2004/0171499 A1****Ravi et al.**(43) **Pub. Date:****Sep. 2, 2004**(54) **CEMENT COMPOSITIONS WITH
IMPROVED MECHANICAL PROPERTIES
AND METHODS OF CEMENTING IN A
SUBTERRANEAN FORMATION****Publication Classification**(51) **Int. Cl.⁷ E21B 43/00**(52) **U.S. Cl. 507/200**(75) **Inventors: Krishna M. Ravi, Kingwood, TX (US);
B. Raghava Reddy, Duncan, OK (US)**(57) **ABSTRACT**

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VICES, INC., DUNCAN, OK**(21) **Appl. No.: 10/745,470**(22) **Filed: Dec. 22, 2003****Related U.S. Application Data**(63) **Continuation-in-part of application No. 10/350,533,
filed on Jan. 24, 2003.**

The present invention relates to subterranean cementing operations, and more particularly, to cement compositions comprising elastic particles and having improved mechanical properties, and methods of using such compositions in subterranean cementing operations. An example of a method of the present invention comprises the steps of: providing a cement composition comprising a base fluid, a hydraulic cement, and a portion of elastic particles; placing the cement composition in a well bore in a subterranean formation; permitting a portion of the cement composition to enter openings in a region of the subterranean formation in fluid communication with the well bore; and permitting the portion of the cement composition to seal the openings off from the well bore. Another example of a method of the present invention comprises the step of adding a portion of elastic particles to a cement composition.

CEMENT COMPOSITIONS WITH IMPROVED MECHANICAL PROPERTIES AND METHODS OF CEMENTING IN A SUBTERRANEAN FORMATION

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application is a continuation-in-part of U.S. patent application Ser. No. 10/350,533 entitled, "Cement Compositions Containing Elastic Particles and Methods of Cementing in Subterranean Formations," filed Jan. 24, 2003, incorporated by reference herein for all purposes, and from which priority is claimed pursuant to 35 U.S.C. §120.

BACKGROUND OF THE INVENTION

[0002] The present invention relates to subterranean cementing operations, and more particularly, to cement compositions comprising elastic particles and having improved mechanical properties, and methods of using such compositions in subterranean cementing operations.

[0003] Hydraulic cement compositions are commonly utilized in subterranean operations, particularly subterranean well completion and remedial operations. For example, hydraulic cement compositions are used in primary cementing operations whereby pipe strings such as casings and liners are cemented in well bores. In performing primary cementing, hydraulic cement compositions are pumped into the annular space between the walls of a well bore and the exterior surface of the pipe string disposed therein. The cement composition is permitted to set in the annular space, thereby forming an annular sheath of hardened substantially impermeable cement therein that substantially supports and positions the pipe string in the well bore and bonds the exterior surfaces of the pipe string to the walls of the well bore. Hydraulic cement 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.

[0004] Subterranean formations transversed by well bores are often weak and extensively fractured. In some cases, the formation may be unable to withstand the hydrostatic head pressure normally associated with cement being pumped in the formation. In such cases, the hydrostatic pressure may be sufficient to force cement into the extensive fractures of the formation, which may result in a significant loss of cement into the formation during cementing operations. This problem of losing fluid into a subterranean formation due to the hydrostatic pressure exerted by the fluid is commonly referred to as "lost circulation." This loss of cement composition is problematic because less cement composition will remain in the annular space to form the protective sheath that bonds the pipe string to the walls of the well bore. Accordingly, the loss of cement composition is of great concern. Resolution of this concern may call for reducing the density of the cement, inter alia, to reduce the hydrostatic pressure applied to the formation.

[0005] A traditional means of reducing the density of the cement composition has been to increase the cement composition's water content, because, generally speaking, the higher the water content, the less dense the cement composition. However, this method may be problematic because the resultant cement composition often requires extensive cure time and lacks the desired strength and mechanical properties.

[0006] As an alternative means of reducing the density of cement compositions, lightweight spherical or substantially spherical particulates have been added to such compositions. Some lightweight spherical or substantially spherical particulates include hollow spheres, which are typically cenospheres, glass hollow spheres, or ceramic hollow spheres. Cenospheres are hollow spheres primarily made from silica (SiO_2) and/or alumina (Al_2O_3), and are filled with gas. These are a naturally occurring by-product of the burning process of a coal-fired power plant. Conventional glass hollow spheres and ceramic hollow spheres reduce the density of the cement composition such that less water is required to form the cement composition. As a result, the curing time of the cement composition is reduced. However, conventional hollow spheres are by nature brittle and fragile, and thus the cement containing the spheres often cannot endure the repeated detrimental stresses that the set cement may encounter in a subterranean well bore during the life of a well. Often, the cement lacks sufficient elasticity to elastically deform, resulting in cracking and breaking of the cement when it is forced to deform under pressure. As a result, failure rates of cement compositions containing microspheres is particularly problematic.

[0007] Cement failure may also be caused by the phenomenon of hydration volume reduction of the cement composition during the curing process. Hydraulic cement compositions typically demonstrate a decrease in volume as the cement composition develops compressive strength and sets. This shrinkage may adversely impact the set cement through the formation of cracks and other imperfections that may occur in the set cement. For instance, any cracks may provide a path for subterranean fluids to penetrate and weaken the cement sheath, and ultimately attack the casing of the well bore, potentially causing the casing to fail during the life of the well. Premature casing failure can result in, inter alia, costly repairs, lost production, and complete loss of the well under certain circumstances.

