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(54) **Title:** TIME-DELAY FLUIDS FOR WELLBORE CLEANUP

(57) **Abstract:** A method for delaying the removal of a majority of an oil-based mud (OBM) filter cake from a hydrocarbon reservoir wellbore that utilizes a multiple phase composition is described. The use of the multiple phase composition allows for a microemulsion, a miniemulsion, or a nanoemulsion to form in situ downhole at a controllable time. The method includes pumping the multiple phase composition comprising an additive into the wellbore. The multiple phase composition may be broken thereby releasing the additive. The broken multiple phase composition and the additive may contact the OBM filter cake particles to form an in situ emulsion selected from the group consisting of a nanoemulsion, a miniemulsion, a microemulsion, a multiple emulsion, a water-continuous emulsion and mixtures thereof. The in situ emulsion may incorporate more of the external oil from the OBM filter cake in order to more easily remove the OBM filter cake.



TIME-DELAY FLUIDS FOR WELLBORE CLEANUP

TECHNICAL FIELD

[0001] The present invention relates to a method for delaying the formation of a downhole emulsion selected from the class consisting of a microemulsion, a miniemulsion, a multiple phase emulsion, a water-continuous emulsion, a nanoemulsion, and mixtures thereof for removal of a majority of an oil-based mud filter cake from a hydrocarbon reservoir wellbore.

BACKGROUND

[0002] 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 should carry cuttings from beneath the bit, transport them through the annulus, and allow their separation at the surface, while 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.

[0003] 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 as defined 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 which are water-in-oil macroemulsions are also called

invert emulsions. The oil in oil-based (invert emulsion) mud can consist of any oil that may include diesel, mineral oil, esters, or alpha olefins. Brine-based drilling fluids, of course are a water-based mud in which the aqueous component is brine. 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.

[0005] Drilling fluids have a number of tasks or functions to perform simultaneously. One specific function of the drilling fluid is to form a filter cake to control the filtrate invasion into the formation. Filter cakes are the residue deposited on a permeable medium, such as a formation surface when a slurry or suspension, such as a drilling fluid, is circulated within the wellbore where the pressure is overbalanced. Filtrate is the liquid that passes through the medium, leaving the filter cake on the medium. Filter cake properties, such as cake thickness, toughness, slickness and permeability are important because the cake that forms on permeable zones in a wellbore can cause stuck pipe and other drilling problems. Reduced hydrocarbon production can result from reservoir or skin damage when a poor filter cake allows deep filtrate invasion.

[0006] In a conventional drilling operation, the filter cake also helps maintain control of the well and isolate formations from drilling fluids. A filter cake may form external to the formation, as well as a small filter cake formed internal to the formation by the spurt loss and solids. However, the external filter cake should be thin but strong enough with low permeability to prevent formation damage or fluid invasion. The internal filter cake has a higher potential for formation damage. It will be appreciated that in the present context the term "filter cake" includes any emulsion or invert emulsion part of the filter cake, and that the filter cake is defined as a combination of any added solids, if any, and drilled solids. It will also be understood that the drilling fluid, e.g. invert emulsion fluid, is concentrated at the bore hole face and partially inside the formation. Further, an open hole completion is understood to be a well completion that has no liner or casing set across the reservoir formation, thus allowing the produced fluids to flow directly into the wellbore. A liner or casing may be

present in other intervals, for instance between the producing interval and the surface.

[0007] Many operators are interested in improving formation clean up after drilling into reservoirs with invert emulsion drilling fluids. More efficient filter cake and formation clean up is desired for a number of open hole completions, including stand-alone and expandable sand screens as well as for gravel pack applications for both production and water injection wells. Skin damage removal from internal and external filter cake deposition during oil well reservoir drilling with invert emulsion drill-in and drilling fluids is desirable to maximize hydrocarbon recovery.

[0008] Further, it is often desirable in the destruction and removal of invert emulsion filter cake to not do so quickly, but rather to delay the destruction and removal of the filter cake. Without control of the destruction rate, massive brine losses may occur quickly and before the work string can be safely pulled out of the open wellbore. Post drill-in treatment and alteration of a majority of filter cake particles can be accomplished by pumping a multiple phase composition downhole to form an in situ emulsion where the in situ emulsion may be a nanoemulsion, a miniemulsion, a microemulsion, a water-continuous emulsion, or mixtures thereof as will be described in more detail.

