



(51) International Patent Classification:
E21B 33/13 (2006.01) *C09K 8/02* (2006.01)
C09K 8/42 (2006.01)

(21) International Application Number:
PCT/US2015/057380

(22) International Filing Date:
26 October 2015 (26.10.2015)

(25) Filing Language: English

(26) Publication Language: English

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

(72) Inventors: **LEOTAUD, Lennox Martin**; 4527 Plantation Colony Drive, Missouri City, Texas 77459 (US). **CHATTERJI, Jiten**; 2213 Scott Lane, Duncan, Oklahoma 73533 (US). **BRENNEIS, Darrell Chad**; 3901 S. Goodrich Road, Marlow, Oklahoma 73055 (US). **BENKLEY, James Robert**; 1810 Terrace, Duncan, Oklahoma 73033 (US). **BROTHERS, Lance Everett**; 800 N.W. 38th, Oklahoma City, Oklahoma 73118 (US). **HARGROVE, Brandi R.**; 11321 Xavier Drive Unit 203, Westminster, Colorado 80031 (US). **DEAN, William J.**; 22602 Crescent Cove Court, Katy, Texas 77494 (US). **ROBERTSON, Logan Todd**; 2801 25th Street W., Williston, North Dakota 58801 (US).

(74) Agent: **TUMEY LLP**; PO Box 22188, Houston, Texas 77227 (US).

[Continued on next page]

(54) Title: USE OF SOLID SURFACTANT COMPOSITES IN WELL CEMENTING

(57) Abstract: Disclosed are spacer fluids and methods of use in subterranean formations. Embodiments may include use of solid surfactant composites in well cementing operations

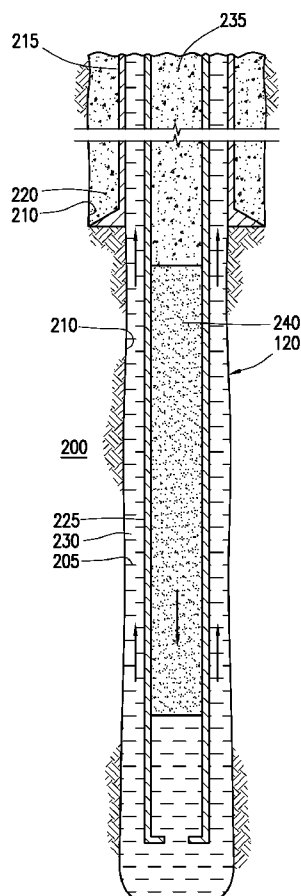


FIG. 2



(81) Designated States (*unless otherwise indicated, for every kind of national protection available*): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (*unless otherwise indicated, for every kind of regional protection available*): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— with international search report (Art. 21(3))

USE OF SOLID SURFACTANT COMPOSITES IN WELL CEMENTING

BACKGROUND

[0001] Embodiments relate well cementing operations and, more particularly, in certain embodiments, to use of solid surfactant composites in well cementing operations.

[0002] In well cementing operations, such as well construction and remedial cementing, cement compositions are commonly utilized. Cement compositions may be used in primary cementing operations whereby pipe strings, such as casing and liners, are cemented in wellbores. In a typical primary cementing operation, a cement composition may be pumped into an annulus between the exterior surface of the pipe string (e.g., casing, liner, etc.) disposed therein and the walls of the wellbore (or a larger conduit in the wellbore). The cement composition may set in the annular space, thereby forming an annular sheath of hardened, substantially impermeable material (i.e., a cement sheath) that may support and position the pipe string in the wellbore and may bond the exterior surface of the pipe string to the wellbore walls (or the larger conduit). Among other things, the cement sheath surrounding the pipe string should function to prevent the migration of fluids in the annulus, as well as protect the pipe string from corrosion. Cement compositions may also be used in remedial cementing methods, such as in squeeze cementing for sealing voids in a pipe string, cement sheath, gravel pack, subterranean formation, and the like.

[0003] Preparation of the wellbore for cementing operations may be important in achieving optimal zonal isolation. Conventionally, wellbores may be cleaned and prepared for the cement composition with a fluid train that precedes the cement composition and can include spacer fluids, flushes, water-based muds, and the like. Spacer fluids may be used in wellbore preparation for drilling fluid displacement before introduction of the cement composition. The spacer fluids may enhance solids removal while also separating the drilling fluid from a physically incompatible fluid, such as a cement composition. Spacer fluids may also be placed between different drilling fluids during drilling change outs or between a drilling fluid and completion brine. A liquid surfactant may be blended with the spacer fluid, for example, to allow the spacer fluid to be compatible with water- or oil-based drilling fluids. Inclusion of the liquid surfactant may enable the spacer fluid to achieve improved cleaning by removal of residual drilling fluid from the wellbore. For wellbores in which oil-based drilling fluids may have been used, the inclusion of liquids surfactants in the spacer fluids may serve the purpose of water-wetting surfaces in the wellbore, such as the wellbore

wall and casing surfaces, resulting in better cement bonding. However, the use of liquid surfactants may be problematic. For example, liquid surfactants require the use of additional equipment on location to mix the spacer fluid and liquid surfactant properly, thus increasing the complexity of the well operation. Additionally, certain liquid surfactants may include one or more flammable components, thus increasing the expense associated with shipment, storage, and handling thereof.

BRIEF DESCRIPTION OF THE DRAWINGS

[0004] These drawings illustrate certain aspects of some of the embodiments of the present invention, and should not be used to limit or define the invention.

[0005] FIG. 1 is a schematic illustration of an example system for the preparation and delivery of a spacer fluid comprising a solid surfactant composite.

[0006] FIG. 2 is a schematic illustration of an example in which a spacer fluid comprising a solid surfactant composite is used between a cement composition and a drilling fluid.

[0007] FIG. 3 is a schematic illustration of the embodiment of FIG. 3 showing displacement of the drilling fluid.

DETAILED DESCRIPTION

[0008] Embodiments relate well cementing operations and, more particularly, in certain embodiments, to use of solid surfactant composites in well cementing operations. The well cementing operations may include the use of the solid surfactant composites in spacer fluids used, for example, in well cementing operations. A solid surfactant composite may be dry blended with particulate solids, wherein the dry blend may be included in a spacer fluid. One of the many potential advantages to these methods and compositions is that the use of a solid surfactant composite instead of liquid surfactants may reduce and potentially eliminate the need for additional mixing equipment for the surfactant at the well site, thus simplifying preparation of the spacer fluid. Additionally, hazards associated with handling of certain liquid surfactants, which may be flammable, at the well site may also be eliminated with the use of a solid surfactant composite.

[0009] A solid surfactant composite may include a water-wetting surfactant and a solid carrier. Optionally, the solid surfactant composite may include a dispersant, a defoaming agent, or a combination thereof. The solid surfactant composite may have a wide variety of shapes and sizes of individual particles suitable for use in cementing applications.

By way of example, individual particles of the solid surfactant composite may have well-defined physical as well as irregular geometries, including the physical shape of platelets, shavings, fibers, flakes, ribbons, rods, strips, spheroids, hollow beads, toroids, pellets, tablets, or any other physical shape. Without limitation, the solid surfactant composite may have a particle size in the range of about 5 microns to about 1,500 microns and, alternatively, a particle size in the range of about 20 microns to about 500 microns. However, particle sizes outside these defined ranges also may be suitable for particular applications.

[0010] Any of a variety of water-wetting surfactants may be included in the solid surfactant composite that may be capable of water-wetting well surfaces, such as the wellbore wall and casing surface. The function that a particular surfactant may perform depends on a variety of factors. These factors may include, but are not limited to, the choice of the hydrophobic and hydrophilic portions and the relative amounts thereof and the presence of any cationic, ionic, non-ionic, amphoteric, or Zwitterionic groups. The water-wetting surfactant may be included in the solid surfactant composite in an amount, without limitation, of from about 5% to about 99.9% by weight of the solid surfactant composite. By way of example, the water-wetting surfactant may be included in an amount of from about 5%, about 10%, about 20%, about 30%, about 40%, about 50%, about 60%, about 70%, about 80%, about 90%, or about 99.9% by weight of the solid surfactant composite. Examples of suitable water-wetting surfactants may include alcohol ethoxylates, alcohol ethoxysulfates, alkyl phenol ethoxylates (e.g., nonyl phenol ethoxylates), glycol ethers, and combinations thereof. Certain of the water-wetting surfactants may be used as water-soluble salts. For example, the water-wetting surfactants may be selected from alkali metal, alkaline earth metal, ammonium, and alkanolammonium salts of alcohol ethoxylates, alcohol ethoxysulfates, and alkyl phenol ethoxylates. One of ordinary skill in the art, with the benefit of this disclosure, should be able to select an appropriate water-wetting surfactant and concentration thereof for a particular application.

