Abstract:

A cement for use in wells in which hydrogen sulfide is present, comprises elastomer particles. In the event of cement-matrix failure, or bonding failure between the cement/casing interface or the cement/borehole-wall interface, the elastomer particles swell when contacted by hydrogen sulfide. The swelling seals voids in the cement matrix, or along the bonding interfaces, thereby restoring zonal isolation.

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METHODS FOR MAINTAINING ZONAL ISOLATION IN A SUBTERRANEAN WELL

BACKGROUND

[0001] The statements in this section merely provide background information related to the present disclosure and may not constitute prior art.

[0002] This disclosure relates to compositions and methods for treating subterranean formations, in particular, compositions and methods for cementing and completing wells into which carbon dioxide is injected, stored or extracted.

[0003] 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.

[0004] 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. However, over time the cement sheath can deteriorate and become permeable. Alternatively, the bonding between the
cement sheath and the tubular body or borehole may become compromised. The principal causes of deterioration and debonding include physical stresses associated with tectonic movements, temperature changes, pressure changes inside the casing and chemical deterioration of the cement.

[0005] Some oil and gas fields have formations whose fluids contain acid gases such as carbon dioxide and hydrogen sulfide. Such wells may be challenging from a zonal isolation point of view.

[0006] Oil and gas that contains elevated amounts of hydrogen sulfide are called "sour." It has been estimated that 15 to 25% of natural gas in the United States may contain hydrogen sulfide. Worldwide, the percentage could be as high as 30%. Hydrogen sulfide is a toxic substance; therefore, it is important to prevent it from escaping through the cement sheath into aquifers or to the surface. Furthermore, hydrogen sulfide is corrosive to steel, and maintaining a competent cement sheath is essential to prevent casing deterioration during the life of the well.

SUMMARY

[0007] The present disclosure presents improvements by describing compositions that form a sustainable cement sheath even in a hydrogen-sulfide environment, and methods by which they may be prepared and applied in subterranean wells.

[0008] In an aspect, embodiments relate to methods for maintaining zonal isolation in a subterranean well having a borehole in which hydrogen sulfide is present. A tubular body is installed inside the borehole of a well, or inside a previously installed
tubular body. An aqueous cement slurry, containing a material that swells when contacted by hydrogen sulfide, is pumped into the borehole. The cement slurry is allowed to set and harden. In the event of cement-matrix or bonding failure, the set cement is exposed to wellbore fluids that contain hydrogen sulfide. The material is allowed to swell, thereby restoring zonal isolation.

[0009] In a further aspect, embodiments relate to methods for cementing a subterranean well having a borehole in which hydrogen sulfide is present. A tubular body is installed inside the borehole of a well, or inside a previously installed tubular body. An aqueous cement slurry, containing a material that swells when contacted by hydrogen sulfide, is pumped into the borehole. The cement slurry is allowed to set and harden. In the event of cement-matrix or bonding failure, the set cement is exposed to wellbore fluids that contain hydrogen sulfide. The material is allowed to swell, thereby restoring zonal isolation.

[0010] In yet a further aspect, embodiments relate to methods for completing a subterranean well having a borehole in which hydrogen sulfide is present. A tubular body is installed inside the borehole of a well, or inside a previously installed tubular body. An aqueous cement slurry, containing a material that swells when contacted by hydrogen sulfide, is pumped into the borehole. The cement slurry is allowed to set and harden. In the event of cement-matrix or bonding failure, the set cement is exposed to wellbore fluids that contain hydrogen sulfide. The material is allowed to swell, thereby restoring zonal isolation.
DETAILED DESCRIPTION

[0011] At the outset, it should be noted that in the development of any such actual embodiment, numerous implementation—specific decisions must be 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 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. 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 and every 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 and every possible number along the continuum between about 1 and about 10. Thus, even if specific data points within the range, or even no data points within the range, are explicitly identified or refer to only a few specific, it is to be understood that the Applicant appreciate and understands that any and all data points within the range are to be considered to have been specified, and that the Applicant possessed knowledge of the entire range and all points within the range.