[0009] It would be desirable if methods could be devised to aid and improve the ability to clean up filter cake, and to remove it more completely, without causing additional formation damage. It is also desirable to delay the rate of destruction and removal of the filter cake by delaying the formation of a nanoemulsion, a miniemulsion, a microemulsions, or mixtures thereof.

SUMMARY

[0010] There is provided, in one form, a method for removing a majority of oil-based mud (OBM) filter cake from a hydrocarbon reservoir wellbore. The method may include delivering a multiple phase composition into the wellbore. The multiple phase composition may be broken downhole thereby releasing an additive. The broken multiple phase composition and the released additive may contact the OBM filter cake to form an in situ emulsion downhole selected

from the group consisting of a nanoemulsion, a miniemulsion, a microemulsion, a multiple emulsion, a water-continuous emulsion, and mixtures thereof. The oil from the OBM filter cake may be incorporated into the in situ emulsion and the filter cake particles are slurrified for subsequent removal of the filter cake from the wellbore.

[0011] There is further provided in another non-limiting embodiment a method for forming an in situ emulsion within a hydrocarbon reservoir wellbore for removing a majority of oil-based mud (OBM) filter cake particles from a hydrocarbon reservoir wellbore. The method may include delivering a multiple phase composition into the wellbore where the multiple phase composition may have an internal phase with at least one component. The multiple phase composition may be broken downhole for release of the at least one internal phase component. The internal phase component may be selected from the group consisting of structural stabilizers, surfactants, co-surfactants, viscosifiers, chelating agents, filtration control additives, suspending agents, dispersants, wetting agents, solvents, co-solvents, acids, and mixtures thereof. The broken multiple phase composition and the released internal phase component may contact the OBM filter cake particles to form an in situ emulsion selected from the group consisting of a nanoemulsion, a miniemulsion, a microemulsion, a water-continuous emulsion, a multiple emulsion, and mixtures thereof. The oily material of the filter cake may be incorporated into the in situ emulsion.

[0012] By forming an in situ emulsion downhole, such as a nanoemulsion, a miniemulsion, a multiple emulsions, a water-continuous emulsion, or a microemulsion, the in situ emulsion may absorb more of the non-polar hydrocarbon phase from the filter cake than if the emulsion were formed at the surface and lowered into the wellbore. Thus, more filter cake particles may be removed.

DETAILED DESCRIPTION

[0013] It has been discovered that post drill-in treatment and alteration of a majority of an OBM filter cake may be accomplished by delaying the formation

of an in situ emulsion selected from the group consisting of a microemulsion, a miniemulsion, a nanoemulsion, and mixtures thereof, so that the formation of the in situ emulsion occurs downhole. The delayed formation of the in situ emulsion downhole may improve, enhance, or increase the ability of the time delayed emulsion to incorporate the oil from the OBM filter cake. The forming of the in situ emulsion may be delayed by delivering an additive from the multiple phase emulsion necessary to form the in situ emulsion that incorporates the oil portion of the OBM filter cake. The multiple phase emulsion should not be confused with the in situ emulsion. The in situ emulsion forms once the multiple phase emulsion has been pumped downhole; said differently, the in situ emulsion cannot form without first delivering the multiple phase emulsion to the desired location.

[0014] The additive is delivered by pumping a multiple phase emulsion downhole and subsequently breaking the multiple phase emulsion and releasing the additive. In a non-limiting embodiment, the additive is in an internal phase of the multiple phase emulsion. The additive then helps create the in situ emulsion that may be a nanoemulsion, a miniemulsion, a multiple emulsion, a water-continuous emulsion, or a microemulsion. The in situ emulsion then incorporates encountered oil from the filter cake.

[0015] Multiple emulsions, also called a multiple phase composition herein, may be defined as an emulsion within an emulsion that is typically stabilized by an emulsifier or a surfactant. An emulsion is a mixture of two or more immiscible liquids. In an emulsion, a dispersed phase is dispersed in a continuous phase. Because the two or more liquids are immiscible, the dispersed phase liquid forms droplets within the continuous phase. In a typical multiple emulsion, the dispersed phase droplets may have smaller dispersed droplets.