[0011] Without limitation, suitable alcohol ethoxylates may include C₆ to C₁₆ alcohols substituted with from about 2 moles to about 15 moles and, alternatively, from about 5 moles to about 12 moles of ethylene oxide. The C₆ to C₁₅ alcohols may be linear or branched. Without limitation, suitable alcohol ethoxylates may include C₄ to C₈ alcohols substituted with about 4 moles to about 8 moles of ethylene oxide, C₈ to C₁₂ alcohols substituted with about 4 moles to about 8 moles of ethylene oxide, and C₁₂ to C₁₄ alcohols substituted with about 10 moles to about 14 moles of ethylene oxide. Specific examples of suitable alcohol ethoxylates may include butanol, hexanol or pentanol substituted with 6 moles of ethylene

oxide, nonyl, decyl alcohol, or dodecyl alcohol substituted with 6 moles of ethylene oxide, or docecyl alcohol, tridecyl alcohol, or tetradecyl alcohol substituted with 12 moles of ethylene oxide. Additional examples of suitable alcohol ethoxylates may include isodecyl alcohol substituted with 6 moles of ethylene oxide or isotridecyl alcohol substituted with 12 moles ethylene oxide. Combinations of suitable alcohol ethoxylates may also be used.

[0012] Without limitation, suitable alcohol ethoxysulfates may include C₁₀ to C₁₆ alcohols substituted with about 2 moles to about 15 moles of ethylene oxide. The C₁₀ to C₁₆ alcohols may be linear or branched. Suitable C₁₀ to C₁₆ alcohol ethoxylates may include docecyl alcohol, tridecyl alcohol, or tetradecyl alcohol substituted with from 2 moles to about 15 moles and, alternatively from about 6 moles to about 12 moles of ethylene oxide. Additional examples of suitable alcohol ethoxylates may include ethoxylated dodecyl alcohol ammonium sulfate or ethoxylated tetradecyl ammonium sulfate. Combinations of suitable alcohol ethoxysulfates may also be used.

[0013] Without limitation, suitable alkyl phenol ethoxylates may include an alkyl group with from 1 to 12 carbon atoms and, alternatively, from about 8 to 12 carbon atoms. The alkyl phenol ethoxylates may have from 2 moles to about 18 moles of ethylene oxide and, alternatively, from about 8 moles to about 12 moles of ethylene oxide. One example of a suitable alkyl phenol ethoxylate is nonyl phenol ethoxylate having from about 8 moles to about 12 moles of ethylene oxide and, alternatively, about 10 moles of ethylene oxide.

[0014] Without limitation, suitable glycol ethers may include an alkyl ether of a mono-, di-, or triethylene glycol. The alkyl ether may include a C₁ to C₅ alkyl ether of a mono-, di-, or triethylene glycol. By way of example, the glycol ether may include diethylene glycol methyl ether, dipropylene glycol methyl ether, 2-butoxy ethanol, ethers of a C₂ to C₆ dihydric alkanol that comprise at least one C₁ to C₆ alkyl group, mono ethers of dihydric alkanols, methoxypropanol, butoxyethanol, hexoxyethanol, isomers thereof, and combinations thereof. One example of a suitable glycol ether may comprise ethylene glycol monobutyl ether. The glycol ethers may be used by themselves in the solid surfactant composite or as a co-surfactant with one or more of the additional water-wetting surfactants described herein. Without limitation, a glycol ether such as ethylene glycol monobutyl ether may be used as a co-surfactant (50% to 90% by weight) with an alcohol ethoxylates, such as butanol, hexanol or pentanol substituted with from 4 moles to about 8 moles and, alternatively, about 6 moles of ethylene oxide.

[0015] As previously described, the water-wetting surfactant may be disposed on a solid carrier. Without limitation, the solid carrier may include any of a variety of solid

materials, such as diatomaceous earth, amorphous silica, starch, clay such as kaolin clay, and combinations thereof. The solid carrier may be included in the solid surfactant composite in an amount, without limitation, of from about 0.1% to about 95% by weight of the solid surfactant composite. By way of example, the solid carrier may be included in an amount of from about 0.1%, about 10%, about 20%, about 30%, about 40%, about 50%, about 60%, about 70%, about 80%, about 90%, or about 95% by weight of the solid surfactant composite. One of ordinary skill in the art, with the benefit of this disclosure, should be able to select an appropriate solid carrier and concentration thereof for a particular application.

[0016] Optionally, the solid surfactant composite may include a dispersant. Without limitation, suitable dispersants may include any of a variety of commonly used cement dispersants, such as sulfonated dispersants; sulfonated polymer dispersants; naphthalene sulfonates; melamine sulfonates; sulfonated melamine formaldehyde condensate; sulfonated naphthalene formaldehyde condensate; sulfonate acetone formaldehyde condensate; ethoxylated polyacrylates; or combinations thereof. One example of a suitable dispersant may include a naphthalene sulfonate condensed with from about 4 moles to about 8 moles and, alternatively, about 6 moles of formaldehyde. The dispersant may be included in the solid surfactant composite in an amount, without limitation, of from about 10% to about 90% by weight of the solid surfactant composite. By way of example, the dispersant may be included in an amount of from about 10%, about 20%, about 30%, about 40%, about 50%, about 60%, about 70%, about 80%, or about 90% by weight of the solid surfactant composite. One of ordinary skill in the art, with the benefit of this disclosure, should be able to select an appropriate dispersant and concentration thereof for a particular application.

[0017] Optionally, the solid surfactant composite may include a defoaming agent. The defoaming agent may be included in the solid surfactant composite in addition to, or separate from, the dispersant. Suitable defoaming agents may include compounds used in well operations to prevent a well treatment fluid from foaming during mixing and pumping. Without limitation, suitable defoaming agents may include polyol compositions, siloxanes such as polydimethyl siloxane, acetylenic diols, and combinations thereof. The defoaming agent may be included in the solid surfactant composite in addition to, or separate from, the dispersant. The defoaming agent may be included in the solid surfactant composite in an amount, without limitation, of from about 0.1% to about 20% by weight of the solid surfactant composite. By way of example, the defoaming agent may be included in an amount of from about 0.1%, about 5%, about 10%, about 15%, or about 20% by weight of the solid surfactant composite. One of ordinary skill in the art, with the benefit of this disclosure,

should be able to select an appropriate defoaming agent and concentration thereof for a particular application.

[0018] Without limitation, a solid surfactant composite may comprise an alcohol ethoxylate, a solid carrier comprising amorphous silica, a dispersant, and a defoaming agent. By way of example, the solid surfactant composite may comprise a C₈ to C₁₂ alcohol substituted with about 4 moles to about 8 moles of ethylene oxide, amorphous silica, a sulfonated naphthalene formaldehyde condensate, and a siloxane. By way of further example, the solid surfactant composite may comprise isodecyl alcohol substituted with 6 moles of ethylene oxide, amorphous silica, naphthalene sulfonate condensed with 6 moles of formaldehyde, and a polydimethyl siloxane.

[0019] Without limitation, a solid surfactant composite may comprise an alcohol ethoxylate, a solid carrier, a dispersant, and a defoaming agent. By way of example, the solid surfactant composite may comprise a C₁₂ to C₁₄ alcohol substituted with about 10 moles to about 14 moles of ethylene oxide, amorphous silica, diatomaceous earth, a sulfonated naphthalene formaldehyde condensate, and a siloxane. By way of further example, the solid surfactant composite may comprise isotridecyl alcohol substituted with 12 moles ethylene oxide, amorphous silica, diatomaceous earth, naphthalene sulfonate condensed with 6 moles of formaldehyde, and a polydimethyl siloxane.

[0020] The solid surfactant composite may be prepared by any suitable technique. By way of example, the components (e.g., water-wetting surfactant, solid carrier, dispersant, and/or defoaming agent) may be combined to form a mixture. This mixture may then be dried, such as by spray drying, to form a substantially dry solid product.

[0021] Without limitation, the solid surfactant composite may be used in a spacer fluid. A spacer fluid may comprise the solid surfactant composite and a base fluid. When added to the base fluid, the water-wetting surfactant on the solid surfactant composite will generally dissolve, with resulting release of the water-wetting surfactant into the base fluid. The solid surfactant composite may be included in the spacer fluid in an amount sufficient for a particular application. Without limitation, the solid surfactant composite may be added to the spacer fluid in an amount in a range of from about 0.1% to about 20% by weight of the spacer fluid and, alternatively, from about 1% to about 5% by weight. For example, the solid surfactant composite may be present in an amount of about 0.1%, about 1%, about 2%, about 4%, about 6%, about 8%, about 10%, about 15%, or about 20% by weight of the spacer fluid.

