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(54) **Title:** COMPOSITIONS AND METHODS FOR CLEANING A WELLBORE PRIOR TO CEMENTING

(57) **Abstract:** Wellbore cleaning compositions comprising water and swellable organically modified silica or glass are useful during cementing operations. The cleaning compositions may be in the form of a spacer fluid or chemical wash, and are designed to remove oily residues from the wellbore wall and the surfaces of tubular bodies such as drillpipe, casing, liner or coiled tubing.



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COMPOSITIONS AND METHODS FOR CLEANING A WELLBORE PRIOR TO CEMENTING

CROSS-REFERENCE TO RELATED APPLICATIONS

[001] This application claims priority to and the benefit from U.S. Provisional Patent Application No. 62/029546, filed July 27, 2014, which is hereby incorporated herein by reference in its entirety.

BACKGROUND

[002] This disclosure relates generally to compositions and methods for treating a subterranean well prior to cementing. More specifically, the present disclosure relates to compositions and methods for cleaning casing and wellbore surfaces with fluids containing a swellable organically modified silica or glass.

[003] Some statements may merely provide background information related to the present disclosure and may not constitute prior art.

[004] During the construction of subterranean wells, it is common, during and after drilling, to place a tubular body in the wellbore. The tubular body may comprise drillpipe, casing, liner, coiled tubing or combinations thereof. The purpose of the tubular body is to act as a conduit through which desirable fluids from the well may travel and be collected. The tubular body is normally secured in the well by a cement sheath. The cement sheath provides mechanical support and hydraulic isolation between the zones or layers that the well penetrates. The latter function is important because it prevents hydraulic communication between zones that may result in contamination. For example, the cement sheath blocks fluids from oil or gas zones from entering the water table and polluting drinking water. In addition, to optimize a well's production efficiency, it may be desirable to isolate, for example, a gas-producing zone from an oil-producing zone. The cement sheath achieves hydraulic isolation because of its low permeability. In addition, intimate bonding between the cement sheath and both the tubular body and borehole is necessary to prevent leaks.

[005] The cement sheath is usually placed in the annular region between the outside of the tubular body and the subterranean borehole wall by pumping the cement slurry down the interior of the tubular body, out the bottom and up into the annulus. The cement slurry may also be placed by the "reverse cementing" method, whereby the slurry is pumped directly down into the annular space. During the cementing process, the cement slurry is frequently preceded by a spacer fluid or chemical wash to prevent commingling with drilling fluid in the wellbore. These fluids also help clean the tubular-body and formation surfaces, promoting better cement bonding and zonal isolation. The cement slurry may also be followed by a displacement fluid such as water, a brine or drilling fluid. This fluid usually resides inside the tubular body after the cementing process is complete. A complete description of the cementing process and the use of spacer fluids and chemical washes is presented in the following publications. Piot B and Cuvillier G: "Primary Cementing Techniques," in Nelson EB and Guillot D (eds.): *Well Cementing—2nd Edition*, Houston, Schlumberger (2006) 459–501. Daccord G, Guillot D and Nilsson F: "Mud Removal," in Nelson EB and Guillot D (eds.): *Well Cementing—2nd Edition*, Houston, Schlumberger (2006) 143–189.

[006] The use of non-aqueous fluids (NAF) as drilling fluids is widespread in many areas for a variety of reasons, including excellent shale inhibition, high rates of penetration and high lubricity. NAF-base drilling fluids generally comprise invert emulsion fluids, where the continuous or external phase is predominantly organic (e.g., mineral oil or synthetic oil), and the inverse or internal phase may be aqueous (e.g., brines). The stability of invert emulsions is generally maintained by one or more additives present in the fluid, such as emulsifiers, emulsion stabilizing agents, and oil-wetting agents. NAFs also include diesel, mineral oil and non-water base solvents.

[007] When drilling is performed with NAFs, the wellbore becomes oil-wet. Prior to cementing, the casing also becomes oil-wet while being run into the hole. This condition commonly results in poor bonding between the set cement and the casing and wellbore surfaces. Poor cement bonding may compromise the hydraulic seal in the annulus, potentially resulting in fluid communication between subterranean zones. Therefore, to ensure successful cementing, two conditions are desirable: (1) the NAF is effectively

removed from the borehole; and (2) the wellbore-wall and casing surfaces are water-wet. Failure to satisfy Condition 1 may cause contamination of the cement slurry, and the cement performance may suffer. Failure to satisfy Condition 2 may lead to poor bonding between the cement and the borehole-wall and casing surfaces.