[0016] Multiple phase compositions are anticipated as being useful to organize a liquid phase to isolate one miscible phase from another. An oil-based vesicle could be used in an invert emulsion, hydrocarbon-based or ester-based or other water immiscible, non-aqueous-based system, while a water-based vesicle could be used in an aqueous system. In another non-limiting

embodiment, alcohol-based vesicles may be used in hydrocarbon-based or other water immiscible, non-aqueous-based systems, or in aqueous systems, depending upon the particulars of the vesicle design.

[0017] In short, the multiple phase compositions may be applied to any two miscible phases such that one phase (the first phase) can be partitioned and isolated from the other phase (the third phase) by the use of a surface active material bilayer membrane (the second phase). The phases need not be "oil" or "water", although such phases are likely to be the most common implementation. One non-limiting example is the combination of a water soluble, relatively low molecular weight glycol that forms an emulsion with brine. The vesicles described herein may also be termed liposomes.

[0018] One important application of this kind of organization would be the controlled release of the internal phase and/or the internal phase contents, such as any conventional additive at least within the innermost (first) phase. A non-limiting example of such an application would be the inclusion of, for instance, structural stabilizers, surfactants, co-surfactants, viscosifiers, chelating agents, filtration control additives, suspending agents, dispersants, wetting agents, solvents, co-solvents, acids, and mixtures thereof alone if liquid or in solution, as a first, internal phase in an aqueous or hydrophilic carrier such as a water-based drilling fluid (third phase) separated by a surface active material bilayer membrane (the second phase).

[0019] The surfactants/emulsifiers, viscosifiers, stabilizers, and mixtures thereof may be added to the surface active material as a structural stabilizer to increase the mechanical stability and to aid in delaying release or breaking of the surface active material bilayer membrane. Any of the surfactants/emulsifiers, viscosifiers, stabilizers, or mixtures thereof previously mentioned may be used in the surface active material bilayer membrane, the inner phase of the multiple phase composition, or both.

[0020] Alternatively, polymerizable surface active materials may be used to form the bilayer membranes followed by polymerization to stabilize the vesicles. Polymerization of the tail portion of the molecule adds stability to the vesicles. Materials suitable to form the surface active material bilayers include, but are

not necessarily limited to phospholipids, alkyl polyglycosides, gemini surfactants, sorbitan monooleate, sorbitan trioleate, glycerol fatty acid esters including mono- and/or dioleates, polyglycerol fatty acid esters, polyglycols, alkanolamines and alkanolamides such as ethoxylated amines, ethoxylated amides, ethoxylated alkanolamides, including non-ethoxylated ethanolamides and diethanolamides, and the like as well as block copolymers, terpolymers and the like, and other polymerizable surface active materials, gelling agents, and the like that can exist as bilayers in aqueous solutions. The hydrophobic portion, that is, the hydrocarbon tails, are shielded in the middle of these bilayers. The hydrophilic portion is exposed on both sides (opposite sides of the respective bilayers) to water or another aqueous solution.

[0021] While surface active material bilayers are more commonly seen in aqueous systems, they are also found in non-aqueous systems where two miscible oil or non-aqueous phases are separated by a surface active material bilayer in which the molecules are arranged oppositely from that described above, i.e. where hydrophobic portions or tails are exposed on both sides of the layer, while the hydrophilic heads are shielded together in the middle or center of the bilayer. Forming multiple phase vesicles using surface active material bilayers may require special but known techniques involving relatively high shear mixing and long shear times, as well as relatively high applications of energy.

[0022] In one non-limiting embodiment, when sorbitan monooleate (SMO) is used to form the surface active material surface active material bilayers, it is difficult to get the SMO into an aqueous fluid. Optionally, a carrier may be used to help introduce the surface active material bilayer compound into the fluid. While SMO can form a surface active material bilayer by itself, generally more time and energy are required than when a carrier is used. Suitable carriers for SMO include, but are not necessarily limited to ethoxylated alcohols and polyalkyleneglycols. It is expected that the carrier may be specific to the surface active material bilayer compound to some extent. The vesicle shape may include, but is not limited to, spherical, ovoid, elongated, cylindrical,

lamellar, onion layered, worm-like, ribbons, hexagonal rods and mixtures thereof.