[0022] The base fluid may be an oil-base fluid or aqueous-base fluid. Examples of aqueous-base fluids may comprise fresh water, salt water (e.g., water containing one or more

dissolved salts), brine, seawater, or any combination thereof. Examples of suitable oil-base fluids may include water-in-oil emulsions. The base fluid may be used to prepare a spacer fluid that is not emulsified. One of ordinary skill in the art with the benefit of this disclosure will recognize which types of aqueous base fluids are appropriate for a particular application. Without limitation, the base fluid may be included in the spacer fluids in an amount in the range of from about 15% to about 99.9% by weight of the spacer fluid and, alternatively, from about 25% to about 85% by weight of the spacer fluid. For example, the base fluid may be present in an amount of about 15%, about 20%, about 30%, about 40%, about 50%, about 60%, about 70%, about 80%, about 90%, about 99%, or about 99% by weight of the spacer fluid.

[0023] The spacer fluids generally should have a density suitable for a particular application as desired by those of ordinary skill in the art, with the benefit of this disclosure. Without limitation, the spacer fluids may have a density in the range of from about 4 pounds per gallon ("ppg") to about 24 ppg, in the range of about 4 ppg to about 17 ppg, or in the range of about 8 ppg to about 13 ppg. Without limitation, the spacer fluids may be foamed or unfoamed or comprise other means to reduce their densities known in the art, such as lightweight additives. Those of ordinary skill in the art, with the benefit of this disclosure, should recognize the appropriate density for a particular application.

[0024] Optionally, the spacer fluid may include a solid particulate additive. The solid particulate additive may be included in the spacer fluid as desired to perform a particular function. By way of example, the solid particulate additive may be included in the spacer fluid to weight the fluid to a desired density, assist in well cleaning by abrasive action in the wellbore, and/or as a viscosifier. Suitable solid particulate additives may include, without limitation, weighting agents, vitrified shale, cement kiln dust, silica flour, bentonite, pumice, fly ash, and combinations thereof. Weighting agents are typically materials may be used to increase the density of a well treatment fluid, such as a spacer fluid, and may have a specific gravity of about 2 or higher (*e.g.*, about 2, about 4, etc.). Examples of weighting agents that may be used include, but are not limited to, hematite, hausmannite, barite, calcium carbonate, and combinations thereof. Without limitation, the solid particulate additive may be included in the spacer fluids in an amount in the range of from about 10% to about 84.9% by weight of the spacer fluid. For example, the solid particulate additive may be present of about 10%, about 20%, about 30%, about 40%, about 50%, about 60%, about 70%, about 80%, or about 84.9 by weight of the spacer fluid.

[0025] Without limitation, the solid particulate additive and the solid surfactant composite may be dry blended prior to combination with the base fluid to form the spacer fluid. This dry blend may be prepared offsite and then transported to the well site, for example, where it may be combined with the base fluid. By dry blending of the solid particulate additive and the solid surfactant, preparation of the spacer fluid may be simplified as only one solid additive may need to be included in the spacer fluid. In addition, costs may be reduced as transporting of multiple individual solid additives may not be needed if all the solid additives for the spacer fluid are included in the dry blend. The dry blend may include the solid particulate additive (or additives) in an amount of from about 80% to about 99.9%, alternatively, from about 90% to about 99.9%, and alternatively, from about 95% to about 99% by weight of the dry blend. The dry blend may include the solid surfactant composite in an amount of from about 0.1% to about 20%, alternatively, from about 0.1% to about 10%, and alternatively, from about 1% to about 5% by weight of the dry blend.

[0026] A wide variety of additional additives may be included in the spacer fluids as deemed appropriate by one skilled in the art, with the benefit of this disclosure. Examples of such additives include, but are not limited to: viscosifying agents (e.g., clays, hydratable polymers, hydroxyl ethyl cellulose), fluid loss control additives, lost circulation materials, filtration control additives, dispersants, foaming additives, defoamers, corrosion inhibitors, scale inhibitors, and formation conditioning agents. A person having ordinary skill in the art, with the benefit of this disclosure, should readily be able to determine the type and amount of additive useful for a particular application and desired result.

[0027] Suitable spacer fluids may be prepared in accordance with any suitable technique. Without limitation, the desired quantity of water may be introduced into a mixer (e.g., a cement blender) followed by the dry blend. Without limitation, the dry blend may comprise the solid surfactant component and the solid particulate additive, as described herein. Additional liquid additives, if any, may be added to the water as desired prior to, or after, combination with the dry blend. This mixture may be agitated for a sufficient period of time to form a pumpable slurry. By way of example, pumps may be used for delivery of this pumpable slurry into the wellbore. As will be appreciated, the spacer fluid and/or the dry blend may be prepared at the well site or prepared offsite and then transported to the well site. If prepared offsite, the dry blend and/or spacer fluid may be transported to the well site using any suitable mode of transportation, including, without limitation, a truck, railcar, barge, or the like. Alternatively, the spacer fluid and/or dry blend may be formulated at the well site, for example, where the components of the spacer fluid and/or dry blend may be delivered

from a transport (e.g., a vehicle or pipeline) and then mixed prior to placement downhole. As will be appreciated by those of ordinary skill in the art, with the benefit of this disclosure, other suitable techniques for preparing the spacer fluids may be used in accordance with embodiments of the present invention.

[0028] With limitation, the spacer fluid (as described herein) may be used for displacing a first fluid from a wellbore, the wellbore penetrating a subterranean formation. The method may comprise combining components comprising a solid surfactant composite, solid particulate additive, and/or a base fluid to provide a spacer fluid. One or more optional additives may also be included in the spacer fluid as discussed herein. The method may further comprise introducing the spacer fluid into the wellbore to displace at least a portion of the first fluid from the wellbore. Without limitation, the spacer fluid may displace the first fluid from a wellbore annulus, such as the annulus between a pipe string and the subterranean formation or between the pipe string and a larger conduit. Non-limiting examples of the first fluid displaced by the spacer fluid may comprise a drilling fluid. By way of example, the spacer fluid may be used to displace the drilling fluid from the wellbore. In addition to displacement of the drilling fluid from the wellbore, the spacer fluid may also remove the drilling fluid from the walls of the wellbore. Additional steps in the method may include, without limitation, introducing a pipe string into the wellbore, introducing a cement composition into the wellbore with the spacer fluid separating the cement composition and the first fluid.

[0029] As described herein, the spacer fluid may prevent the cement composition from contacting the first fluid, such as a drilling fluid. The spacer fluid may also remove the drilling fluid, dehydrated/gelled drilling fluid, and/or filter cake solids from the wellbore in advance of the cement composition. Removal of these compositions from the wellbore may enhance bonding of the cement composition to surfaces in the wellbore.

[0030] The displaced drilling fluid may include, for example, any number of fluids, such as solid suspensions, mixtures, and emulsions. A non-limiting example of a suitable drilling fluid may comprise an oil-based drilling fluid. An example of a suitable oil-based drilling fluid comprises an invert emulsion. Without limitation, the oil-based drilling fluid may comprise an oleaginous fluid. Examples of suitable oleaginous fluids that may be included in the oil-based drilling fluids include, but are not limited to, α -olefins, internal olefins, alkanes, aromatic solvents, cycloalkanes, liquefied petroleum gas, kerosene, diesel oils, crude oils, gas oils, fuel oils, paraffin oils, mineral oils, low-toxicity mineral oils, olefins,

esters, amides, synthetic oils (e.g., polyolefins), polydiorganosiloxanes, siloxanes, organosiloxanes, ethers, dialkylcarbonates, hydrocarbons, and combinations thereof.

[0031] The cement composition introduced into the wellbore may comprise hydraulic cement and water. A variety of hydraulic cements may be utilized in accordance with the present invention, including, but not limited to, those comprising calcium, aluminum, silicon, oxygen, iron, and/or sulfur, which set and harden by reaction with water. Suitable hydraulic cements include, but are not limited to, Portland cements, pozzolana cements, gypsum cements, high alumina content cements, slag cements, silica cements, and combinations thereof. In certain embodiments, the hydraulic cement may comprise a Portland cement. In some embodiments, the Portland cements may include cements classified as Classes A, C, H, or G cements according to American Petroleum Institute, *API Specification for Materials and Testing for Well Cements*, API Specification 10, Fifth Ed., July 1, 1990. In addition, in some embodiments, the hydraulic cement may include cements classified as ASTM Type I, II, or III.