[0008] Despite efforts to prepare the borehole properly prior to cementing, Cement Bond Logs (CBL) commonly reveal poor or no bonding, or poor-quality cement behind casing. Current solutions to achieve mud removal and water wetting include pumping fluids that separate the cement slurry from the drilling fluid. The fluid may be a single-stage, viscous, water-base spacer that contains surfactants with strong water-wetting tendencies. Or, a two-stage spacer system may be pumped that comprises base oil, solvents, or water-base chemical washes with surfactants, in combination with a viscous water-base spacer that contains water-wetting surfactants.

SUMMARY

[0009] This summary is provided to introduce a selection of concepts that are further described below in the detailed description. This summary is not intended to identify key or essential features of the claimed subject matter, nor is it intended to be used as an aid in limiting the scope of the claimed subject matter.

[0010] The present disclosure describes improved compositions for removing NAFs from wellbore and tubular-body surfaces. Aqueous fluids including spacer fluids, chemical washes, drilling fluids and cement slurries are provided that are compatible with NAFs and have the ability to remove them from a wellbore during a cementing treatment.

[0011] In an aspect, embodiments relate to compositions comprising water and a swellable organically modified silica or glass.

[0012] In a further aspect, embodiments relate to methods for cleaning a subterranean well having a borehole having an oily residue thereon. A composition is prepared that comprises water and a swellable organically modified silica or glass. The composition is circulated in the wellbore such that the composition contacts the wellbore wall. The composition is then allowed to remove the oily residue from the wellbore wall.

[0013] In yet a further aspect, embodiments relate to methods for cementing a subterranean well having a borehole wall having an oily residue thereon. A composition is prepared that comprises water and a swellable organically modified silica or glass. The composition is circulated in the wellbore such that the composition contacts the wellbore wall. The composition is then allowed to remove the oily residue from the wellbore wall. A cement slurry is prepared that comprises water and an inorganic cement. The cement slurry is then placed in the wellbore such that the composition is displaced.

DETAILED DESCRIPTION

[0014] At the outset, it should be noted that in the development of any such actual embodiment, numerous implementation—specific decisions are made to achieve the developer's specific goals, such as compliance with system related and business related constraints, which will vary from one implementation to another. Moreover, it will be appreciated that such a development effort might be complex and time consuming but would nevertheless be a routine undertaking for those of ordinary skill in the art having the benefit of this disclosure. In addition, the composition used/disclosed herein can also comprise some components other than those cited. In the summary of the disclosure and this detailed description, each numerical value should be read once as modified by the term "about" (unless already expressly so modified), and then read again as not so modified unless otherwise indicated in context. The term about should be understood as any amount or range within 10% of the recited amount or range (for example, a range from about 1 to about 10 encompasses a range from 0.9 to 11). Also, in the summary and this detailed description, it should be understood that a concentration range listed or described as being useful, suitable, or the like, is intended that any concentration within the range, including the end points, is to be considered as having been stated. For example, "a range of from 1 to 10" is to be read as indicating each possible number along the continuum between about 1 and about 10. Furthermore, one or more of the data points in the present examples may be combined together, or may be combined with one of the data points in the specification to create a range, and thus include each possible value or

number within this range. Thus, even if specific data points within the range, or even no data points within the range, are explicitly identified or refer to a few specific, it is to be understood that inventors appreciate and understand that any data points within the range are to be considered to have been specified, and that inventors possessed knowledge of the entire range and the points within the range.

[0015] In an aspect, embodiments relate to compositions comprising water and a swellable organically modified silica or glass.

[0016] In a further aspect, embodiments relate to methods for cleaning a subterranean well having a borehole having an oily residue thereon. A composition is prepared that comprises water and a swellable organically modified silica or glass. The composition is circulated in the wellbore such that the composition contacts the wellbore wall. The composition is then allowed to remove the oily residue from the wellbore wall. The swellable organically modified silica or glass particles do not swell in water, thereby allowing them to be added to an aqueous fluid and subject to swelling when they are exposed to a hydrocarbon in the well.

[0017] The well may further comprise at least one tubular body having surfaces with an oily residue thereon, and circulating the composition in the well removes the oily residue from the surfaces.

[0018] The tubular body may comprise drillpipe, casing, liner or coiled tubing or a combination thereof.

[0019] In yet a further aspect, embodiments relate to methods for cementing a subterranean well having a borehole wall having an oily residue thereon. A composition is prepared that comprises water and a swellable organically modified silica or glass. The composition is circulated in the wellbore such that the composition contacts the wellbore wall. The composition is then allowed to remove the oily residue from the wellbore wall. The particles swell upon exposure to the oily residue and, in so doing, entrap and carry the residue away from the borehole wall. A cement slurry is prepared that comprises water and an inorganic cement. The cement slurry is then placed in the wellbore such that the composition is displaced.

