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(54) **PROCESS FOR DOWNHOLE HEATING**

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(57) **ABSTRACT**

Neutral electrolytes, relatively neutral electrolytes, metal oxides, metal hydroxides and/or organic exothermic hydration chemicals may be hydrated with water at a controlled location in a subterranean formation to generate sufficient exothermic heat to at least soften and possibly melt and flow bitumen at or near the location. This controlled and localized heating would be useful in drilling through relatively thick bitumen or "tar" beds. In one non-limiting embodiment the exothermic hydration reaction does not generate appreciable amounts of gas. Alternatively, the exothermic reaction may be used to liberate hydrocarbons from gas hydrates in an embodiment where the evolution of gas is acceptable.

PROCESS FOR DOWNHOLE HEATING

CROSS-REFERENCE TO RELATED APPLICATION

[0001] This application claims the benefit of U.S. provisional application No. 60/614,129 filed Sep. 29, 2004.

FIELD OF THE INVENTION

[0002] The present invention relates to methods and compositions for providing controlled downhole heating, such as in a subterranean reservoir during a hydrocarbon recovery operation.

BACKGROUND OF THE INVENTION

[0003] Drilling fluids used in the drilling of subterranean oil and gas wells along with other drilling fluid applications and drilling procedures are known. In rotary drilling there are a variety of functions and characteristics that are expected of drilling fluids, also known as drilling muds, or simply "muds". The drilling fluid is expected to carry cuttings up from beneath the bit, transport them up the annulus, and allow their separation at the surface while at the same time the rotary bit is cooled and cleaned. A drilling mud is also intended to reduce friction between the drill string and the sides of the hole while maintaining the stability of uncased sections of the borehole. The drilling fluid is formulated to prevent unwanted influxes of formation fluids from permeable rocks penetrated and also often to form a thin, low permeability filter cake which temporarily seals pores, other openings and formations penetrated by the bit. The drilling fluid may also be used to collect and interpret information available from drill cuttings, cores and electrical logs. It will be appreciated that within the scope of the claimed invention herein, the term "drilling fluid" also encompasses "drill-in fluids" and "completion fluids".

[0004] Drilling fluids are typically classified according to their base fluid. In water-based muds, solid particles are suspended in water or brine. Oil can be emulsified in the water. Nonetheless, the water is the continuous phase. Oil-based muds are the opposite or inverse. Solid particles are suspended in oil, and water or brine is emulsified in the oil and therefore the oil is the continuous phase. Oil-based muds that are water-in-oil emulsions are also called invert emulsions. Brine-based drilling fluids, of course are a water-based mud in which the aqueous component is brine.

[0005] It is apparent to those selecting or using a drilling fluid for oil and/or gas exploration that an essential component of a selected fluid is that it be properly balanced to achieve the necessary characteristics for the specific end application. Because drilling fluids are called upon to perform a number of tasks simultaneously, this desirable balance is not always easy to achieve.

[0006] Sometimes during drilling operations subterranean bitumen or "tar" beds are encountered. These beds are commonly found during sub-salt drilling in the Gulf of Mexico, but also at other locations. Indeed, the bitumen occurs so frequently in the Gulf of Mexico formations that it has been likened to a "river" of tar. Drilling through thin bitumen beds is generally no more than a minor nuisance, but thick beds can result in stuck pipe, stuck casing, sidetracks, loss of hole and other problems that can cost the well operators millions of dollars. One of the most precarious operations is running casing after drilling through a bitumen bed due to the movement or "flow" of the bitumen into the borehole before casing can be picked up and run to bottom.

[0007] As the price of crude oil has risen, recovery of hydrocarbons from oil sands, such as those found in Alberta, Canada, and elsewhere has become more economically attractive. Oil sands are a mixture of grit and bitumen. The deposits are generally either minded in massive open pits, or if too deep for surface mining, are injected with steam to coax the viscous bitumen to flow into wells.