[0032] As will be appreciated, the solid surfactant composite may be used in a wide variety of subterranean operations, including well cementing operations. An example method may comprise providing a solid surfactant composite comprising a water-wetting surfactant and a solid carrier; mixing components comprising the solid surfactant composite and a base fluid to provide a spacer fluid; and introducing a spacer fluid into a wellbore such that the spacer fluid displaces a drilling fluid in the wellbore. The solid surfactant composite may be spray dried. The solid surfactant composite may further comprise at least one additive selected from the group consisting of a dispersant, a defoaming agent, and any combination thereof. The water-wetting surfactant comprises at least one surfactant selected from the group consisting of an alcohol ethoxylate, an alcohol ethoxysulfate, an alkyl phenol ethoxylate, a glycol ether, and any combination thereof. The water-wetting surfactant may comprise an alcohol ethoxylate, wherein the alcohol ethoxylate comprises C₈ to C₁₂ alcohol ethoxylated with about 4 moles to about 8 moles of ethylene oxide. The solid carrier may comprise amorphous silica, and wherein the solid surfactant composite further comprises a naphthalene sulfonate formaldehyde condensate and a polydimethyl siloxane. The water-wetting surfactant may comprise an alcohol ethoxylate, wherein the alcohol ethoxylate comprises C₁₂ to C₁₄ alcohol ethoxylated with about 10 moles to about 14 moles of ethylene oxide. The solid carrier may comprise amorphous silica and diatomaceous earth, and wherein the solid surfactant composite further comprises a naphthalene sulfonate formaldehyde condensate and a polydimethyl siloxane. The components mixed to prepare the spacer fluid

may further comprise a solid particulate additive, and the mixing comprising mixing a dry blend comprising the solid surfactant and the solid particulate additive with the base fluid. The solid particulate additive comprises at least one solid material selected from the group consisting of a weighting agent, vitrified shale, cement kiln dust, silica flour, bentonite, pumice, fly ash, hematite, hausmannite, barite, calcium carbonate, and any combination thereof. The base fluid may comprise an aqueous-base fluid selected from the group consisting of fresh water, salt water, brine, seawater, and any combination thereof. The spacer fluid may not be emulsified. The spacer fluid may be introduced into a wellbore annulus.

[0033] A composition may be provided that comprises a solid surfactant composite comprising a water-wetting surfactant and a solid carrier; and a solid particulate additive dry blended with the solid surfactant composite. The solid surfactant composite may be spray dried. The solid surfactant composite may further comprise at least one additive selected from the group consisting of a dispersant, a defoaming agent, and any combination thereof. The water-wetting surfactant comprises at least one surfactant selected from the group consisting of an alcohol ethoxylate, an alcohol ethoxysulfate, an alkyl phenol ethoxylate, a glycol ether, and any combination thereof. The water-wetting surfactant may comprise an alcohol ethoxylate, wherein the alcohol ethoxylate comprises C₈ to C₁₂ alcohol ethoxylated with about 4 moles to about 8 moles of ethylene oxide. The solid carrier may comprise amorphous silica, and wherein the solid surfactant composite further comprises a naphthalene sulfonate formaldehyde condensate and a polydimethyl siloxane. The water-wetting surfactant may comprise an alcohol ethoxylate, wherein the alcohol ethoxylate comprises C₁₂ to C₁₄ alcohol ethoxylated with about 10 moles to about 14 moles of ethylene oxide. The solid carrier may comprise amorphous silica and diatomaceous earth, and wherein the solid surfactant composite further comprises a naphthalene sulfonate formaldehyde condensate and a polydimethyl siloxane. The solid particulate additive comprises at least one solid material selected from the group consisting of a weighting agent, vitrified shale, cement kiln dust, silica flour, bentonite, pumice, fly ash, hematite, hausmannite, barite, calcium carbonate, and any combination thereof.

[0034] A system may be provided that may comprise a solid surfactant composite for use in a spacer fluid, wherein the solid surfactant component comprises a water-wetting surfactant and a solid carrier; a base fluid for use in the spacer fluid; and a pump fluid fluidly coupled to a tubular in fluid communication with a wellbore, wherein the tubular is configured to convey the spacer fluid to the wellbore. The system may further comprise a vessel disposed upstream of the pump, wherein the spacer fluid is disposed in the vessel. The

solid surfactant composite may be spray dried. The solid surfactant composite may further comprise at least one additive selected from the group consisting of a dispersant, a defoaming agent, and any combination thereof. The water-wetting surfactant comprises at least one surfactant selected from the group consisting of an alcohol ethoxylate, an alcohol ethoxysulfate, an alkyl phenol ethoxylate, a glycol ether, and any combination thereof. The water-wetting surfactant may comprise an alcohol ethoxylate, wherein the alcohol ethoxylate comprises C₈ to C₁₂ alcohol ethoxylated with about 4 moles to about 8 moles of ethylene oxide. The solid carrier may comprise amorphous silica, and wherein the solid surfactant composite further comprises a naphthalene sulfonate formaldehyde condensate and a polydimethyl siloxane. The water-wetting surfactant may comprise an alcohol ethoxylate, wherein the alcohol ethoxylate comprises C₁₂ to C₁₄ alcohol ethoxylated with about 10 moles to about 14 moles of ethylene oxide. The solid carrier may comprise amorphous silica and diatomaceous earth, and wherein the solid surfactant composite further comprises a naphthalene sulfonate formaldehyde condensate and a polydimethyl siloxane. The components mixed to prepare the spacer fluid may further comprise a solid particulate additive, and the mixing comprising mixing a dry blend comprising the solid surfactant and the solid particulate additive with the base fluid. The solid particulate additive comprises at least one solid material selected from the group consisting of a weighting agent, vitrified shale, cement kiln dust, silica flour, bentonite, pumice, fly ash, hematite, hausmannite, barite, calcium carbonate, and any combination thereof. The base fluid may comprise an aqueous-base fluid selected from the group consisting of fresh water, salt water, brine, seawater, and any combination thereof. The spacer fluid may not be emulsified. The spacer fluid may be introduced into a wellbore annulus.

[0035] Without limitation, methods of using the spacer fluids described herein in well cementing will now be described in more detail with reference to FIGS. 1-3. Any of the embodiments of a spacer fluid described herein may apply in the context of FIGS. 1-3. FIG. 1 illustrates an example system 100 that may be used for preparation and delivery of a spacer fluid downhole. It should be noted that while FIG. 1 generally depicts a land-based operation, those skilled in the art will readily recognize that the principles described herein are equally applicable to subsea operations that employ floating or sea-based platforms and rigs, without departing from the scope of the disclosure. As illustrated on FIG. 1, the system 100 may include a vessel 105 and a pump 110. The pump 110 may be positioned downstream of the vessel 105 and may be fluidly coupled to a tubular 115 that is in fluid communication with the wellbore 120. The tubular 115 may be configured to circulate or otherwise deliver the

spacer fluid to the wellbore 120. The tubular 115 may be comprised, for example, of one or more different pipes that extend into the wellbore 120. The pump 110 may be, for example, one or more high pressure or low pressure pumps, which may be depend on, without limitation, the viscosity and density of the spacer fluid. Without limitation, the pump 110 may draw the spacer fluid from the vessel 105, elevate the spacer fluid to an appropriate pressure, and then introduce the spacer fluid to the tubular 115 for delivery downhole. Without limitation, the vessel 105 and pump 110 may be disposed on one or more cement trucks, for example. While not illustrated, system 100 may further include a recirculating mixer, a batch mixer and/or a jet mixer, which may be used for example, in preparation and/or storage of the spacer fluid. Non-limiting additional components that may be present include, but are not limited to, supply hoppers, valves, condensers, adapters, joints, gauges, sensors, compressors, pressure controllers, pressure sensors, flow rate controllers, flow rate sensors, temperature sensors, and the like.

[0036] FIG. 2 depicts one or more subterranean formations 200 penetrated by wellbore 120 with drilling fluid 205 disposed therein. The drilling fluid 205 may include the example drilling fluids disclosed herein as well as other suitable drilling fluids that will be readily apparent to those of ordinary skill in the art. While the wellbore 120 is shown extending generally vertically into the one or more subterranean formations 200, the principles described herein are also applicable to wellbores that extend at an angle through the one or more subterranean formations 200, such as horizontal and slanted wellbores. As illustrated, the wellbore 120 comprises walls 210. Without limitation, a surface casing 215 may be cemented to the walls 210 of the wellbore 120 by cement sheath 220. Without limitation, one or more additional pipe strings (e.g., intermediate casing, production casing, liners, etc.), shown here as casing 225 may also be disposed in the wellbore 120. As illustrated, there is a wellbore annulus 230 formed between the casing 225 and the walls 210 of the wellbore 120 (and/or a larger conduit such as the surface casing 215). While not shown, one or more centralizers may be attached to the casing 225, for example, to centralize the casing 225 in the wellbore 120 prior to and during the cementing operation.