[0008] In some cases, the problem of hydration volume reduction has been addressed through the use of particulate expanding additives. When added to the cement slurry, these expanding additives react with the slurry to produce a gas. The volume of the slurry is increased by the generation of this gas, which compensates for hydration volume reduction. The use of expanding additives to compensate for hydration volume reduction may necessitate testing to optimize the cement composition. Furthermore, the particulate nature of these expanding additives may necessitate the incorporation of additional procedures. Thus, the existing methods of resolving the dilemma of hydration volume reduction during the curing process are challenging. Failure to properly resolve this dilemma may lead to the increased probability of failure of the set cement in the well bore, which may result in, inter alia, radial or circumferential cracking of the set cement as well as a breakdown of the bonds between the set cement and the pipe or between the cement sheath and the surrounding subterranean formation. Such failures can result in at least lost production, environmental pollution, hazardous rig operations, and/or hazardous production operations. A common undesirable result is the presence of pressure at the well head in the form of trapped gas between casing strings.

[0009] To successfully meet the subterranean challenges that a cement composition may encounter, a cement com-

position should develop high bond strength after setting, and also should have sufficient mechanical properties including elasticity, flexibility, compressibility, and ductility to resist loss of pipe or formation bonding, cracking, and/or shattering as a result of all of the stressful conditions that may plague the well, including impacts and/or shocks generated by drilling and other well operations.

SUMMARY OF THE INVENTION

[0010] The present invention relates to subterranean cementing operations, and more particularly, to cement compositions comprising elastic particles and having improved mechanical properties, and methods of using such compositions in subterranean cementing operations.

[0011] An example of a method of the present invention is a method of avoiding the loss of circulation of a cement composition in a subterranean formation, comprising the steps of: providing a cement composition comprising a base fluid, a hydraulic cement, and a portion of elastic particles; placing the cement composition in a well bore in a subterranean formation; permitting a portion of the cement composition to enter openings in a region of the subterranean formation in fluid communication with the well bore; and permitting the portion of the cement composition to seal the openings off from the well bore.

[0012] Another example of a method of the present invention is a method of improving the ability of a cement composition to resist the loss of circulation, comprising the step of adding to the cement composition a portion of elastic particles.

[0013] The features and advantages of the present invention will be readily apparent to those skilled in the art upon a reading of the description of the preferred embodiments that follows.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

[0014] The present invention relates to subterranean cementing operations, and more particularly, to cement compositions comprising elastic particles and having improved mechanical properties, and methods of using such compositions in subterranean cementing operations. While the methods of the present invention are useful in a variety of subterranean applications, they are particularly useful in well completion and remedial operations, including primary cementing, e.g., cementing casings and liners in well bores, including those in multi-lateral subterranean wells.

[0015] The cement compositions useful with the methods of the present invention generally comprise a hydraulic cement, a portion of elastic particles, and a base fluid. Other additives suitable for use in conjunction with subterranean cementing operations also may be added to these cement compositions if desired. In certain embodiments, the cement compositions useful with the present invention have a density in the range of from about 6 lb/gallon to about 22 lb/gallon. In certain preferred embodiments, the density is in the range of from about 8 lb/gallon to about 18 lb/gallon.

[0016] Any known cement may be utilized in the cement compositions used with the present invention, including hydraulic cements composed of calcium, aluminum, silicon, oxygen, and/or sulfur, which set and harden by reaction with

water. Examples of suitable hydraulic cements are Portland cements, pozzolanic cements, gypsum cements, high alumina content cements, silica cements, and high alkalinity cements.

[0017] The base fluid may be aqueous-based, nonaqueous-based, or a mixture thereof. Where the base fluid is aqueous-based, it may comprise fresh water, salt water (e.g., water containing one or more salts dissolved therein), brine (e.g., saturated salt water), or seawater. Generally, the water can be from any source provided that it does not contain an excess of compounds that may adversely affect other components in the cement composition. Where the base fluid is nonaqueous-based, the base fluid may comprise any number of organic liquids. Examples of suitable organic liquids include, but are not limited to, mineral oils, synthetic oils, esters, and the like. Generally, any organic liquid in which a water solution of salts can be emulsified is suitable for use as a base fluid in the cement compositions used with the present invention. The base fluid may be present in an amount sufficient to form a pumpable slurry. More particularly, in certain embodiments the base fluid is present in the cement compositions in an amount in the range of from about 25% to about 150% by weight of cement ("bwoc"). In certain preferred embodiments, the base fluid is present in the cement compositions in the range of from about 30% to about 75% bwoc.