[0008] Another type of formation encountered during drilling operations is in situ gas hydrates, also called clathrates. Gas hydrates are solid inclusion compounds resembling ice. Gas hydrates occur when water molecules form a cage-like structure around smaller "guest molecules". The most common guest molecules are methane, ethane, propane, isobutene, n-butane, nitrogen, carbon dioxide and hydrogen sulfide, of which methane occurs most abundantly in naturally-occurring hydrates. In nature, one cubic meter of hydrate may contain up to about 164 m^3 of methane. Gas hydrates occur wherever the conditions within the sediments are in a methane-hydrate stability region and where methane and water are available. This stability is limited by temperature and pressure: gas hydrates are stable at low temperatures and/or high pressure. Because of the requirements of pressure and temperature, and because of the requirement of relatively large amounts of organic matter of bacterial methanogenesis, gas hydrates are primarily restricted to two regions: high latitudes and along the continental margins in oceans. In polar regions, the gas hydrates are commonly linked to permafrost occurrence onshore and on the continental shelves. In the oceans, gas hydrates are found in outer continental margins, where the supply of organic material is high enough to generate enough methane, and with water temperatures close to freezing. These solid crystals, upon melting, can release up to 170 scf of natural gas per cubic foot of hydrate. The oceanic gas hydrate reservoir has been estimated to be about 10,000 to 11,000 GtC (Gigatons carbon). The permafrost reservoir has been estimated at about 400 GtC, but no estimates have been made of possible Antarctic reservoirs. Given the amount of hydrocarbons bound in gas hydrates, many are exploring the possibility of recovering hydrocarbons from this source.

[0009] It would be desirable if compositions and methods could be devised to provide localized heating to soften the bitumen to help facilitate movement of the casing or liner through the bitumen to the bottom. It would also be desirable if compositions and methods could be devised to provide controlled localized heating to melt in-situ gas hydrates in order to produce the large quantities of natural gas they contain. Further, it would be helpful to facilitate controlled localized heating of oil sands to improve recovery of hydrocarbons from that source.

SUMMARY OF THE INVENTION

[0010] Accordingly, it is an object of the present invention to provide a method for heating a location or region downhole in a subterranean location in a controlled manner.

[0011] It is another object of the present invention to provide a method and composition for heating a location or

region downhole in a subterranean location containing bitumen or tar in a controlled manner that does not generate appreciable amounts of gas.

[0012] Further, it is an object of the invention to provide methods and compositions to assist in the recovery of hydrocarbons from gas hydrates whether or not appreciable amounts of gas are created.

[0013] In carrying out these and other objects of the invention, there is provided, in one non-limiting form, a method for providing localized heating in a subterranean formation that involves placing at a location in the subterranean formation in any order: an exothermic hydration chemical and an amount of water in contact with the exothermic hydration chemical effective to cause an exothermic reaction thereby heating the location and a suitable medium for transporting the heat source to the desired location.

[0014] In another non-limiting embodiment there is created a method for providing localized heating in a subterranean formation that involves placing at a location in the subterranean formation where bitumen is present in any order: an exothermic hydration chemical and an effective amount of water in contact with the exothermic hydration chemical to cause an exothermic reaction without generating an appreciable amount of gas; and heating the location sufficiently to at least soften the bitumen.

[0015] Alternatively, there is facilitated a method for providing localized heating in a subterranean formation that involves placing at a location in the subterranean formation containing gas hydrates an exothermic hydration chemical, and reacting at least a portion of the water in the gas hydrates with the exothermic hydration chemical to cause an exothermic reaction to release at least a portion of hydrocarbons bound in the hydrates. In this embodiment an appreciable amount of gas may or may not be released and water may or may not be added to the formation.

DETAILED DESCRIPTION OF THE INVENTION

[0016] A method has been discovered to generate localized heat remotely downhole using heat of hydration as a heat source. It has been estimated in one non-limiting embodiment, if the bitumen in the "river of tar" beneath the Gulf of Mexico is heated to about 220 to about 230° F. (about 104 to about 110° C.), the material would be 10 times less viscous. Most exothermic oxidation/combustion reactions require temperatures that would compromise mud/spot stability, if not tubular integrity, would tend to be difficult to initiate and would be problematic to formulate as a liquid or mud for downhole use. Initiating the reaction at the surface would tend to expend and dissipate most of the heat before placement in the target or the mud for downhole use. Hydration of acidic electrolytes (such as aluminum chloride, $AlCl_3$) or acids would be expected to be corrosive and at high temperatures could compromise the integrity of the tubular goods, tools and other equipment in many circumstances. For instance, hydration of aluminum chloride would produce a product environment of about pH 0.8, as contrasted with using NaOH, which would generally yield a product environment of about pH 14. Oil field chemistries are generally and preferably alkaline at least in part to avoid or minimize corrosion concerns.