[0037] As illustrated, a cement composition 235 may be introduced into the wellbore 120. For example, the cement composition 235 may be pumped down the interior of the casing 225. A pump (e.g. pump 110 on FIG. 1) may be used for delivery of the cement composition 235 into the wellbore 120. It may be desired to circulate the cement composition 235 in the wellbore 120 until it is in the wellbore annulus 230. The cement composition 235 may include the example cement compositions disclosed herein as well as other suitable

cement compositions that will be readily apparent to those of ordinary skill in the art. While not illustrated, other techniques may also be utilized for introduction of the cement composition 235. By way of example, reverse circulation techniques may be used that include introducing the cement composition 235 into the wellbore 120 by way of the wellbore annulus 230 instead of through the casing 225.

[0038] Without limitation, the spacer fluid 240 may be used to separate the drilling fluid 205 from the cement composition 235. The previous description with reference to FIG. 1 for preparation of a spacer fluid may be used for delivery of the spacer fluid 240 into the wellbore 120. Moreover, a pump (e.g., pump 110 on FIG. 1) may also be used for delivery of the spacer fluid 240 into the wellbore 120. The spacer fluid 240 may be used with the cement composition 235 for displacement of the drilling fluid 205 from the wellbore 120 as well as preparing the wellbore 120 for the cement composition 235. By way of example, the spacer fluid 240 may function, *inter alia*, to remove the drilling fluid 205, drilling fluid 205 that is dehydrated/gelled, and/or filter cake solids from the wellbore 120 in advance of the cement composition 235. While not shown, one or more plugs or other suitable devices may be used to physically separate the drilling fluid 205 from the spacer fluid 240 and/or the spacer fluid 240 from the cement composition 235.

[0039] Referring now to FIG. 3, the drilling fluid 205 has been displaced from the wellbore annulus 230. As illustrated, the spacer fluid 240 and the cement composition 235 may be allowed to flow down the interior of the casing 225 through the bottom of the casing 225 (e.g., casing shoe 300) and up around the casing 225 into the wellbore annulus 230, thus displacing the drilling fluid 205. At least a portion of the displaced drilling fluid 205 may exit the wellbore annulus 230 via a flow line 125 and be deposited, for example, in one or more retention pits 130 (e.g., a mud pit), as shown in FIG. 1. Turning back to FIG. 3, the cement composition 235 may continue to be circulated until it has reached a desired location in the wellbore annulus 230. The spacer fluid 240 (or a portion thereof) and/or the cement composition 235 may be left in the wellbore annulus 230. As illustrated, the spacer fluid 240 may be disposed in the wellbore annulus 230 above or on top of the cement composition 235. The cement composition 235 may set in the wellbore annulus 230 to form an annular sheath of hardened, substantially impermeable material (i.e., a cement sheath) that may support and position the casing 225 in the wellbore 120.

[0040] The exemplary spacer fluid disclosed herein may directly or indirectly affect one or more components or pieces of equipment associated with the preparation, delivery, recapture, recycling, reuse, and/or disposal of the sugar cane ash and associated spacer fluids.

For example, the spacer fluid (or components thereof) may directly or indirectly affect one or more mixers, related mixing equipment, mud pits, storage facilities or units, composition separators, heat exchangers, sensors, gauges, pumps, compressors, and the like used generate, store, monitor, regulate, and/or recondition the exemplary sugar cane ash and fluids containing the same. The disclosed spacer fluid (or components thereof) may also directly or indirectly affect any transport or delivery equipment used to convey the spacer fluid (or components thereof) to a well site or downhole such as, for example, any transport vessels, conduits, pipelines, trucks, tubulars, and/or pipes used to compositionally move the spacer fluid (or components thereof) from one location to another, any pumps, compressors, or motors (e.g., topside or downhole) used to drive the spacer fluid (or components thereof), into motion, any valves or related joints used to regulate the pressure or flow rate of the spacer fluid, and any sensors (i.e., pressure and temperature), gauges, and/or combinations thereof, and the like. The disclosed spacer fluid may also directly or indirectly affect the various downhole equipment and tools that may come into contact with the spacer fluid such as, but not limited to, wellbore casing, wellbore liner, completion string, insert strings, drill string, coiled tubing, slickline, wireline, drill pipe, drill collars, mud motors, downhole motors and/or pumps, cement pumps, surface-mounted motors and/or pumps, centralizers, turbolizers, scratchers, floats (e.g., shoes, collars, valves, etc.), logging tools and related telemetry equipment, actuators (e.g., electromechanical devices, hydromechanical devices, etc.), sliding sleeves, production sleeves, plugs, screens, filters, flow control devices (e.g., inflow control devices, autonomous inflow control devices, outflow control devices, etc.), couplings (e.g., electro-hydraulic wet connect, dry connect, inductive coupler, etc.), control lines (e.g., electrical, fiber optic, hydraulic, etc.), surveillance lines, drill bits and reamers, sensors or distributed sensors, downhole heat exchangers, valves and corresponding actuation devices, tool seals, packers, cement plugs, bridge plugs, and other wellbore isolation devices, or components, and the like.

EXAMPLES

[0041] 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, or to define, the scope of the invention.

Example 1

[0042] Two solid surfactant composites were prepared in accordance with the following procedures. The solid surfactant composites are identified as Solid Surfactant Composite A (SSCA) and Solid Surfactant Composite B (SSSB).

[0043] The following components were used in preparation of SSCA: 14.9% by weight of isodecyl alcohol with 6 moles of ethylene oxide; 84.2% by weight of naphthalene sulfonate condensed with 6 moles of formaldehyde, 0.45% by weight of a polydimethyl siloxane emulsion, and 0.45% by weight of amorphous silica. First, the isodecyl alcohol was added to the naphthalene sulfonate formaldehyde condensate and mixed until a homogeneous mixture was formed. To this mixture, the polydimethyl siloxane emulsion was added with the resulting mixture stirred until a homogenous mixture was formed. Thereafter, the amorphous silica was added with the resulting mixture spray dried to produce SSCA.

[0044] The following components were used in preparation of SSCB: 20% by weight of naphthalene sulfonate condensed with 6 moles of formaldehyde; 23% by weight of diatomaceous earth; 17% by weight of amorphous silica; 30% by weight of isotridecyl alcohol with 12 moles of ethylene oxide; and 10% by weight of polydimethyl siloxane emulsion. First, the naphthalene sulfonate formaldehyde condensate was mixed in a blender with the diatomaceous earth followed by addition of the amorphous silica. This mixture was mixed until a homogenous mixture was formed. The isotridecyl alcohol was then added to the blender containing this mixture and mixed until homogenous. Next, the polydimethyl siloxane emulsion was added to the blender and mixed until homogenous. Thereafter, the resulting mixture was spray dried to produce SSCB.

Example 2

[0045] The performance of Solid Surfactant Composite A (SSCA) prepared as described in Example 1 was tested in a spacer fluid using a synthetic oil-based mud (OBM) having a density of 12.6 ppg. The OBM and spacer fluid were conditioned at the test temperature for 30 minutes. The spacer fluid and the OBM were mixed in various proportions. The rheology was measured at the test temperature (190 °F) using a FANNTM Model 35 viscometer. The composition of the spacer fluid and the test results are provided below.

Table 1. Spacer Fluid Formulation

Additive	Amount	Fluid Density
Fresh Water	12.6 gps	13.5 ppg
Tune Spacer TM III Blend	27.5 lb/bbl	

Barite	261.69 lb/bbl
D-AIR-5000™ Defoamer	0.5% lb/bbl
Fe-2™ Agent	1 lb/bbl
SSCA	3 g

[0046] In Table 1, the abbreviation “gps” refers to gallons of the additive per 30-pound sack of the Tuned Spacer™ III Blend and the abbreviation “lb/bbl” refers to pounds of the additive per 42 gallon barrel of the spacer fluid. Tuned Spacer™ III Blend is a dry blend available from Halliburton Energy Services, Inc., that comprises from about 60-80 weight % vitrified shale, from about 5-20 weight % sepiolite, from about 5-20 weight % diatomaceous earth, and from about 1-10 weight percent welan gum. Fe-2™ Agent is an organic acid available from Halliburton Services, Inc. D-AIR-5000™ Defoamer is a defoaming additive available from Halliburton Energy Services, Inc.

Table 2

Compatibility of Spacer Fluid with OBM at 190°F							
Spacer Fluid/OBM Ratio	Viscometer Readings						
	300	200	100	60	30	6	30
100:0	70	50	38	30	24	10	8
95:5	78	60	46	38	28	12	10
75:25	108	86	66	52	40	20	12
50:50	120	100	70	56	44	24	14
25:75	126	100	72	62	48	26	16
5:95	82	60	40	28	22	20	12
0:100	80	56	36	30	26	12	8

Example 3

[0047] The performance of Solid Surfactant Composite B (SSCB) prepared as described in Example 1 was tested in a spacer fluid using a synthetic oil-based mud (OBM) having a density of 15.7 ppg. The OBM and spacer fluid were conditioned at the test temperature for 30 minutes. The spacer fluid and the OBM were mixed in various proportions. The rheology was measured at the test temperature (190 °F) using a FANN™ Model 35 viscometer. The composition of the spacer fluid and the test results are provided below.