[0018] The cement compositions useful with the methods of the present invention further comprise a portion of elastic particles. As referred to herein, the term "elastic" will be understood to mean the tendency for a particle to deform or compress under an applied force, and then re-expand as the force is removed, without substantial adverse effect to the structure of the particle. Any elastic particle that is compatible with a cement (e.g., that is relatively chemically stable over time upon incorporation into the cement) and that is substantially impermeable to the fluids typically encountered during cementing operations may be suitable for use with the cement compositions used in the present invention. In certain exemplary embodiments, the elastic particles have a specific gravity in the range of at least about 0.05. In certain preferred embodiments, the elastic particles have a specific gravity in the range of from about 0.3 to about 0.99. Further, the elastic particles will also have an isothermal compressibility factor. As referred to herein, the term "isothermal compressibility factor" will be understood to mean a particle's change in volume with pressure per unit volume of the particle while temperature is held constant. Any elastic particle having an isothermal compressibility factor in the range of from about 1.5×10^{-3} (1/psi) to about 1.5×10^{-9} (1/psi) may be suitable for use with the present invention. Generally, the elastic particles are present in the cement compositions useful with the present invention in an amount sufficient to provide a cement composition having a desired density and desired mechanical properties such as, inter alia, a desired Young's modulus and tensile strength. More particularly, the elastic particles may be present in the cement compositions in an amount in the range of from about 1% to about 200% bwoc. In certain exemplary embodiments, the elastic particles are present in the cement composition in an amount in the range of from about 5% to about 100% bwoc. In certain exemplary embodiments, the elastic particles are present in the cement composition in an amount in the range of from about 5% to about 10% bwoc.

[0019] In certain embodiments, the elastic particles will further comprise an internal fluid. Where the elastic particles comprise an internal fluid, the internal fluid may become incorporated within the elastic particles, so that the elastic particle forms a boundary around the fluid, by any suitable means. For example, the internal fluid may be injected into the elastic particle. As another example, the internal fluid may become incorporated within the elastic particle as a natural consequence of the process of manufacturing the elastic particle. One of ordinary skill in the art with the benefit of this disclosure will recognize an appropriate means by which the internal fluid may become incorporated within the elastic particle. The incorporation of an internal fluid within the elastic particles, inter alia, permits adjustment of the density of the elastic particles by pre-expanding them to a desired density. In certain embodiments, the elastic particles comprising the internal fluid may be thermally pre-expanded. In certain embodiments, the elastic particles may be pre-expanded up to about 40 times their original volume before being added to the cement composition. The internal fluid within the elastic particles may comprise air, nitrogen, carbon dioxide, butane, fluorinated hydrocarbons, hydrochlorofluorocarbons, or the like. The preceding list is not intended to be an exhaustive list, but rather is intended merely to provide an illustration of some types of fluids that may be suitable for use as internal fluids in accordance with the present invention. Other fluids may also be suitable for use as internal fluids, and one of ordinary skill in the art with the benefit of this disclosure will be able to identify an appropriate internal fluid for a particular application.

[0020] Generally, the elastic particles may be configured in any shape. The elastic particles may generally be of any size sufficient to permit the particle to behave elastically. In certain exemplary embodiments, the elastic particles are spherical or substantially spherical in shape. In certain exemplary embodiments, the elastic particles have a substantially spherical shape and a diameter of at least 1 micrometer when measured at about 25° C. and about atmospheric pressure. For example, in one exemplary embodiment, the elastic particles have a substantially spherical shape and a diameter of about 3,000 micrometers when measured at about 25° C. and about atmospheric pressure. In another exemplary embodiment, the elastic particles have a substantially spherical shape and a diameter in the range of from about 2 to about 150 micrometers when, measured at about 25° C. and about atmospheric pressure. An example of a suitable elastic particle comprises a polymer that, over the range of temperatures and pressures encountered in the well bore, changes volume by expansion and contraction, and consequently may impart desired mechanical properties to the cement composition. Suitable polymers may include those that possess sufficient rubbery and elastic characteristics to allow the elastic particles to respond to changes in volume of the fluid within the elastic particles at temperatures and pressures commonly encountered in the well bore. In certain exemplary embodiments of the present invention, the elastic particles comprise a copolymer of styrene and divinylbenzene. Another example of suitable elastic particles comprises either a copolymer of styrene and acrylonitrile or a terpolymer of styrene, acrylonitrile, and vinylidene chloride, and a fluid, such as isobutane or the like. Such particles are commercially available under the trade name "EXPANCEL" from Akzo Nobel, Inc., of Duluth, Ga. Several grades of EXPANCEL elastic particles with differ-

ent polymer-softening temperatures, allowing for expansion and contraction at different temperature ranges, are available. Depending on the conditions of the subterranean well bore in which the elastic particles may be placed, a particular grade of EXPANCEL elastic particles may be suitable.

[0021] The substantial impermeability of the elastic particles to the fluids typically encountered during cementing operations (e.g., to a fluid in the cement composition or in the subterranean formation) may also be achieved by appropriately encapsulating or coating a prefabricated elastic particle with appropriate materials. For example, an elastic particle intended for use, inter alia, in a nonaqueous-based cement composition, may be coated or encapsulated with a hydrophilic material. An elastic particle intended for use in an aqueous-based cement composition may be coated or encapsulated with a hydrophobic material. Examples of suitable hydrophobic materials include, inter alia, silanes, silicone polymers, latexes, and the like. Examples of suitable hydrophilic materials include, inter alia, ethylene oxide, propylene oxide, acrylic acid, 2-acrylamido-2-methylpropane sulfonic acid, aminoalkoxysilanes, and the like. The preceding lists are not intended to be exhaustive lists, but rather are intended merely to provide an illustration of some types of materials that may be suitable for use in accordance with the present invention. Other materials may also be suitable, and one of ordinary skill in the art with the benefit of this disclosure will be able to identify an appropriate material for a particular application.