[0017] The process in one non-limiting embodiment uses a binary design where in one non-limiting embodiment the "fuel" is placed first as a slurry or suspension or fluid combined with an "initiator", e.g. water that produces heat precisely at the point or location of interest. Although the binary components may be placed at the location in any order, in most embodiments it is expected that the "initiator" (e.g. water) would be placed last in sequence.

[0018] Heat of hydration is defined as the heat evolved (or absorbed) when a hydrate of a compound is formed. In one non-limiting embodiment, the exothermic hydration chemical has a heat of hydration of at least 40 kJ/mol, and alternatively has a heat of hydration of at least 80 kJ/mol. In general, the exothermic hydration chemical should be a material that when combined with the initiator generates sufficient heat to soften, melt or flow the bitumen, but without generating an appreciable amount of gas. Many exothermic reactions give large amounts of heat, but produce relatively large amounts of gas—a thermite reaction, for example. However, such an exothermic reaction downhole could cause a blowout of the well and is extremely undesirable. At worst, such a reaction would be like setting off a bomb downhole. Herein the term "an appreciable amount of gas" is defined as an amount that would interfere with normal hydrocarbon recovery operations and does not include incidental or non-problematic amounts. It should be understood that avoiding the generation of an appreciable amount of gas does not mean that water vapor may not be evolved. It is acceptable in all embodiments herein for water vapor to be evolved or generated in the process of remote heating a location or formation.

[0019] With respect to the case where the method herein is used to deliver heat to a remote location having tar or bitumen, such as oil sands or subterranean bitumen layers, it may be understood that these environments are generally non-aqueous, that is, they do not contain appreciable amounts of water. The water is delivered as part of the method to be a co-reactant with the exothermic hydration chemical.

[0020] In the alternative embodiment of the invention where the exothermic hydration chemical is used to generate heat in a subterranean gas hydrate formation (e.g. in a permafrost region on land or sub-ocean), the generation of appreciable amounts of gas is acceptable—and in fact is desirable since it is expected to be the primary way in which hydrocarbons (e.g. methane) is released. Further, this embodiment uses a unitary design; it is contemplated that in most cases only the exothermic hydration chemical would be delivered or pumped to the gas hydrate formation or region since the hydrates themselves would provide the source of most of the water. Alternatively, additional water may be added as necessary or desired. As expected, a goal of recovering hydrocarbons from gas hydrates is to either deliver heat (increase temperature) or reduce pressure, or both. In many cases it is expected that the temperature of the gas hydrates need only be raised 2 or 3° C. for the gas hydrate to decompose and the guest molecules released.

[0021] There are further a smaller group of exothermic reactions that would not produce an appreciable amount of gas, but that would involve reactants—either the "fuel" or "initiator" that would be too exotic or expensive to use in the quantities necessary for heating a location in a subterranean

reservoir. Thus, although such systems could be used, it would be desirable if both the "fuel" and the "initiator" were relatively inexpensive and readily available. Since water is a highly accessible and cheap material, it is one non-limiting choice for initiator that may be used. Additionally, water has a very high specific heat and thus will retain the heat well for a period of time for the purpose of softening and/or melting the bitumen or heating in situ gas hydrate formations.