[0020] The well may further comprise at least one tubular body having surfaces with an oily residue thereon, and circulating the composition in the well removes the oily residue from the surfaces.

[0021] The tubular body may comprise drillpipe, casing, liner or coiled tubing or a combination thereof.

[0022] The inorganic cement may comprise portland cement, calcium aluminate cement, fly ash, blast furnace slag, lime-silica blends, zeolites, geopolymers or chemically bonded phosphate ceramics or combinations thereof.

[0023] The cement slurry may be placed during a primary or remedial cementing operation.

[0024] For each aspect, the swellable organically modified silica or glass (SOMS) may comprise OSORB™, marketed by Absorbent Materials Company LLC of Wooster, Ohio, USA. The OSORB™ material may rapidly swell to about 5 to about 10 times its original amount when contacted by a hydrocarbon fluid. The SOMS may be a hydrophobic material that selectively absorbs non-polar liquids. The swelling process may be reversible allowing the SOMS to serve a type of “sponge-like” material for various other materials. Examples of SOMS are described in U.S. Patent Application Pub. No. 2010/0096334 and U.S. Patent No. 7,790,830, the disclosures of which are incorporated by reference herein in their entirety.

[0025] For each aspect, the swellable organically modified silica or glass may be present in the composition at a concentration between 0.1 vol% and 20 vol%, or between 0.1 vol% and 10 vol% or between 0.1 vol% and 5 vol%.

[0026] For each aspect, the composition may be a spacer fluid, and further comprise silica flour, barite, hematite, ilmenite, manganese tetraoxide, fly ash, blast furnace slag, glass microspheres, ceramic microspheres or nitrogen or combinations thereof.

[0027] For each aspect, the composition may be a chemical wash or a scavenger slurry. Chemical washes are fluids having a density and viscosity close to that of water. They may contain surfactants that help clean wellbore and casing surfaces. Scavenger slurries

are dilute suspensions of cement in water, and frequently contain water soluble polymer thickeners, surfactants and salts.

EXAMPLE 1

[0028] The following example serves to further illustrate the disclosure.

[0029] A rotor test is conducted to evaluate the ability of treatment-fluid compositions to remove a SBM/OBM fluid from casing surfaces. The test equipment is a Chan 35™ rotational rheometer, available from Chandler Engineering, Tulsa, OK, USA. The rheometer is equipped with an 85-mm diameter cup for tests conducted at 25°C. A closed rotor, 73.30 mm long and 40.70 mm in diameter, is employed to simulate the casing surface. The rotor has a sand blasted stainless-steel surface with an average roughness of 1.4 micrometers.

[0030] A base spacer fluid is prepared that comprises water, a viscosifier, and antifoam agent and optionally a dispersant. The viscosifier may be bentonite, a water soluble polymer a mixed metal hydroxide or a combination thereof. The antifoam agent may be a silicone or polypropylene glycol or a combination thereof. The dispersant may be a sulfonated aromatic polymer such as polynaphthalene sulfonate, polymelamine sulfonate and the like. An example of such a fluid is MUDPUSH™ spacer fluid, available from Schlumberger.

[0031] An 80/20 oil/water emulsion (SBM), obtained from a field location, is provided.

[0032] The rotor is lowered into the SBM and allowed to remain stationary for 10 min. When the rotor is removed, a smooth and homogenous layer of drilling fluid will cover the rotor. The rotor is allowed to remain stationary for 2 min to allow excess SBM to drip off. Then the rotor is placed in a test fluid and rotated at 100 RPM for 2 min. After the rotation period the rotor is removed and visually inspected for SBM remaining on the rotor surface.

[0033] Two fluids are prepared: the base spacer only and the base spacer plus 5 vol% OSORB™ particles.

[0034] The first fluid in which the rotor is lowered is the base spacer. After the rotation period and the removal of the rotor, SBM will be observed coating the rotor surface. The rotor is weighed to determine how much SBM has been removed.

[0035] The rotor is cleaned and then lowered into the second fluid: the base spacer plus OSORB™ particles. After the rotation period and the removal of the rotor, less SBM or no SBM will be observed coating the rotor surface. The rotor weight will be lower than that measured when the rotor was immersed in the first fluid.

[0036] Although the preceding description has been described herein with reference to particular means, materials and embodiments, it is not intended to be limited to the particulars disclosed herein; rather, it extends to all functionally equivalent structures, methods and uses, such as are within the scope of the appended claims.