[0023] If appropriate or desirable, the additive may be in aqueous or hydrocarbon solution. In some non-limiting embodiments, the additive to be delivered may be in both the first phase and the second phase, and in identical or different concentrations. Such a system could provide a two-stage delivery of the additive. The first or internal phase may be soluble in the external or continuous phase (the third phase). Thus, if the continuous phase (third phase) is an aqueous fluid, the first, internal phase should be aqueous; if the continuous phase (third phase) is non-aqueous or hydrophobic, the first, internal phase should be non-aqueous or hydrophobic.

[0024] Vesicles have several advantages over multiple emulsions. The lack of appreciable amounts of an immiscible intermediate (second) carrier phase of different density helps prevent gravity separation of the final multiphase system. Leaving out the second phase carrier fluid maximizes the viscosity/consistency of the surface active material bilayer membrane and helps stabilize the membrane. Leaving out the second phase carrier fluid also minimizes the amount of "inert" material in a product, which can add to the storage and shipping costs of that product undesirably. Indeed, an important advantage of vesicles in many embodiments is the increased stability of the product and/or liquid they exist in.

[0025] The speed of stirring or mixing of the two phases would depend upon the desired size of the vesicles, and the particular system used. It is expected that the size of the first phase vesicles would range from about 0.01 to about 1000 micrometers or less, in another non-limiting embodiment, from about 1 to about 100 micrometers or less, as non-limiting examples. In one non-limiting embodiment, the vesicles would be as large as is practical.

[0026] The proportion of the first, internal phase to the overall multiple phase composition may range from about 1 vol % independently to about 90 vol% independently, 40 vol% independently to about 60 vol%, or in another non-limiting embodiment about 50 vol% or less, as non-limiting examples. A lower threshold of 1 vol% may be appropriate in some embodiments. The

multiple phase vesicles may be suspended in the drilling and/or completion fluid (the third phase). If the third phase is non-aqueous, in one non-restrictive embodiment, the phase may, in some non-limiting embodiments, be a synthetic material, and, for instance, may include, but is not necessarily limited to, esters, iso-olefins, alpha-olefins, polyolefins, poly(alpha-olefins), paraffins, Fischer-Tropsch reaction products, and the like. The non-aqueous phase may be a mixture or blend of petroleum distillates and synthetic hydrocarbons. Suitable petroleum distillates include, but are not limited to, diesel oil, kerosene, mineral oils, food grade mineral oils, paraffinic oils, cycloparaffinic oils, aromatic oils, or n-paraffins, isoparaffins and similar hydrocarbons.

[0027] Crude oil could be used in some cases. In the case where the third phase is an oil-based phase, it is anticipated that any of these hydrocarbons may be used. In the case where first and third miscible phases are aqueous, the aqueous phases may be brine. It is expected that brine will be a common component of the multiple phase composition, and any of the commonly used brines, and salts to make them, are expected to be suitable in the methods herein. Careful adjustment of the internal phase salinity may be required (osmotic pressure gradient adjustment). Too much salt in a first aqueous phase may make the vesicles unstable. However, this mechanism may be intentionally used to cause failure or rupture of the vesicles or liposomes downhole. For example, the droplets could be designed to grow on the journey downhole and break at or near the desired zone.

[0028] Dilution is prevented, suppressed, or delayed until the surface active material bilayer membrane is intentionally broken. A likely area for breakage of the multiple phase composition is the high shear environment of and below the drilling bit, where the additive is released to the borehole and cuttings in concentrated form on a localized basis. It may be noted that the high shear conditions used in making the compositions are at surface pressures and temperatures, and that downhole temperatures and pressures will be higher. Further, it is expected that in some high shear applications, vesicles may be created at the same time others are broken to maintain a pseudo-steady state, or in some cases an increase in vesicle content. It will also be understood in

the context described herein that the internal phase or first phase may be the same as or co-extensive with the agent or the product being delivered. Of course, emulsifiers, viscosifiers, or other structural stabilizers may also be added to increase the mechanical stability of the vesicles in some cases to delay release of the contents (additive).