[0022] Factors to be considered in selecting the binary reactants include, but are not necessarily limited to the expected amount of heat output (for instance measured in kJ/mol), the cost, the acidity of the resulting products, the solubility of the "fuel" or exothermic hydration chemical, HS&E profile (Health, Safety & Environmental) and the like. In one non-limiting embodiment a suitable "fuel" or exothermic hydration chemical to react with water in a hydration reaction includes, but is not necessarily limited to, a relatively neutral electrolyte, a metal oxide, a metal hydroxide, and an organic compound. Examples of relatively neutral electrolytes include, but are not necessarily limited to, halogen salts such as calcium chloride, magnesium chloride, lithium chloride, and lithium bromide and mixtures thereof and the like. Other examples of relatively neutral electrolytes include sulfate salts such as magnesium sulfate, calcium sulfate, and the like. "Relatively neutral" refers to an electrolyte that is not strictly neutral, but which is sufficiently neutral for the purposes of the process described herein. An example of a non-neutral electrolyte that could be considered is aluminum chloride, which could be useful under certain specialized situations. Examples of metal oxides include, but are not necessarily limited to, calcium oxide, strontium oxide, barium oxide, and mixtures thereof and the like. Examples of metal hydroxides include, but are not necessarily limited to, sodium hydroxide (NaOH), potassium hydroxide (KOH), lithium hydroxide (LiOH), cesium hydroxide (CsOH) and mixtures thereof and the like. Examples of suitable organic compounds include, but are not necessarily limited to, peroxides, epoxides and monomers whose polymerization would generate heat such as acrylates, methacrylates and mixtures thereof and the like.

[0023] Other reactants that can be used to generate localized heating but might be limited in their uses due to appreciable amounts of gas produced are acid compounds such as hydrogen bromide, hydrogen chloride, hydrogen iodide, and percholoric acid. Reactions other than exothermic hydration reactions could be used to provide localized heating in certain situations. These reactions are typically not desirable for the bitumen-heating embodiment of the invention due to the by-products produced.

[0024] Slurry placement of the "fuel" or exothermic hydration chemical is anticipated where the "fuel" would settle out in the zone of interest to concentrate the fuel as much as possible in the desired location. There may be instances where a stable slurry may be desirable or preferred in a method of delivery and/or placement at the desired location. By "stable" is meant that the slurry does not separate or settle upon standing for periods of time. In the case of the stable slurry, it would be pumped downhole to a location or against a structure and pack off like a packed bed. The more densely packed the bed, the more heat generated, and the more effective the process. The slurry must consist of an organic base fluid and preferably one that has a low specific heat. The fluid should also a high thermal conductivity in order to transfer the generated heat effectively. Examples of fluid mediums include, but are not necessarily limited to, alcohols, glycols, alcohol/glycol blends, specifically designed heat transfer fluids, such as Dowtherm® fluids (available from Dow Chemical Company) and Therminol® fluids (available from Solutia Inc.), esters either natural such as vegetable oils and/or animal oils or synthetic esters such as 2-ethylhexyl esters of fatty acids and hydrocarbon oils either distillates or synthetic.

[0025] Alternatively, placement could involve encapsulating the fuel or exothermic hydration chemical, such as with a wax; a polymer wax or other polymer or material that melts or disintegrates or dissociates at the location. Of course, the encapsulating material or carrier should not prematurely react with the exothermic hydration chemical or fuel. Specific examples of suitable polymeric materials include, but are not necessarily limited to, hydrocarbon waxes such as paraffin waxes and microcrystalline waxes, vegetable or animal waxes, solid relatively weak acids such as tallow or hydrogenated tallow fatty acid, polybutylene, polymethacrylates, polyethylene glycol (PEG), methoxylated PEG, polyethylene oxide (PEO), polyethylene waxes, polypropylene glycol (PPG), and the like. In one non-limiting embodiment of the invention, suitable encapsulating material includes ionomeric waxes, including, but not necessarily limited to, PEG (e.g. CARBOWAX available from Union Carbide Corporation, Danbury, Conn.), alkoxy terminated PEG (e.g. methoxylated PEG or mPEG), PEO, and polypropylene oxide (PPO). The encapsulation may be extended to PEG/PPG, PEG/PEO, and mPEG/PEG blends of different molecular weights. Polymerization of these polymer shells is well known in the art. Other extended release forms include, but are not necessarily limited to, pelletization with binder compounds, absorbed or some other method of layering on a small particle or porous substrate, and/or a combination thereof. Specifically, the fuel or exothermic hydration chemical may be encapsulated to permit slow or timed release thereof. In non-limiting examples, the coating material may slowly dissolve or be removed by any conventional mechanism, or the coating could have very small holes or perforations therein for the exothermic hydration chemicals within to diffuse through slowly. For instance, polymer encapsulation coatings such as used in fertilizer technology available from Scotts Company, specifically POLY-S® product coating technology, or polymer encapsulation coating technology from Fritz Industries could possibly be adapted to the methods herein. The sources could also be absorbed onto zeolites, such as Zeolite A, Zeolite 13X, Zeolite DB-2 (available from PQ Corporation, Valley Forge, Pa.) or Zeolites Na-SKS5, Na-SKS6, Na-SKS7, Na-SKS9, Na-SKS10, and Na-SKS13, (available from Hoechst Aktiengesellschaft, now an affiliate of Aventis S.A.), and other porous solid substrates such as MICROSPONGE™ (available from Advanced Polymer Systems, Redwood, Calif.) and cationic exchange materials such as bentonite clay or microscopic particles such as carbon nanotubes or buckminster fullerenes. Further, the component sources may be both absorbed into and onto porous substrates and then encapsulated or coated, as described above.