[0012] Cement systems that form durable cement sheath in an environment
containing hydrogen sulfide would be positively received by the industry. The Applicant has determined that cement compositions comprising materials that swell in the presence of hydrogen sulfide would respond to the industry challenges. When incorporated into a cement composition, such hydrogen sulfide swelling compounds may enable the cement sheath to close its own voids and/or cracks that may appear.

[0013] The Applicant has determined that certain elastomers may fulfill the required swellable capacity in the presence of hydrogen sulfide. Such elastomers comprise fluorinated elastomers, ethylene-propylene copolymers and combinations thereof.

[0014] In an aspect, embodiments relate to methods for maintaining zonal isolation in a subterranean well having a borehole, in which hydrogen sulfide is present. A tubular body is installed inside the borehole of a well, or inside a previously installed tubular body. An aqueous cement slurry, containing a material that swells when contacted by hydrogen sulfide, is pumped into the borehole. The cement slurry is allowed to set and harden. In the event of cement-matrix or bonding failure, the set cement is exposed to wellbore fluids that contain hydrogen sulfide. The material is allowed to swell, thereby restoring zonal isolation.

[0015] In a further aspect, embodiments relate to methods for cementing a subterranean well having a borehole, in which hydrogen sulfide is present. A tubular body is installed inside the borehole of a well, or inside a previously installed tubular body. An aqueous cement slurry, containing a material that swells when contacted by hydrogen sulfide, is pumped into the borehole. The cement slurry is allowed to set and harden. In the event of cement-matrix or bonding failure, the set cement is exposed to
wellbore fluids that contain hydrogen sulfide. The material is allowed to swell, thereby restoring zonal isolation.

[0016] In yet a further aspect, embodiments relate to methods for completing a subterranean well having a borehole, in which hydrogen sulfide is present. A tubular body is installed inside the borehole of a well, or inside a previously installed tubular body. An aqueous cement slurry, containing a material that swells when contacted by hydrogen sulfide, is pumped into the borehole. The cement slurry is allowed to set and harden. In the event of cement-matrix or bonding failure, the set cement is exposed to wellbore fluids that contain hydrogen sulfide. The material is allowed to swell, thereby restoring zonal isolation.

[0017] For all aspects, the borehole penetrates at least one fluid-containing reservoir, the reservoir containing fluid with a hydrogen sulfide concentration greater than about 5 moles per liter of fluid. The hydrogen sulfide may be supercritical, wet, dry or dissolved in oil or water.

[0018] For all aspects, the material may be a fluorinated elastomer, an ethylene-propylene copolymer or a combination thereof. The concentration of the material may be between about 5% and 50% by volume of solids in the cement slurry, also known as "by volume of blend (BVOB)." Or the range may be between about 10% and 40% BVOB. For optimal performance, the particle-size distribution of the material may be such that the average particle size is between about 10 µm and about 1000 µm. The average particle size may also be between about 100 µm and 900 µm.

[0019] Example fluorinated elastomers may comprise FKM elastomers as defined by ASTM D1418. FKM elastomers may comprise polyvinyl fluoride,
polyvinylidene fluoride, polyhexafluoropropylene, polytetrafluoroethylene, polychlorotrifluoroethylene, perfluoroalkoxy polymers, fluorinated ethylene-propylene, polyethylenetetrafluoroethylene, polyethylenechlorotrifluoroethylene and perfluoromethylvinylether. Other example fluorinated elastomers may comprise perfluoroelastomers, which are given the designation FFKM in the elastomer industry. FFKM elastomers are fully fluorinated and may comprise commercial elastomers that include KALREZ™, AFLAS™, TECNOFLON™, VITON™ and NAFION™.

[0020] Persons skilled in the art will recognize that the present use of elastomers is different and distinct from their use as cement extenders (i.e., to reduce the amount of cement or to reduce the cement-slurry density) or as materials to improve cement flexibility.