[0022] Optionally, certain exemplary embodiments of the elastic particles may be expanded before mixing with the cement by heating the elastic particles, thereby increasing the pressure of the fluid therein. In determining whether or not to heat a particular elastic particle, the benefit from expanding the elastic particle may be weighed against the cost in terms of manpower and energy to achieve such expansion. Further, while expansion by heating may be suitable for certain embodiments of the elastic particles (e.g., the EXPANCEL particles), other embodiments of the elastic particles may be susceptible to thermal degradation from such heating. One of ordinary skill in the art, with the benefit of this disclosure, will be able to determine whether expansion by heating is appropriate for a particular type of elastic particle. The expansion of the elastic particles generally may be measured by a corresponding reduction in the specific gravity of the expanded elastic particle. In certain exemplary embodiments, the elastic particles are capable of expanding up to about 40 times their original volume, e.g., the volume at about 25° C. and about atmospheric pressure. The temperature to which the elastic particles are heated depends on factors such as the chemical composition of the particle. For example, the glass transition temperature of the polymer used to make the particles could affect the temperature to which the particles are heated. The temperature to which the elastic particles are heated also depends on other factors including, but not limited to, the desired density of the cement composition. One of ordinary skill in the art, with the benefit of this disclosure, will be able to determine the appropriate temperature to which a particular type of elastic particle may be safely heated for a particular application.

[0023] Among other benefits, the addition of the elastic particles to a cement composition may reduce the density of the cement composition. Among other benefits, the presence of the elastic particles in the cement compositions used in

the present invention provides improved elasticity, resiliency, and ductility to the ensuing hardened cement sheath, and protects it from experiencing brittle failure during the life of the well. The elastic particle contracts, to some extent, under pressure, and subsequently expands when the pressure is removed. Certain exemplary embodiments of the elastic particles of the present invention can withstand pressures in excess of about 21,000 psi without crushing, and may rebound upon release of the pressure to about their original dimensions. Accordingly, the elastic particles provide a mechanism for the cement compositions used in the present invention to absorb stress imposed by the temperature and pressure conditions encountered in a subterranean formation. Among other benefits, the elastic particles also enable the cement composition to endure the reduction in hydration volume ("shrinkage") and associated changes that may occur while the cement sets in the subterranean formation.

[0024] Among other benefits, the elastic particles in the cement compositions used in the present invention may reduce the problem of loss of circulation of the cement composition into the fractures of the subterranean formation, because they permit the density of the cement compositions to vary. For example, the cement composition may have a lower density at shallower depths, and subsequently have a higher density at greater depths, due to factors such as the compressibility of the elastic particles. This may permit the cement compositions to have a sufficiently low density at shallow depths to avoid lost circulation at such low depths, yet also have a sufficiently high density at greater depths to prevent fluid influx from the subterranean formation surrounding the well bore. If the zones within the subterranean formation where circulation may potentially be lost are at a shallow depth, then the cement compositions may be able to prevent or minimize lost circulation, because the cement composition will have a sufficiently low density at such shallow depth to avoid fracturing the subterranean formation. This lower density reduces the hydrostatic pressure exerted by the column of cement composition at such shallow depth that might otherwise cause the cement composition to enter the fractures within the lost circulation zone. Furthermore, where the cement compositions are actually lost to any extent to a lost circulation zone, the presence of the elastic particles in the cement compositions may minimize such loss of the cement composition due to factors such as the expansion of the elastic particles as they enter lower pressure zones within the formation, so as to seal off such lower pressure zones from the well bore, which will prevent further loss of circulation. Lower pressures may exist within the lost circulation zones in the formation for reasons including the fact that such zones may provide a broad flow area, as well as because frictional losses may occur as the cement composition travels through such zones within the formation. One of ordinary skill in the art with the benefit of this disclosure will recognize the amount and type of elastic particles to include within the cement compositions in order to optimize the expansion and sealing capability of the cement compositions for a particular application.

[0025] Optionally, the cement compositions used in the present invention may comprise fibers. Where fibers are included in the cement compositions, the fibers are, in certain exemplary embodiments, high tensile modulus carbon fibers that have a high tensile strength. In certain preferred embodiments, the tensile modulus of the fibers

may exceed 180 GPa, and the tensile strength of the fibers may exceed 3000 MPa. In certain exemplary embodiments, the fibers may have a mean length of about 1 mm or less. In certain embodiments, the mean length of the carbon fibers is from about 50 to about 500 microns. In certain exemplary embodiments, the fibers have a mean length in the range of from about 100 to about 200 microns. In certain exemplary embodiments, the fibers are milled carbon fibers. An example of suitable fibers includes "AGM-94" carbon fibers commercially available from Asbury Graphite Mills, Inc., of Asbury, N.J. AGM-94 fibers have a mean length of about 150 microns and a diameter of about 7.2 microns. Another example of suitable fibers includes the "AGM-99" carbon fibers, also available from Asbury Graphite Mills, Inc., which have a mean length of about 150 microns and a diameter of about 7.4 microns. One of ordinary skill in the art with the benefit of this disclosure will recognize where fibers may be suitable for a particular application, and in what amount they may appropriately be included within the cement composition.