Table 3. Spacer Fluid Formulation

Additive	Amount	Fluid Density
Fresh Water	6.42 gps	16.7 ppg
Tune Spacer™ III Blend	23.7 lb/bbl	
Barite	440.2 lb/bbl	
D-AIR-5000™ Defoamer	0.5% lb/bbl	
Fe-2™ Agent	1.6 lb/bbl	
SSCB	4 g	

[0048] In Table 3, the abbreviation “gps” refers to gallons of the additive per 30-pound sack of the Tuned Spacer™ III Blend and the abbreviation “lb/bbl” refers to pounds of the additive per 42 gallon barrel of the spacer fluid.

Table 4

Compatibility of Spacer Fluid with OBM at 190°F							
Spacer Fluid/OBM Ratio	Viscometer Readings						
	300	200	100	60	30	6	30
100:0	110	94	72	60	50	28	22
95:5	162	188	102	78	60	36	22
75:25	264	230	200	176	156	120	100
50:50	470	350	266	165	102	62	50
25:75	222	154	92	66	50	44	36
5:95	146	104	60	44	26	10	6
0:100	150	112	66	48	38	24	20

Example 4

[0049] The performance of Solid Surfactant Composite A (SSCA) and Solid Surfactant Composite B (SSCB) prepared as described in Example 1 were further tested in a spacer fluid using a synthetic oil-based mud (OBM) having a density of 15.7 ppg. The OBM and spacer fluid conditioned at the test temperature for 30 minutes. The spacer fluid and the OBM were mixed in various proportions. The rheology was measured at the test temperature (190 °F) using a FANN™ Model 35 viscometer. The composition of the spacer fluid and the test results are provided below.

Table 5. Spacer Fluid Formulation

Additive	Amount	Fluid Density
----------	--------	---------------

Fresh Water	6.42 gps	16.7 ppg
Tune Spacer™ III Blend	23.7 lb/bbl	
Barite	440.2 lb/bbl	
D-AIR-5000™ Defoamer	0.5 lb/bbl	
Fe-2™ Agent	1.6 lb/bbl	
SSCA	5.33 g	
SSCB	5.33 g	

[0050] In Table 5, the abbreviation “gps” refers to gallons of the additive per 30-pound sack of the Tuned Spacer™ III Blend and the abbreviation “lb/bbl” refers to pounds of the additive per 42 gallon barrel of the spacer fluid.

Table 6

Compatibility of Spacer Fluid with OBM at 190°F							
Spacer Fluid/OBM Ratio	Viscometer Readings						
	300	200	100	60	30	6	30
100:0	104	86	66	56	46	34	30
95:5	136	118	90	78	64	46	36
75:25	172	156	120	96	72	50	42
50:50	180	172	130	100	76	52	44
25:75	176	152	104	82	62	42	34
5:95	60	44	28	20	14	8	8
0:100	58	44	28	20	16	10	8

Example 5

[0051] Additional dry surfactant composites were prepared to test the wettability of the dry surfactant composites and their compatibility with an oil-based drilling fluid (OBM). The additional dry surfactants comprised different water-wetting surfactants as provided below:

[0052] Solid Surfactant Composite C (SSCC): Nonylphenol with 10.5 moles of ethylene oxide (Surfactant C)

[0053] Solid Surfactant Composite D (SSCD): Ethoxylated tetradecyl ammonium sulfate (Surfactant D).

[0054] Solid Surfactant Composite E (SSCE): Ethylene glycol monobutyl ether and hexanol with 6 moles of ethylene oxide in weight ratio of 9:1 (Surfactant E).

[0055] To test wettability and compatibility with the OBM's, combinations of the dry surfactant composites in different ratios were included in a spacer fluid and then combined with the OBM.

[0056] The wettability of the solid surfactant composite was tested by including 8.932 lb/bbl of SSCC and 10.556 lb/bbl of SSCE in the spacer fluid. An apparent wettability meter test was used to measure Hogan (HN) readings. The conductivity of the pure spacer fluid and the spacer fluid/OBM combination were determined, Table 7.

Table 7

Starting OBM volume (mL)	Conductivity of Pure Spacer Fluid (Hn)	Conditioning Time (min)	Temp. (°F)	Spacer Vol. Added (mL)	Spacer Fluid (%)	Conductivity (Hn)
200	150	30	135	200	50	200

[0057] The rheological values for different ratios of the spacer fluid to the OBM are provided in Tables 8-10 below. For comparative purposes, the rheological values of the combined spacer fluid/OBM were also determined with no water-wetting surfactant and with a corresponding liquid surfactant.

Table 8

Spacer Fluid/OBM Ratio	3 lb/bbl SSCD with Surfactant D + 3 lb/bbl SSCE with Surfactant E			0.5 gal/bbl Liquid Surfactant D + 0.5 gal/bbl Liquid Surfactant E			No Surfactant		
	30 RPM	60 RPM	100 RPM	30 RPM	60 RPM	100 RPM	30 RPM	60 RPM	100 RPM
100:0	25	28	31	25	29	32	24	27	30
95:5	33	35	37	35	38	41	25	29	32
75:25	29	35	41	32	36	41	38	46	53
50:50	12	17	21	14	16	20	14	21	30
25:75	8	11	14	7	10	14	7	10	14
5:95	5	7	9	5	7	9	5	7	8
0:100	6	7	9	6	8	9	5	7	9

Table 9

Spacer Fluid/OBM Ratio	3 lb/bbl SSCD with Surfactant D + 3 lb/bbl SSC with Surfactant C			0.5 gal/bbl Liquid Surfactant D + 0.5 gal/bbl Liquid Surfactant C			No Surfactant		
	30 RPM	60 RPM	100 RPM	30 RPM	60 RPM	100 RPM	30 RPM	60 RPM	100 RPM
100:0	22	24	27	20	26	30	24	27	30
95:5	28	31	33	21	28	33	25	29	32
75:25	18	23	29	27	34	39	38	46	53
50:50	11	15	19	12	16	20	14	21	30
25:75	7	10	13	6	10	13	7	10	14
5:95	5	7	9	4	7	9	5	7	8
0:100	5	7	9	4	6	8.5	5	7	9

Table 10

Spacer Fluid/OBM Ratio	2 lb/bbl SSCD with Surfactant D + 2 lb/bbl SSC with Surfactant C			0.25 gal/bbl Liquid Surfactant D + 0.25 gal/bbl Liquid Surfactant C			No Surfactant		
	30 RPM	60 RPM	100 RPM	30 RPM	60 RPM	100 RPM	30 RPM	60 RPM	100 RPM
100:0	20	29	32	23	28	33	24	27	30
95:5	26	31	36	32	36	42	25	29	32
75:25	29	35	40	24	32	38	38	46	53
50:50	15	22	27	14	18	21	14	21	30
25:75	9	12	15	9	13	16	7	10	14
5:95	6.5	8	11	8	10	12	5	7	8
0:100	6	7.5	10	7	9	11	5	7	9

[0058] Tables 4-6 inclusion spacer fluid comprising a solid surfactant composite provide comparable drilling fluid compatibility as corresponding liquid surfactants.

[0059] The preceding description provides various embodiments of the spacer fluids containing different additives and concentrations thereof, as well as methods of using the spacer fluids. It should be understood that, although individual embodiments may be discussed herein, the present disclosure covers all combinations of the disclosed

embodiments, including, without limitation, the different additive combinations, additive concentrations, and fluid properties.

[0060] It should be understood that the compositions and methods are described in terms of “comprising,” “containing,” or “including” various components or steps, the compositions and methods can also “consist essentially of” or “consist of” the various components and steps. Moreover, the indefinite articles “a” or “an,” as used in the claims, are defined herein to mean one or more than one of the element that it introduces.

[0061] For the sake of brevity, only certain ranges are explicitly disclosed herein. However, ranges from any lower limit may be combined with any upper limit to recite a range not explicitly recited, as well as, ranges from any lower limit may be combined with any other lower limit to recite a range not explicitly recited, in the same way, ranges from any upper limit may be combined with any other upper limit to recite a range not explicitly recited. Additionally, whenever a numerical range with a lower limit and an upper limit is disclosed, any number and any included range falling within the range are specifically disclosed. In particular, every range of values (of the form, “from about a to about b,” or, equivalently, “from approximately a to b,” or, equivalently, “from approximately a-b”) disclosed herein is to be understood to set forth every number and range encompassed within the broader range of values even if not explicitly recited. Thus, every point or individual value may serve as its own lower or upper limit combined with any other point or individual value or any other lower or upper limit, to recite a range not explicitly recited.