[0026] Melting would occur at the location temperature, and disintegration or dissociation may occur due to a change in temperature, pressure, chemical environment, a combination of these or other forces. An encapsulated exothermic hydration chemical could be suspended in an aqueous carrier at the surface and pumped downhole for placement, such as

in the previously mentioned slurries. The wax or other coating would be chosen to melt at the temperature of the target zone or just before exposing the fuel and/or chemical to the water in the carrier at that time. In the non-limiting case where the encapsulating or shell material is melted or the disintegration is temperature triggered, as heat is generated when the exothermic hydration chemical is reacted, more of the shell or capsules would melt, further accelerating the process. Alternatively, the capsule shell could be designed to be dissolved in the initiator (e.g. water). In the context of the compositions and methods herein, encapsulation includes, but is not necessarily limited to, microencapsulation.

[0027] In summary, one non-limiting example of the invention would be drilling out the bitumen inside of a stuck liner, spotting a caustic soda/"oil" or hydrocarbon slurry inside the liner opposite or adjacent to the bitumen zone, allowing the caustic soda beads/powder to settle, and slowly pumping an aqueous fluid to hydrate the caustic soda to generate localized heating.

[0028] The invention will be further illustrated with respect to the following Examples which are not intended to limit the invention, but rather simply to additionally illuminate it.

EXAMPLE 1

[0029] Use of 40 wt % NaOH in oil does not generate heat, but when contacted with a water-based mud would give 186,000 Btu/bbl.

EXAMPLE 2

[0030] The use of 42 wt % $CaCl_2$ in oil does not generate heat, but when contacted with water would give 44,000 Btu/bbl.

EXAMPLE 3

[0031] The use of 70 wt % $AlCl_3$ when contacted with water, gives 296,000 Btu/bbl as well.

[0032] In the foregoing specification, the process has been described with reference to specific embodiments thereof, and has been suggested as effective in providing components downhole for controlled release of heat in space and time, such as to soften, melt or flow bitumen and possibly for other purposes. However, it will be evident that various modifications and changes can be made thereto without departing from the broader spirit or scope of the invention as set forth in the appended claims. Accordingly, the specification is to be regarded in an illustrative rather than a restrictive sense. For example, specific combinations of exothermic hydration chemicals, initiators and proportions as well as various encapsulation or suspending techniques, thereof falling within the claimed parameters, but not specifically identified or tried in a particular composition or example to deliver heat locally and controllably, are anticipated to be within the scope of this invention. For instance the compositions and methods described herein may be used to help recover hydrocarbons from oil sands.

We claim:

1. A method for providing localized heating in a subterranean formation comprising:

placing at a location in the subterranean formation in any order:

an exothermic hydration chemical, and

an effective amount of water in contact with the exothermic hydration chemical to cause an exothermic reaction; and

heating the location.

2. The method of claim 1 where bitumen is present at the location, the exothermic reaction does not generate an appreciable amount of gas, and the heating is sufficient to at least soften the bitumen.

3. The method of claim 2 where the exothermic hydration chemical is selected from the group consisting of a relatively neutral electrolyte, a metal oxide, a metal hydroxide, and an organic compound, all capable of exothermic reaction without generating an appreciable amount of gas.

4. The method of claim 3 where the exothermic hydration chemical is selected from the group consisting of aluminum chloride, NaOH, KOH, halogen salts, sulfate salts, calcium oxide, barium oxide, and mixtures thereof.