[0026] Optionally, the cement compositions useful with the present invention may further comprise an expanding additive, for providing a foamed cement. The expanding additive may be any component suitable for performing the desired function of incorporating gas into the cement composition. Further, foaming of the cement composition can be accomplished by any suitable method. Where the expanding additive is a gas, for instance, foaming of the cement composition is achieved at the surface in one preferred embodiment, and the foamed cement composition is then introduced into the subterranean formation and permitted to set therein into a resilient, ductile, and tough foamed cement mass. Where the cement compositions are to be foamed, the cement composition is foamed in one preferred embodiment by direct injection of the expanding additive into the cement composition. For instance, where the cement composition is foamed by the direct injection of gas into the composition, the gas utilized can be air or any suitable inert gas, such as nitrogen, or even a mixture of such gases. Preferably, nitrogen is used. Where foaming is achieved by direct injection of gas, the gas may be present in the composition in an amount sufficient to foam the composition, generally in an amount in the range of from about 0.01% to about 60% by volume of the composition. In another preferred embodiment, the cement composition is foamed by gas generated by a reaction between the cement slurry and an expanding additive present in the cement composition in particulate form. For example, the composition may be foamed by hydrogen gas generated in situ as the product of a reaction between the slurry and fine aluminum powder present in the cement composition. Where an expanding additive in particulate form is used, aluminum powder, gypsum blends, and deadburned magnesium oxide are preferred. Preferred expanding additives comprising aluminum powder are commercially available under the trade names "GAS-CHEK®" and "SUPER CBL" from Halliburton Energy Services of Duncan, Okla.; a preferred expanding additive comprising a blend containing gypsum is commercially available under the trade name "MICROBOND" from Halliburton Energy Services of Duncan, Okla.; and preferred expanding additives comprising deadburned magnesium oxide are commercially available under the trade names "MICROBOND M" and "MICROBOND HT" from Halliburton Energy Services, Inc., of Duncan, Okla. Such preferred expanding

additives are described in commonly-owned U.S. Pat. Nos. 4,304,298; 4,340,427; 4,367,093; 4,450,010; and 4,565,578, the relevant disclosures of which are hereby incorporated herein by reference.

[0027] Additional additives may be added to the cement compositions used with the methods of the present invention as deemed appropriate by one skilled in the art with the benefit of this disclosure. Examples of such additives include, inter alia, fluid loss control additives, salts, vitrified shale, fly ash, fumed silica, bentonite, fixed-density weighting agents, set retarders, and the like. An example of a preferred fixed-density weighting agent is "HI-DENSE® No. 4," commercially available from Halliburton Energy Services, Inc., of Duncan, Okla. An example of a preferred fly ash is "POZMIX® A," commercially available from Halliburton Energy Services, Inc., of Duncan, Okla. An example of a preferred source of fumed silica is "SILICALITE," commercially available from Halliburton Energy Services, Inc., of Duncan, Okla.

[0028] Optionally, other nonflexible particles may be added, in conjunction with the elastic particles, to the cement compositions used in the present invention. Particularly suitable nonflexible particles are cenospheres, which are commercially available from, for example, Halliburton Energy Services, Inc., of Duncan, Okla., under the trade name "SPHERELITE"; other suitable nonflexible particles are commercially available from PQ Corporation of Valley Forge, Pa., under the trade name "EXTENDOSPHERES"; and from Trelleborg Fillite, Inc., of Atlanta, Ga., under the trade name "FILLITE". Alternatively, the nonflexible particles may be glass particles or ceramic particles. In some cases, the nonflexible particles are relatively inexpensive compared to the elastic particles. This is particularly true in the case of cenospheres, which are nonflexible particles that are formed as an industrial waste by-product. However, the nonflexible particles may be more likely to break when subjected to downhole temperature and pressure changes. In determining the relative amounts of elastic particles and nonflexible particles to add to the cement composition when using them in combination, the cost savings produced by the use of nonflexible particles may be considered in light of the mechanical properties needed to withstand the stresses on the cement sheath during the life of the well. One of ordinary skill in the art with the benefit of this disclosure will recognize the appropriate balance of elastic particles and nonflexible particles to provide the best technical and economic solution for a given application.

[0029] The cement compositions used with the methods of the present invention may be prepared by dry blending the elastic particles with the cement before the addition of water, or by mixing the elastic particles with the water before the water is added to the cement, or by mixing the elastic particles with the cement slurry consecutively with or after the addition of the water. In certain preferred embodiments, the elastic particles are dry-blended with the cement before the addition of water. In other embodiments, the elastic particles also may be pre-suspended in water and injected into the cement mix fluid or into the cement composition as an aqueous slurry, if desired. In embodiments where the elastic particles are pre-suspended in water before injection into the cement composition, a preferred elastic particle comprising a styrene divinylbenzene copolymer may be surface-modified so that it will remain suspended in water,

despite the natural tendency of such elastic particles to float. In other embodiments where elastic particles are used that have not been so modified, surfactants may be added to the cement compositions, if desired, to water-wet the surface of the elastic particles so that the elastic particles—the density of which is less than that of water—will remain suspended in the aqueous phase. One of ordinary skill in the art with the benefit of this disclosure will recognize when the use of a surfactant is appropriate with the cement compositions.