[0021] For all aspects, the cement may additionally comprise one or more members of the list comprising Portland cement, calcium aluminate cement, fly ash, blast furnace slag, lime-silica blends, zeolites, geopolymers, Sorel cements or chemically bonded phosphate ceramics, and mixtures thereof. The composition shall be pumpable. Those skilled in the art will recognize that a pumpable fluid in the context of well cementing has a viscosity lower than about 1000 mPa-s at a shear rate of 100 s⁻¹ at the temperatures to which the fluid is exposed during a cementing operation, and during the time necessary to place the composition in the well. Also, the tubular body may comprise one or more members of the list comprising drillpipe, casing, liner and coiled tubing. In addition, the borehole may penetrate at least one fluid-containing reservoir, the reservoir preferably containing fluid with a hydrogen sulfide concentration greater than about five moles per liter.
The cement slurry may further comprise dispersing agents, fluid-loss-control agents, set retarders, set accelerators, foaming agents, gas generating agents, antifoaming agents, extenders, weighting agents, lost-circulation control agents and combinations thereof. Other compounds may also be present such as coal, petroleum coke, graphite or gilsonite and mixtures thereof. Further, the hydrogen sulfide swellable elastomers may be coupled to water super absorbent polymers such as those described in EP 1623089 incorporated herein in its entirety. A further association may be with one or more compounds from the list comprising an aqueous inverse emulsion of polymer comprising a betaine group, poly-2, 2, 1-bicyclo heptene (polynorbornene), alkylstyrene, crosslinked substituted vinyl acrylate copolymers, diatomaceous earth, natural rubber, vulcanized rubber, polyisoprene rubber, vinyl acetate rubber, polychloroprene rubber, acrylonitrile butadiene rubber, hydrogenated acrylonitrile butadiene rubber, ethylene propylene diene monomer, ethylene propylene monomer rubber, styrene-butadiene rubber, styrene/propylene/diene monomer, brominated poly(isobutylene-co-4-methylstyrene), butyl rubber, chlorosulphonated polyethylenes, polyacrylate rubber, polyurethane, silicone rubber, brominated butyl rubber, chlorinated butyl rubber, chlorinated polyethylene, epichlorohydrin ethylene oxide copolymer, ethylene acrylate rubber, ethylene propylene diene terpolymer rubber, sulphonated polyethylene, fluoro silicone rubbers, fluoroelastomers, substituted styrene acrylate copolymers and bivalent cationic compounds or any other particles such as those described in WO2004/101951 that swells when exposed to liquid hydrocarbons, the international application being incorporated herein by reference in its entirety. Further combinations may be made with thermoplastic block polymers including for example styrene-isoprene-styrene (SIS),
styrene-butadiene-styrene (SBS) and mixtures thereof.

[0023] The cement slurry may further comprise materials that swell in the presence of another acid gas. The materials may be an elastomer comprising chlorofluorocarbons, tetrafluoroethylene-propylene copolymers, ethylene-propylene copolymers, isobutene-isoprene rubbers, nitrile rubbers, hydrogenated nitrile butadiene rubbers, or tetrafluoroethylene-perfluorovinyl methyl ether copolymers and combinations thereof.

[0024] Persons skilled in the art will recognize that these methods may be performed during a primary cementing operation or a remedial cementing operation. The primary cementing operation may be performed the traditional way (i.e., the slurry is pumped down the casing and up the annulus) or by "reverse cementing," which consists of pumping the slurry down the annulus.
CLAIMS

1. A method for maintaining zonal isolation in a subterranean well having a borehole in which hydrogen sulfide is present, comprising:
   (i) installing a tubular body inside the borehole of the well, or inside a previously installed tubular body;
   (ii) pumping an aqueous cement slurry comprising a material that swells when contacted by hydrogen sulfide into the borehole;
   (iii) allowing the cement slurry to set and harden;
   (iv) in the event of cement-matrix or bonding failure, exposing the set cement to wellbore fluids that contain hydrogen sulfide; and
   (v) allowing the material to swell, thereby restoring zonal isolation.

2. The method of claim 1, wherein the material comprises a fluorinated elastomer, or an ethylene-propylene copolymer or a combination thereof.

3. The method of claim 1, wherein the concentration of the material in the cement slurry is between about 5 percent and about 50 percent by volume of solid blend (BVOB).