[0029] In one embodiment, the vesicles may be as large as possible. The larger the first phase vesicles in the second phase, all things being equal, the easier it would be to break the surface active material bilayers to release the agents and/or internal phase contents from the first phase. The proportions of the vesicles in the second phase as a product completion fluid (additional second phase) may range from about 0.5 vol% independently to about 90 vol%. Alternatively the lower limit of this range may be about 1 vol% independently or about 2 vol%, while the upper limit of this range may be about 40 vol%, in one non-limiting embodiment about 10 vol%, in another embodiment up to about 5 vol%, and in still another non-restrictive embodiment up to about 6 vol%, as non-limiting examples, to make the overall multiple phase composition.

[0030] The method described may find particular usefulness in increasing the local concentration of an additive downhole after rupture of the surface active material bilayers, while keeping the overall concentration of the agent in the drilling mud (including the entire multiple phase composition) low. For example, polymers or copolymers, such as styrene-butadiene rubber (SBR) in one non-limiting embodiment, may be useful as viscosifiers and/or filtration control additives, could be the additive in the first phase and be in relatively low concentrations overall. However, once the surface active material bilayers of the vesicles are broken or caused to fail, the local concentration of SBR at the vesicle failure zone would be relatively increased.

[0031] However, the multiple phase composition is designed to be broken in one non-limiting embodiment. That is, the internal phase or first phase which contains an additive or where the internal phase is the additive itself is released or delivered from within the surface active material bilayer. Indeed, the vesicles are desirably and controllably broken within a certain area of the wellbore at

designated and relatively controlled time. The preparation of the vesicles would typically involve the mixing of the first phase with the second phase, in the presence of the surface active material bilayer material, where any emulsifier or structural stabilizer might also be present. Alternatively, one liquid may be used which contains the surface active material bilayer compound, with or without a structural stabilizer.

[0032] Using the multiple phase composition is straightforward and requires no special equipment. The vesicles are injected into a fluid that is pumped downhole. The fluid may be a drilling fluid, drill-in fluid, a completion fluid or the like. In one non-restrictive embodiment, the fluid is a drilling fluid or drill-in fluid. A number of mechanisms could be used to break the multiple phase composition at a particular time, including, but not necessarily limited to, a change in energy input, e.g. a change in temperature, a change in pressure, an increase in shear stress, an increase in shear rate, mechanical action (e.g. a rotating drill bit or drill string), a change in pH, a change in electrical potential, a change in magnetic flux, solvent thinning, presence of a chemical agent, presence of a catalyst, and the like, and combinations thereof.

[0033] A non-limiting, but useful method is breaking the multiple phase composition by subjecting it to a high shear environment, in particular the fluid stream exiting a nozzle impinging on the borehole such as below a bit or opposite a reamer or hole opener. In one non-limiting embodiment, the surface active material bilayers are broken within a required period of time, and within a required physical volume. In another non-limiting embodiment, if the additive being delivered could be delivered essentially instantaneously to the borehole and cuttings in a concentrated form on a localized basis. It would also be understood that more than one additive may be delivered downhole, and that two or more additives may interact or react with each other to provide a beneficial effect. For example, cross-linkers could be transported in a first vesicle product in the same aqueous third phase as second vesicle product containing the agent to be crosslinked.

[0034] It may be necessary or desirable to add surfactants/emulsifiers, viscosifiers, stabilizers, and mixtures thereof as structural stabilizers to increase

the mechanical stability of the internal phase. Emulsifiers should be understood to include, but are not limited to, surfactants and the like, and viscosifiers should be understood to include, but are not limited to, gelling agents and the like. The emulsifiers and viscosifiers may be in liquid or solid (e.g. powder) form. Suitable emulsifiers may include, but are not necessarily limited to, nonionic, anionic, cationic, amphoteric, zwitterionic, and extended surfactants and in particular, blends thereof. Co-solvents or co-surfactants such as alcohols are optional additives within the multiple phase composition that may aid in filter cake removal once the in situ emulsion has formed downhole.