[0030] An example of a cement composition suitable for use with the methods of the present invention comprises Class G Portland cement, 49.4% water bwoc, 20% silica fume bwoc, 20% fly ash bwoc, and 52% elastic particles bwoc. Another example of a cement composition suitable for use with the methods of the present invention comprises Class G Portland cement, 39.3% water bwoc, 24% fixed-density weighting agent, and 4.5% elastic particles bwoc.

[0031] An example of a method of the present invention is a method of avoiding the loss of circulation of a cement composition in a subterranean formation, comprising the steps of: providing a cement composition comprising a base fluid, a hydraulic cement, and a portion of elastic particles; placing the cement composition in a well bore in a subterranean formation; permitting a portion of the cement composition to enter openings in a region of the subterranean formation in fluid communication with the well bore; and permitting the portion of the cement composition to seal the openings off from the well bore. Additional steps include, but are not limited to, selectively placing the cement composition in a region of the well bore that is in fluid communication with openings in a region of the subterranean formation.

[0032] Another example of a method of the present invention is a method of improving the ability of a cement composition to resist the loss of circulation, comprising the step of adding to the cement composition a portion of elastic particles.

[0033] To facilitate a better understanding of the present invention, the following examples of some of the preferred embodiments are given. In no way should such examples be read to limit the scope of the invention.

EXAMPLE 1

[0034] A test sample was made of an exemplary embodiment of a cement composition useful in accordance with the present invention. To prepare Sample Composition No. 1, Class G Portland cement was mixed with 49.4% water bwoc, 20% silica fume bwoc, 20% fly ash bwoc, and 52% elastic particles bwoc. The density of Sample Composition No. 1 was measured at 9 lb/gallon.

EXAMPLE 2

[0035] Example 2 compares the physical properties of Sample Composition No. 2, which is a cement composition prepared without elastic particles, with the physical properties of Sample Composition No. 3, which is a cement composition that comprises elastic particles.

[0036] Sample Composition No. 2 comprises Class G Portland cement mixed with 39.8% water bwoc, and 24% fixed density weighting agent bwoc. The resultant density of Sample Composition No. 2 was 18 lb/gallon.

[0037] Sample Composition No. 3 is a cement composition of the present invention comprising Class G Portland cement mixed with 39.3% water bwoc, 24% fixed density weighting agent bwoc, and 4.5% elastic particles bwoc. The resultant density of Sample Composition No. 3 was 16.2 lb/gallon. This demonstrates, inter alia, that the addition of 4.5 weight percent elastic particles provides a resultant 11.1% decrease in the density of a cement composition.

EXAMPLE 3

[0038] The effect of the elastic particles on the cement compositions used in the methods of the present invention may be illustrated by considering a hypothetical cement composition of the present invention comprising Class H cement, further comprising 50% aqueous base fluid bwoc, 20% POZMIX® Abwoc, 20% SILICALITE bwoc, and 50% elastic particles bwoc, the elastic particles having a specific gravity of about 0.41 and an isothermal compressibility factor of about 1.5×10^{-4} (1/psi). The density of such hypothetical cement composition at sea level is 9.2 lb/gallon. The following equations may be used to calculate the density of the cement composition at different depths.

[0039] The change in volume of the elastic particle as the external pressure changes may be determined from the relationship:

$$dv = \left(\frac{\partial v}{\partial p} \right) dp \quad \text{Equation 1}$$

or

$$\frac{dv}{v} = \frac{1}{v} \left(\frac{\partial v}{\partial p} \right) dp = C dp \quad \text{Equation 2}$$

[0040] In Equation 2, the value "C" is the compressibility of the elastic particle. If the elastic particle is subjected to a change in pressure of dp, then the new volume of the elastic particle is given by:

$$v_{\text{new}} = v_{\text{old}} + dv \quad \text{Equation 3}$$

[0041] and the new density is then calculated.

[0042] From the surface to a depth of 2,500 feet, the change in pressure is 1,129 psi, which will cause the volume of the elastic particles to change by 17%, using Equation 2. Using Equation 3, the density at 2,500 feet is then calculated to be 10.2 lb/gallon. The calculated density of the hypothetical cement composition at increasing depths is shown in Table 1 below.

TABLE 1

Depth (feet)	Equivalent Cement Composition Density (lb/gallon)
0	9.2
2,500	10.2
5,000	11.4
7,500	13.1

[0043] Therefore, the present invention is well adapted to carry out the objects and attain the ends and advantages mentioned as well as those that are inherent therein. While

the invention has been depicted, described, and is defined by reference to exemplary embodiments of the invention, such a reference does not imply a limitation on the invention, and no such limitation is to be inferred. The invention is capable of considerable modification, alternation, and equivalents in form and function, as will occur to those ordinarily skilled in the pertinent arts and having the benefit of this disclosure. The depicted and described embodiments of the invention are exemplary only, and are not exhaustive of the scope of the invention. Consequently, the invention is intended to be limited only by the spirit and scope of the appended claims, giving full cognizance to equivalents in all respects.