CLAIMS

1. A composition, comprising:
(i) water; and
(ii) a swellable organically modified silica or glass.
2. The composition of claim 1, wherein the composition is a spacer fluid.
3. The composition of claim 1, wherein the composition further comprises silica flour, barite, hematite, ilmenite, manganese tetraoxide, fly ash, blast furnace slag, glass microspheres, ceramic microspheres or nitrogen or combinations thereof.
4. The composition of claim 1, wherein the composition is a chemical wash or a scavenger slurry.
5. The composition of claim 1, wherein the swellable organically modified silica or glass is present at a concentration between 0.1 and 20 volume percent.
6. A method for cleaning a subterranean well having a borehole wall having an oily residue thereon, comprising:
(i) preparing a composition comprising water and a swellable organically modified silica or glass;
(ii) circulating the composition in the wellbore such that the composition contacts the wellbore wall; and
(iii) allowing the composition to remove the oily residue from the wellbore wall.
7. The method of claim 6, wherein the well further comprises at least one tubular body having surfaces with an oily residue thereon, and circulating the composition in the well removes the oily residue from the surfaces.
8. The method of claim 7, wherein the tubular body comprises drillpipe, casing, liner or coiled tubing or a combination thereof.
9. The method of claim 6, wherein the composition is a spacer fluid.
10. The method of claim 6, wherein the composition further comprises silica flour, barite, hematite, ilmenite, manganese tetraoxide, fly ash, blast furnace slag, glass microspheres, ceramic microspheres or nitrogen or combinations thereof.
11. The method of claim 6, wherein the composition is a chemical wash or a scavenger slurry.

12. A method for cementing a subterranean well having a borehole wall having an oily residue thereon, comprising:
 - (i) preparing a composition comprising water and a swellable organically modified silica or glass;
 - (ii) circulating the composition in the wellbore such that the composition contacts the wellbore wall;
 - (iii) allowing the composition to remove oily residue from the wellbore wall;
 - (iv) preparing a cement slurry comprising water and an inorganic cement; and
 - (v) placing the cement slurry in the wellbore such that the composition is displaced.
13. The method of claim 12, wherein the well further comprises at least one tubular body having surfaces with an oily residue thereon, and circulating the composition in the well removes the oily residue from the surfaces.
14. The method of claim 13, the tubular body comprises drillpipe, casing, liner or coiled tubing or a combination thereof.
15. The method of claim 12, wherein the composition is a spacer fluid.
16. The method of claim 12, wherein the composition further comprises silica flour, barite, hematite, ilmenite, manganese tetraoxide, fly ash, blast furnace slag, glass microspheres, ceramic microspheres or nitrogen or combinations thereof.
17. The method of claim 12, wherein the composition is a chemical wash or a scavenger slurry.
18. The method of claim 12, wherein the inorganic cement comprises portland cement, calcium aluminate cement, fly ash, blast furnace slag, lime-silica blends, zeolites, geopolymers or chemically bonded phosphate ceramics or combinations thereof.
19. The method of claim 12, wherein the cement slurry is placed during a primary cementing operation.
20. The method of claim 12, wherein the cement slurry is placed during a remedial cementing operation.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2015/042001**A. CLASSIFICATION OF SUBJECT MATTER****C09K 8/42(2006.01)i, C09K 8/46(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)

C09K 8/42; A61F 13/53; B09B 5/00; C08K 5/01; E21B 43/22; C08L 83/04; E21B 33/13; C02F 5/10; E21B 43/08; C09K 8/50; C09K 8/46

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: water, swellable organically modified silica, glass, oil-swellable, tubular, cement, bridging group, clean, remove, crude oil

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 2014-011071 A1 (SCHLUMBERGER CANADA LIMITED et al.) 16 January 2014 See paragraph [0015]; and claims 1-11.	1-20
Y	US 2010-0113856 A1 (EDMISTON, PAUL L.) 06 May 2010 See paragraph [0051]; and claims 1-4.	1-20
A	WO 2014-011546 A1 (M-I L.L.C.) 16 January 2014 See paragraphs [0001], [0009], [0016] and [0020]-[0025]; and claims 1-6.	1-20
A	US 2009-0171308 A1 (FOSSUM, RENAE DIANNA et al.) 02 July 2009 See paragraph [0118]; and claim 1.	1-20
A	US 4359545 A (ONA, ISAO et al.) 16 November 1982 See abstract; column 3, lines 23-27; and claim 1.	1-20



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:

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"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

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Information on patent family members

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