5. The method of claim 1 where the exothermic hydration chemical is encapsulated in a material selected from the group consisting of wax, polymer wax, solid fatty acids, polymers, or is absorbed onto or bound to a substrate material where the material melts or disintegrates at the location.

6. The method of claim 1 where the exothermic hydration chemical has a heat of hydration of at least 40 kJ/mol.

7. The method of claim 1 where gas hydrates are present at the location, the exothermic reaction may generate an appreciable amount of gas, and the heating is sufficient to release at least a portion of hydrocarbons bound in the hydrates.

8. The method of claim 1 where the exothermic reaction chemical is placed at the location in a delivery medium selected from the group consisting of alcohols, glycols, heat transfer fluids, organic oils, and mixtures thereof.

9. A method for providing localized heating in a subterranean formation comprising:

placing at a location in the subterranean formation where bitumen is present in any order:

an exothermic hydration chemical selected from the group consisting of a relatively neutral electrolyte, a metal oxide, a metal hydroxide, and an organic compound, and

an effective amount of water in contact with the exothermic hydration chemical to cause an exothermic reaction without generating an appreciable amount of gas; and

heating the location sufficiently to at least soften the bitumen.

10. The method of claim 9 where the exothermic hydration chemical is selected from the group consisting of aluminum chloride, NaOH, KOH, halogen salts, sulfate salts, calcium oxide, barium oxide, and mixtures thereof.

11. The method of claim 9 where the exothermic hydration chemical is encapsulated in a material selected from the group consisting of wax, polymer wax, solid fatty acids, polymers, or is absorbed onto or bound to a substrate material, where the material melts or disintegrates at the location.

12. The method of claim 9 where the exothermic hydration chemical has a heat of hydration of at least 40 kJ/mol.

13. The method of claim 9 where the exothermic reaction chemical is placed at the location in a delivery medium selected from the group consisting of alcohols, glycols, heat transfer fluids, organic oils, and mixtures thereof.

14. A method for providing localized heating in a subterranean formation comprising:

placing at a location in the subterranean formation in any order:

an exothermic hydration chemical selected from the group consisting of a relatively neutral electrolyte, a metal oxide, a metal hydroxide, and an organic compound, where the exothermic hydration chemical has a heat of hydration of at least 40 kJ/mol, and

an effective amount of water in contact with the exothermic hydration chemical to cause an exothermic reaction without generating an appreciable amount of gas; and

heating the location.

15. The method of claim 14 where bitumen is present at the location and the heating is sufficient to at least soften the bitumen.

16. The method of claim 14 where the exothermic hydration chemical is selected from the group consisting of aluminum chloride, NaOH, KOH, halogen salts, sulfate salts, calcium oxide, barium oxide, and mixtures thereof.

17. The method of claim 14 where the exothermic hydration chemical is encapsulated in a material selected from the group consisting of wax, polymer wax, solid fatty acids, polymers, or is absorbed onto or bound to a substrate material, where the material melts or disintegrates at the location.

18. A method for providing localized heating in a subterranean formation comprising:

placing at a location in the subterranean formation containing gas hydrates an exothermic hydration chemical, and

reacting at least a portion of the water in the gas hydrates with the exothermic hydration chemical to cause an exothermic reaction to release at least a portion of hydrocarbons bound in the hydrates.

19. The method of claim 18 where the exothermic hydration chemical is selected from the group consisting of a relatively neutral electrolyte, a metal oxide, a metal hydroxide, an organic compound, a hydrogen halide and perchloric acid.

20. The method of claim 19 where the exothermic hydration chemical is selected from the group consisting of aluminum chloride, NaOH, KOH, halogen salts, sulfate salts, calcium oxide, barium oxide, hydrogen halides, perchloric acid, and mixtures thereof.

21. The method of claim 18 where the exothermic hydration chemical is encapsulated in a material selected from the group consisting of wax, polymer wax, solid fatty acids, polymers, or is absorbed onto or bound to a substrate material where the material melts or disintegrates at the location.

22. The method of claim 18 where the exothermic hydration chemical has a heat of hydration of at least 40 kJ/mol.

23. The method of claim 18 where the exothermic reaction chemical is placed at the location in a delivery medium selected from the group consisting of alcohols, glycols, heat transfer fluids, organic oils, and mixtures thereof.

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