What is claimed is:

1. A method of avoiding the loss of circulation of a cement composition in a subterranean formation, comprising the steps of:

providing a cement composition comprising a hydraulic cement and a portion of elastic particles;

placing the cement composition in a well bore in a subterranean formation;

permitting a portion of the cement composition to enter openings in a region of the subterranean formation in fluid communication with the well bore; and

permitting the portion of the cement composition to seal the openings off from the well bore.

2. The method of claim 1 wherein the hydraulic cement comprises Portland cements, pozzolana cements, gypsum cements, high alumina content cements, silica cements, or high alkalinity cements.

3. The method of claim 1 wherein the cement composition further comprises a base fluid, and wherein the base fluid comprises water, a nonaqueous fluid, or a mixture thereof.

4. The method of claim 3 wherein the nonaqueous fluid comprises an organic liquid.

5. The method of claim 3 wherein the base fluid is present in the cement composition in an amount sufficient to form a pumpable slurry.

6. The method of claim 5 wherein the base fluid is present in the cement composition in an amount in the range of from about 25% to about 150% by weight of the cement.

7. The method of claim 1 wherein the elastic particles have a specific gravity of at least about 0.05.

8. The method of claim 7 wherein the elastic particles have a specific gravity in the range of from about 0.05 to about 0.99.

9. The method of claim 1 wherein the portion of elastic particles comprises elastic particles comprising a copolymer of styrene and divinylbenzene; a copolymer of styrene and acrylonitrile; or a terpolymer of styrene, vinylidene chloride, and acrylonitrile.

10. The method of claim 1 wherein the elastic particles have a compressibility factor in the range of from about 1.5×10^{-5} (1/psi) to about 1.5×10^{-9} (1/psi).

11. The method of claim 1 wherein a portion of the elastic particles has a diameter of at least about 1 micrometer at a temperature of about 25° C. and at about atmospheric pressure.

12. The method of claim 1 wherein the portion of elastic particles is present in the cement composition in an amount in the range of from about 1% to about 200% by weight of cement.

13. The method of claim 12 wherein the portion of elastic particles is present in the cement composition in an amount in the range of from about 5% to about 100% by weight of cement.

14. The method of claim 13 wherein the portion of elastic particles is present in the cement composition in an amount in the range of from about 5% to about 10% by weight of cement.

15. The method of claim 1 wherein a portion of the elastic particles is substantially impermeable to a fluid present in the cement composition or in the subterranean formation.

16. The method of claim 1 wherein the surface of a portion of the elastic particles is coated with a substantially impermeable material to render the elastic particles substantially impermeable to a fluid present in the cement composition or in the subterranean formation.

17. The method of claim 16 wherein the material is hydrophilic or hydrophobic.

18. The method of claim 17 wherein the hydrophobic material comprises silanes, silicone polymers, latexes, or a mixture thereof.

19. The method of claim 17 wherein the hydrophilic material comprises ethylene oxide, propylene oxide, acrylic acid, 2-acrylamido-2-methylpropanesulfonic acid, aminoalkoxysilanes, or a mixture thereof.

20. The method of claim 1 wherein the elastic particles further comprise an internal fluid.

21. The method of claim 20 wherein the internal fluid comprises air, nitrogen, carbon dioxide, propane, isobutane, normal butane, normal or branched pentane, ammonia, fluorinated hydrocarbons, hydrochlorofluorocarbons, argon, helium, or a mixture thereof.

22. The method of claim 20 wherein a portion of the elastic particles is capable of expanding up to about 40 times its original volume.

23. The method of claim 1 wherein a portion of the elastic particles can withstand a pressure of about 21,000 psi without crushing.

24. The method of claim 1 wherein a portion of the elastic particles can rebound upon release of pressure.

25. The method of claim 1 wherein the cement composition has a density, and wherein the density of the cement composition may vary with pressure.

26. The method of claim 1 wherein the cement composition comprising the portion of elastic particles has a density sufficient to prevent fluid influx from a region of the subterranean formation adjacent to the well bore without fracturing a region of the formation.

27. The method of claim 26 wherein the cement composition comprising the portion of the elastic particles has a density in a range of from about 6 pounds per gallon to about 22 pounds per gallon.

28. The method of claim 1 wherein the cement composition further comprises a surfactant, a dispersant, an accelerator, a retarder, a salt, mica, fibers, a formation-conditioning agent, a fixed-density weighting agent, vitrified shale, fumed silica, fly ash, a fluid loss control additive, an expanding additive, a defoamer, a viscosifier, a cenosphere, a glass sphere, a ceramic sphere, or a mixture thereof.

29. The method of claim 20 further comprising the step of expanding a portion of the elastic particles before introducing the elastic particles to the cement composition.

30. The method of claim 1 wherein the step of permitting the portion of the cement composition to seal the openings

off from the well bore comprises permitting the portion of elastic particles within the portion of the cement composition to expand upon entering the openings such that the openings are sealed off from the well bore.

31. The method of claim 1 wherein the step of placing the cement composition in a well bore in a subterranean formation involves selectively placing the cement composition in a region of the well bore that is in fluid communication with openings in a region of the subterranean formation.