[0062] Therefore, the present invention is well adapted to attain the ends and advantages mentioned as well as those that are inherent therein. The particular embodiments disclosed above are illustrative only, as the present invention may be modified and practiced in different but equivalent manners apparent to those skilled in the art having the benefit of the teachings herein. Furthermore, no limitations are intended to the details of construction or design herein shown, other than as described in the claims below. Also, the terms in the claims have their plain, ordinary meaning unless otherwise explicitly and clearly defined by the patentee. It is therefore evident that the particular illustrative embodiments disclosed above may be altered or modified and all such variations are considered within the scope and spirit of the present invention. If there is any conflict in the usages of a word or term in this specification and one or more patent(s) or other documents that may be incorporated herein by reference, the definitions that are consistent with this specification should be adopted.

CLAIMS

What is claimed is:

1. A method comprising:
 - providing a solid surfactant composite comprising a water-wetting surfactant and a solid carrier;
 - mixing components comprising the solid surfactant composite and a base fluid to provide a spacer fluid; and
 - introducing a spacer fluid into a wellbore such that the spacer fluid displaces a drilling fluid in the wellbore.
2. The method of claim 1, wherein the solid surfactant composite is spray dried.
3. The method of claim 1, wherein the solid surfactant composite further comprise at least one additive selected from the group consisting of a dispersant, a defoaming agent, and any combination thereof.
4. The method of claim 1, wherein the water-wetting surfactant comprises at least one surfactant selected from the group consisting of an alcohol ethoxylate, an alcohol ethoxysulfate, an alkyl phenol ethoxylate, a glycol ether, and any combination thereof.
5. The method of claim 1, wherein the water-wetting surfactant comprises an alcohol ethoxylate, wherein the alcohol ethoxylate comprises C₈ to C₁₂ alcohol ethoxylated with about 4 moles to about 8 moles of ethylene oxide.
6. The method of claim 5, wherein the solid carrier comprises amorphous silica, and wherein the solid surfactant composite further comprises a naphthalene sulfonate formaldehyde condensate and a polydimethyl siloxane.
7. The method of claim 1, wherein the water-wetting surfactant comprises an alcohol ethoxylate, wherein the alcohol ethoxylate comprises C₁₂ to C₁₄ alcohol ethoxylated with about 10 moles to about 14 moles of ethylene oxide.
8. The method of claim 7, wherein the solid carrier comprises amorphous silica and diatomaceous earth, and wherein the solid surfactant composite further comprises a naphthalene sulfonate formaldehyde condensate and a polydimethyl siloxane.

9. The method of claim 1, wherein the components mixed to prepare the spacer fluid further comprise a solid particulate additive, and the mixing comprising mixing a dry blend comprising the solid surfactant and the solid particulate additive with the base fluid.
10. The method of claim 1, wherein the base fluid comprises an aqueous-base fluid selected from the group consisting of fresh water, salt water, brine, seawater, and any combination thereof.
11. The method of claim 1, wherein the spacer fluid is not emulsified.
12. The method of claim 1, wherein spacer fluid is introduced into a wellbore annulus.
13. A composition comprising:
 - a solid surfactant composite comprising a water-wetting surfactant and a solid carrier; and
 - a solid particulate additive dry blended with the solid surfactant composite.
14. The composition of claim 13, wherein the solid surfactant composite is spray dried.
15. The composition of claim 13, wherein the solid surfactant composite further comprise at least one additive selected from the group consisting of a dispersant, a defoaming agent, and any combination thereof.
16. The composition of claim 13, wherein the water-wetting surfactant comprises at least one surfactant selected from the group consisting of an alcohol ethoxylate, an alcohol ethoxysulfate, an alkyl phenol ethoxylate, a glycol ether, and any combination thereof.
17. The composition of claim 13, wherein the water-wetting surfactant comprises an alcohol ethoxylate, wherein the alcohol ethoxylate comprises C₈ to C₁₂ alcohol ethoxylated with about 4 moles to about 8 moles of ethylene oxide, and wherein the solid carrier comprises amorphous silica, and wherein the solid surfactant composite further comprises a naphthalene sulfonate formaldehyde condensate and a polydimethyl siloxane.
18. The composition of claim 13, wherein the water-wetting surfactant comprises an alcohol ethoxylate, wherein the alcohol ethoxylate comprises C₁₂ to C₁₄ alcohol ethoxylated with about 10 moles to about 14 moles of ethylene oxide, and wherein the solid carrier comprises amorphous silica and diatomaceous earth, and wherein the solid surfactant

composite further comprises a naphthalene sulfonate formaldehyde condensate and a polydimethyl siloxane.

19. The composition of claim 13, wherein the solid carrier comprises at least one solid material selected from the group consisting of amorphous silica, diatomaceous earth, and any combination thereof.

20. The composition of claim 13, wherein the solid particulate additive comprises at least one solid material selected from the group consisting of a weighting agent, vitrified shale, cement kiln dust, silica flour, bentonite, pumice, fly ash, hematite, hausmannite, barite, calcium carbonate, and any combination thereof.

21. A system comprising:

- a solid surfactant composite for use in a spacer fluid, wherein the solid surfactant component comprises a water-wetting surfactant and a solid carrier;

- a base fluid for use in the spacer fluid; and

- a pump fluid fluidly coupled to a tubular in fluid communication with a wellbore, wherein the tubular is configured to convey the spacer fluid to the wellbore.

22. The system of claim 21, further comprising a vessel disposed upstream of the pump, wherein the spacer fluid is disposed in the vessel.