4. The method of claim 1, wherein the average particle size of the material is between about 10 \( \mu \text{m} \) and about 1000 \( \mu \text{m} \).

5. The method of claim 1, wherein the hydrogen sulfide is supercritical, wet, dry or dissolved in oil or water.

6. The method of claim 1, wherein the borehole penetrates at least one fluid-containing reservoir, the reservoir containing fluid with a hydrogen sulfide concentration greater than about five moles per liter.
7. The method of claim 1, wherein the cement slurry comprises one or more members of the list comprising Portland cement, calcium aluminate cement, fly ash, blast furnace slag, lime-silica blends, zeolites, geopolymers, Sorel cements and chemically bonded phosphate ceramics.

8. The method of claim 1, wherein the cement slurry further comprises dispersing agents, fluid-loss-control agents, set retarders, set accelerators, foaming agents, gas generating agents, antifoaming agents, extenders, weighting agents, lost-circulation control agents and combinations thereof.

9. The method of claim 1, wherein the tubular body comprises one or more members of the list comprising drillpipe, casing, liner and coiled tubing.

10. The method of claim 1, wherein the cement slurry further comprises dispersing agents, fluid-loss-control agents, set retarders, set accelerators, foaming agents, gas generating agents, antifoaming agents, extenders, weighting agents, lost-circulation control agents and combinations thereof.

11. A method for cementing a subterranean well having a borehole in which hydrogen sulfide is present, comprising:

(i) installing a tubular body inside the borehole of the well, or inside a previously installed tubular body;

(ii) pumping an aqueous cement slurry comprising a material that swells when contacted by hydrogen sulfide into the borehole;

(iii) allowing the cement slurry to set and harden;

(iv) in the event of cement-matrix or bonding failure, exposing the set cement to wellbore fluids that contain hydrogen sulfide; and

(v) allowing the material to swell, thereby restoring zonal isolation.
12. The method of claim 11, wherein the material comprises a fluorinated elastomer, or an ethylene-propylene copolymer or a combination thereof.

13. The method of claim 11, wherein the concentration of the material in the cement slurry is between about 5 percent and about 50 percent by volume of solid blend (BVOB).

14. The method of claim 11, wherein the average particle size of the material is between about 10 µm and about 1000 µm.

15. The method of claim 11, wherein the hydrogen sulfide is supercritical, wet, dry or dissolved in oil or water.

16. The method of claim 11, wherein the borehole penetrates at least one fluid-containing reservoir, the reservoir containing fluid with a hydrogen sulfide concentration greater than about five moles per liter.

17. The method of claim 11, wherein the cement comprises one or more members of the list comprising Portland cement, calcium aluminate cement, fly ash, blast furnace slag, lime-silica blends, zeolites, geopolymers, Sorel cements and chemically bonded phosphate ceramics.

18. The method of claim 11, wherein the cement slurry further comprises dispersing agents, fluid-loss-control agents, set retarders, set accelerators, foaming agents, gas generating agents, antifoaming agents, extenders, weighting agents, lost-circulation control agents and combinations thereof.
19. The method of claim 11, wherein the tubular body comprises one or more members of the list comprising drillpipe, casing, liner and coiled tubing.

20. The method of claim 11, wherein in the cement slurry further comprises dispersing agents, fluid-loss-control agents, set retarders, set accelerators, foaming agents, gas generating agents, antifoaming agents, extenders, weighting agents, lost-circulation control agents and combinations thereof.
INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2013/064935

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - C09K 8/473 (2014.01)
USPC - 507/926

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)
IPC(8) - C04B 24/24, 24/28, 28/02; C09K 8/42, 8/473, 8/50 (2014.01)
USPC - 507/200, 202, 205, 269, 901, 926

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
CPC - C09K 8/14, 8/18, 8/42, 8/46, 8/473, 8/50 (2014.01)

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

Orbit.com, Google Patents, Google Scholar, Public AppFT and PatFT

C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y</td>
<td>US 4,524,982 A (HERTZ, JR) 25 June 1985 (25.06.1985) entire document</td>
<td>2, 12</td>
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Further documents are listed in the continuation of Box C.

* Special categories of cited documents:

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

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