32. The method of claim 1 wherein the cement composition is placed in a well bore in the subterranean formation; wherein the cement composition has a density that may vary with pressure; wherein the cement composition comprising the portion of elastic particles has a density sufficient to prevent fluid influx from a region of the subterranean formation adjacent to the well bore without fracturing a region of the formation; wherein the portion of elastic particles is present in the cement composition in an amount in the range of from about 1% to about 200% by weight of cement; wherein the portion of elastic particles comprises elastic particles comprising a copolymer of styrene and divinylbenzene; a copolymer of styrene and acrylonitrile; or a terpolymer of styrene, vinylidene chloride and acrylonitrile; and wherein the elastic particles have a compressibility factor in the range of from about 1.5×10^{-3} (1/psi) to about 1.5×10^{-9} (1/psi).

33. A method of improving the ability of a cement composition to resist the loss of circulation, comprising the step of adding to the cement composition a portion of elastic particles.

34. The method of claim 33 wherein the cement composition further comprises a hydraulic cement, and wherein the hydraulic cement comprises Portland cements, pozzolana cements, gypsum cements, high alumina content cements, silica cements, or high alkalinity cements.

35. The method of claim 33 wherein the cement composition further comprises a base fluid, and wherein the base fluid comprises water, a nonaqueous fluid, or a mixture thereof.

36. The method of claim 35 wherein the nonaqueous fluid comprises an organic liquid.

37. The method of claim 35 wherein the base fluid is present in the cement composition in an amount sufficient to form a pumpable slurry.

38. The method of claim 37 wherein the base fluid is present in the cement composition in an amount in the range of from about 25% to about 150% by weight of the cement.

39. The method of claim 33 wherein the elastic particles have a specific gravity of at least about 0.05.

40. The method of claim 39 wherein the elastic particles have a specific gravity in the range of from about 0.05 to about 0.99.

41. The method of claim 33 wherein the portion of elastic particles comprises elastic particles comprising a copolymer of styrene and divinylbenzene; a copolymer of styrene and acrylonitrile; or a terpolymer of styrene, vinylidene chloride, and acrylonitrile.

42. The method of claim 33 wherein the elastic particles have a compressibility factor in the range of from about 1.5×10^{-3} (1/psi) to about 1.5×10^{-9} (1/psi).

43. The method of claim 33 wherein a portion of the elastic particles has a diameter of at least about 1 micrometer at a temperature of about 25° C. and at about atmospheric pressure.

44. The method of claim 33 wherein the portion of elastic particles is present in the cement composition in an amount in the range of from about 1% to about 200% by weight of cement.

45. The method of claim 44 wherein the portion of elastic particles is present in the cement composition in an amount in the range of from about 5% to about 100% by weight of cement.

46. The method of claim 45 wherein the portion of elastic particles is present in the cement composition in an amount in the range of from about 5% to about 10% by weight of cement.

47. The method of claim 33 wherein a portion of the elastic particles is substantially impermeable to a fluid present in the cement composition or in a subterranean formation.

48. The method of claim 33 wherein the surface of a portion of the elastic particles is coated with a substantially impermeable material to render the elastic particles substantially impermeable to a fluid present in the cement composition or in a subterranean formation.

49. The method of claim 48 wherein the material is hydrophilic or hydrophobic.

50. The method of claim 49 wherein the hydrophobic material comprises silanes, silicone polymers, latexes, or a mixture thereof.

51. The method of claim 49 wherein the hydrophilic material comprises ethylene oxide, propylene oxide, acrylic acid, 2-acrylamido-2-methylpropane sulfonic acid, aminoalkoxysilanes, or a mixture thereof.

52. The method of claim 33 wherein the elastic particles further comprise an internal fluid.

53. The method of claim 52 wherein the internal fluid comprises air, nitrogen, carbon dioxide, propane, isobutane, normal butane, normal or branched pentane, ammonia, flu-

orinated hydrocarbons, hydrochlorofluorocarbons, argon, helium, or a mixture thereof.

54. The method of claim 52 wherein a portion of the elastic particles is capable of expanding up to about 40 times its original volume.

55. The method of claim 33 wherein a portion of the elastic particles can withstand a pressure of about 21,000 psi without crushing.

56. The method of claim 33 wherein a portion of the elastic particles can rebound upon release of pressure.

57. The method of claim 33 wherein the cement composition has a density, and wherein the density of the cement composition may vary with pressure.

58. The method of claim 33 wherein the cement composition comprising the portion of elastic particles has a density sufficient to prevent fluid influx from a region of a subterranean formation adjacent to a well bore without fracturing a region of the formation.

59. The method of claim 58 wherein the cement composition comprising the portion of the elastic particles has a density in a range of from about 6 pounds per gallon to about 22 pounds per gallon.

60. The method of claim 33 wherein the cement composition further comprises a surfactant, a dispersant, an accelerator, a retarder, a salt, mica, fibers, a formation-conditioning agent, a fixed-density weighting agent, vitrified shale, fumed silica, fly ash, a fluid loss control additive, an expanding additive, a defoamer, a viscosifier, a cenosphere, a glass sphere, a ceramic sphere, or a mixture thereof.

61. The method of claim 52 further comprising the step of expanding a portion of the elastic particles before introducing the elastic particles to the cement composition.

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