1/2

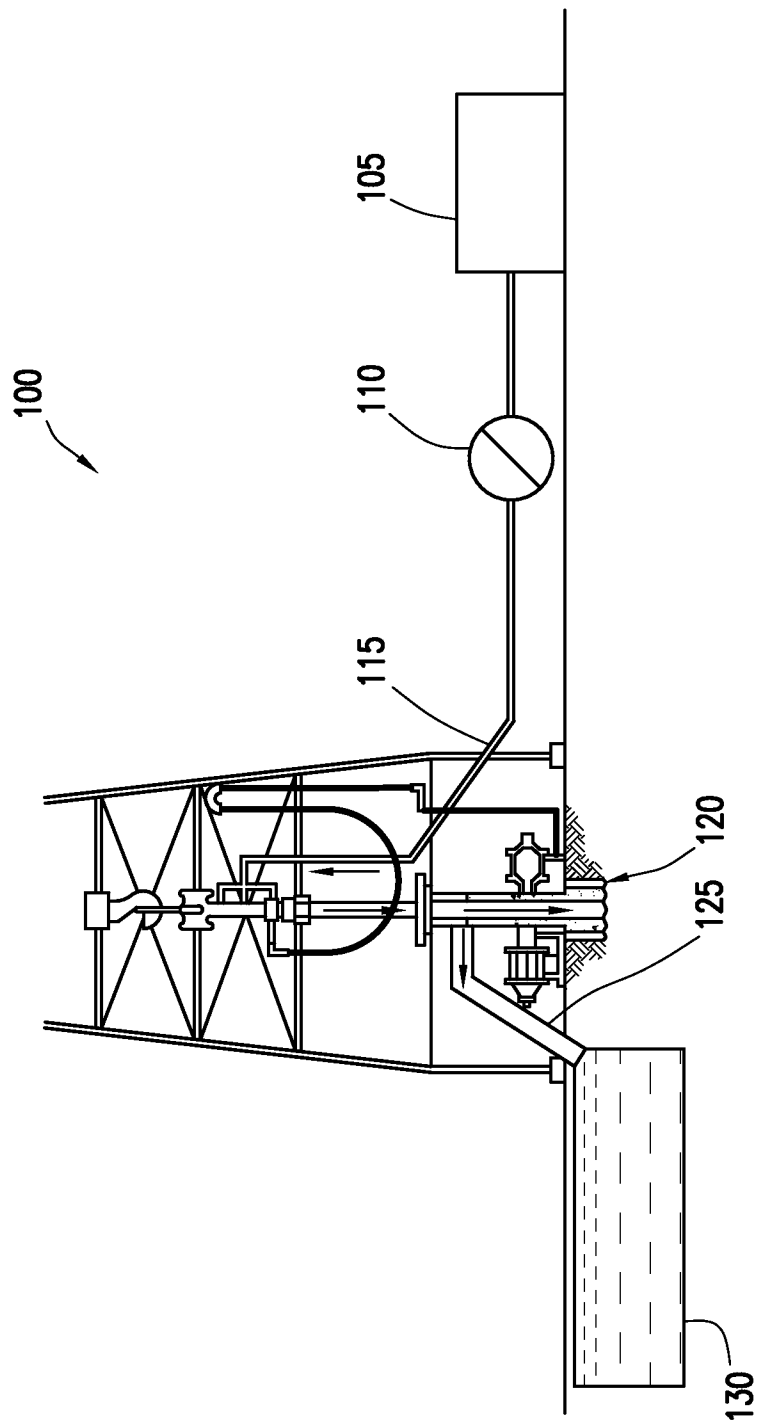


FIG. 1

2/2

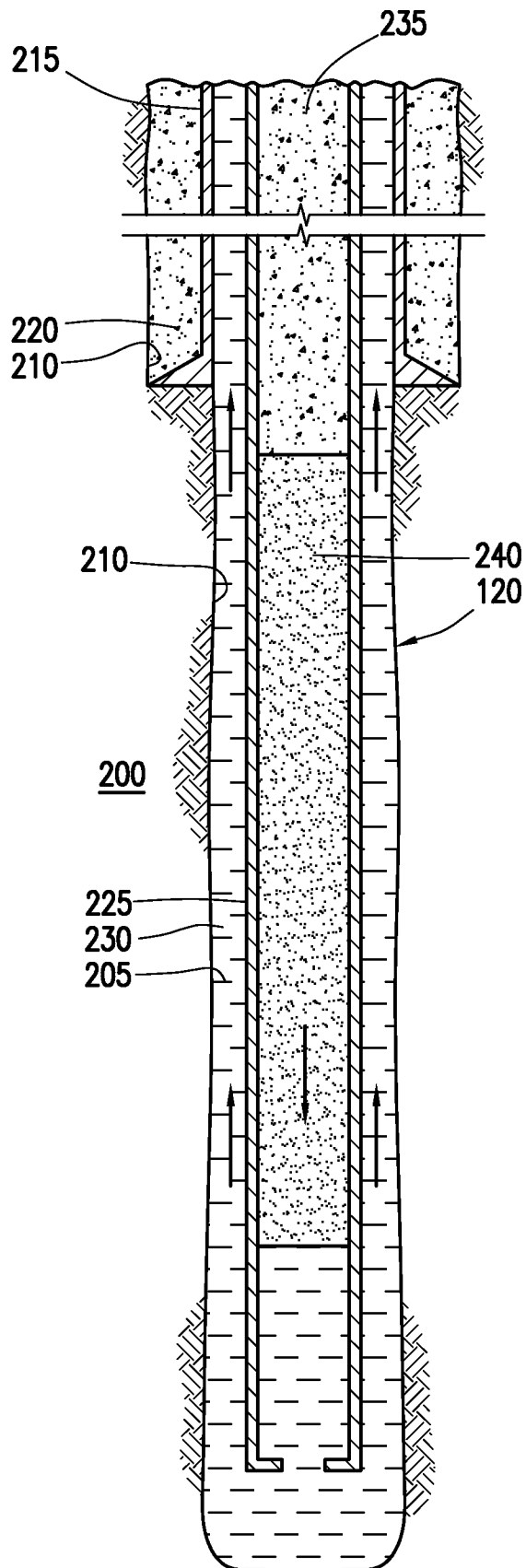


FIG. 2

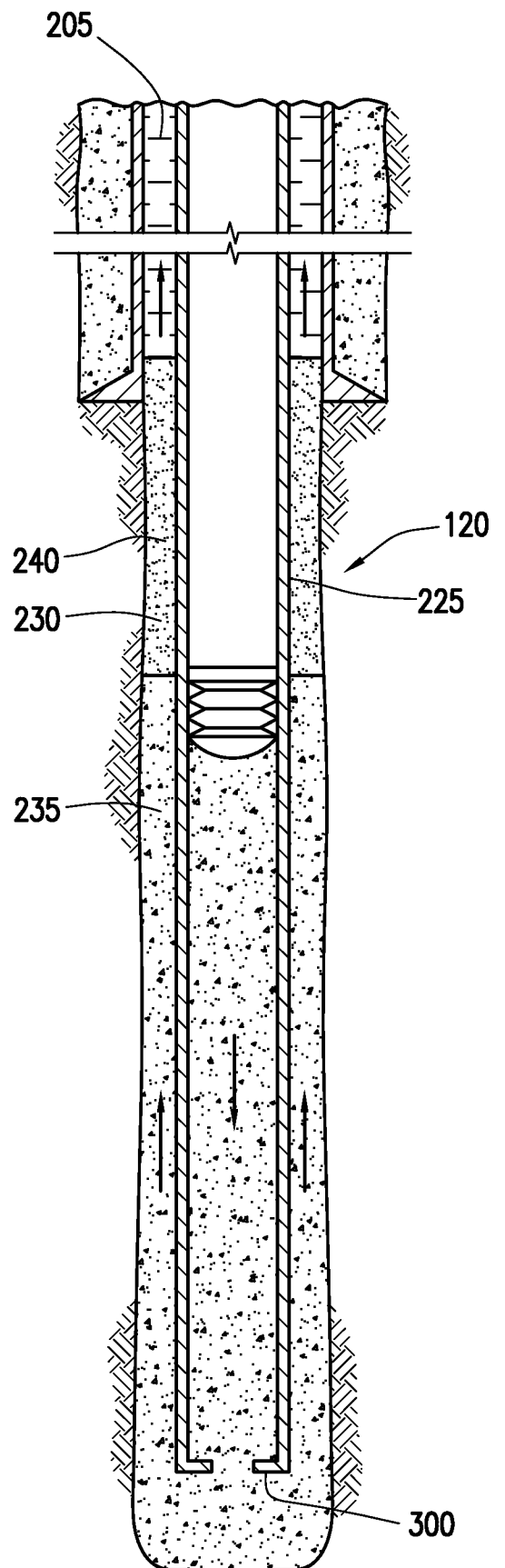


FIG. 3

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2015/057380**A. CLASSIFICATION OF SUBJECT MATTER****E21B 33/13(2006.01)i, C09K 8/42(2006.01)i, C09K 8/02(2006.01)i**

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

E21B 33/13; E21B 33/138; C09K 8/68; C09K 8/46; E21B 37/00; E21B 43/25; E21B 43/16; C09K 8/10; E21B 33/16; C09K 8/42; C09K 8/02

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

Korean utility models and applications for utility models

Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

eKOMPASS(KIPO internal) & Keywords: solid surfactant composite, water-wetting surfactant, solid carrier, spacer fluid, wellbore

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3850248 A (CARNEY, LEROY I.) 26 November 1974 See abstract; column 2, lines 34-44; column 3, lines 27-42; column 4, lines 10-29; column 5, line 33 - column 6, line 19; and claim 1.	1-20
Y		21-22
Y	WO 2015-076845 A1 (HALLIBURTON ENERGY SERVICES, INC.) 28 May 2015 See claims 19-20; and figure 1.	21-22
A	EP 0814232 B1 (HALLIBURTON ENERGY SERVICES, INC. et al.) 03 December 2003 See paragraphs [0038]-[0040]; and claims 1, 8-12.	1-22
A	US 2015-0129217 A1 (BAKER HUGHES INCORPORATED) 14 May 2015 See abstract; paragraphs [0012], [0017]; and claims 1-2, 5-7.	1-22
A	US 6668927 B1 (CHATTERJI, JITEN et al.) 30 December 2003 See abstract; column 4, lines 7-30; and claims 1-6.	1-22



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

19 July 2016 (19.07.2016)

Date of mailing of the international search report

20 July 2016 (20.07.2016)

Name and mailing address of the ISA/KR

International Application Division

Korean Intellectual Property Office

189 Cheongsa-ro, Seo-gu, Daejeon, 35208, Republic of Korea

Facsimile No. +82-42-481-8578

Authorized officer

PARK, Tae Wook

Telephone No. +82-42-481-3405



INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2015/057380

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 3850248 A	26/11/1974	US 03896031 A US 04108779 A US 04233162 A	22/07/1975 22/08/1978 11/11/1980
WO 2015-076845 A1	28/05/2015	None	
EP 0814232 B1	03/12/2003	CA 2208205 A1 CA 2208205 C DE 69726495 D1 DE 69726495 T2 EP 0814232 A2 EP 0814232 A3 NO 972446 A NO 972446 D0 US 5789352 A	19/12/1997 26/04/2005 15/01/2004 27/05/2004 29/12/1997 14/01/1998 22/12/1997 29/05/1997 04/08/1998
US 2015-0129217 A1	14/05/2015	US 9359254 B2 WO 2015-073121 A1	07/06/2016 21/05/2015
US 6668927 B1	30/12/2003	AR 041483 A1 US 2004-0182577 A1 US 2006-0258545 A1 US 6852676 B1 US 7143827 B2 WO 2004-083599 A1 WO 2005-059058 A2 WO 2005-059058 A3	18/05/2005 23/09/2004 16/11/2006 08/02/2005 05/12/2006 30/09/2004 30/06/2005 03/01/2008