[0035] In another non-restrictive embodiment, the additive may be a co-surfactant which is an alcohol having from about 3 to about 10 carbon atoms, in another non-limiting embodiment from about 4 to about 6 carbon atoms. A specific example of a suitable co-surfactant includes, but is not necessarily limited to butanol. In one non-limiting embodiment, the multiple phase composition contains non-polar liquid, which may include a synthetic fluid including, but are not necessarily limited to, ester fluids; paraffins (such as PARA-TEQ™ fluids from Baker Hughes Drilling Fluids) and isomerized olefins (such as ISO-TEQ™ from Baker Hughes Drilling Fluids). However, mineral oils such as Escaid 110 (from Exxon) or ECD 99-DW oils (from TOTAL) can also be used as a non-polar liquid in preparing the fluid systems herein. It will be appreciated that the amount of emulsion-forming components to be used is difficult to determine and predict with much accuracy since it is dependent upon a number of interrelated factors including, but not necessarily limited to, the brine type, the bridging particle type, the temperature of the formation, the particular surfactant or surfactant blend used, whether a chelating agent is present and what type, etc. Nevertheless, in order to give some idea of the quantities used, in one non-limiting embodiment, the proportion of non-brine components in the multiple phase composition may range from about 1 vol% independently to about 50 vol%, from about 5 vol % independently to about 20 vol%, and in another non-limiting embodiment may range from about 5 vol% to about 20 vol%.

[0036] Suitable nonionic surfactants include, but are not necessarily limited to, alkyl polyglycosides, sorbitan esters, methyl glucoside esters, amine ethoxylates, diamines ethoxylates, polyglycerol esters, alkyl ethoxylates, polypropoxylated and/or ethoxylated alcohols, sorbitan fatty acid esters including phospholipids, alkyl polyglycosides, gemini surfactants, sorbitan monooleate, sorbitan trioleate, glycerol fatty acid esters including mono- and/or dioleates, polyglycols, alkanolamines and alkanolamides such as ethoxylated amines, ethoxylated amides, ethoxylated alkanolamides, including non-ethoxylated ethanolamides and diethanolamides, and the like as well as block copolymers, terpolymers and the like. Suitable cationic surfactants include, but are not necessarily limited to, arginine methyl esters, alkanolamines and alkylenediamides. In one non-limiting embodiment the suitable anionic surfactants include alkali metal alkyl sulfates, alkyl ether sulfonates, alkyl sulfonate, branched ether sulfonates, alkyl disulfonate, alkyl disulfate, alkyl sulfosuccinate, alkyl ether sulfate, branched ether sulfates.

[0037] Amphoteric or zwitterionic surfactants include, but are not necessarily limited to alkyl betaines and sulfobetaines. Others surfactants, such as extended surfactants may include, but are not necessarily limited to surfactants having a non-ionic spacer-arm between the polar head and the lipophilic tail. The non-ionic spacer-arm central extension may result from a process that may include, but is not necessarily limited to polypropoxylation, polyethoxylation, or combinations thereof. Viscosifiers and gelling agents may include, but are not necessarily limited to, polymers of ethylene, propylene, butylenes, butadiene, styrene, vinyltoluene, and various copolymers and terpolymers thereof, organophilic clays, aluminum soaps and alkoxides and other aluminum salts, alkaline earth soaps, lithium soaps, fumed silica and alumina and the like and mixtures thereof.

[0038] Other suitable stabilizers may include, but are not necessarily limited to, cholesterol and long chain oil soluble waxy alcohols, and the like. These structural stabilizers may be added directly to the second phase prior to the addition of the first phase, directly to the first and second phase emulsion, or they may be added to the fully formed multiple phase vesicle system, if that is

more convenient. In one non-limiting embodiment, the proportion of structural stabilizer based on the total of the first and second phases, prior to injection into the third phase for transport, may range from about 0.1 vol % independently to about 90 vol.%, in another non-limiting embodiment from about 1 to about 50 vol. %. As used herein with respect to a range, "independently" means that any lower threshold may be used together with any upper threshold to give a suitable alternative range.

[0039] The internal phase may optionally include a chelating agent. The chelating agent improves the incorporation of the external oil in the filter cake particles into the in situ emulsion as compared to an identical in situ emulsion formed absent the chelating agent. The use of the multiple phase composition in open hole completion optionally allows for the direct contact of a chelating agent once the multiple phase composition has broken and the chelating agent has been released. The chelating agent may be an acid and/or an acid blend mixed in conventional brine completion fluids, without causing a high viscosity oil continuous emulsion (sludge) and formation blockage. The action of the in situ emulsion formed alters the deposited filter cake, which allows the chelating agent such as an acid or a salt of an acid, such as a polyamino carboxylic acid (PACA) and/or a mineral acid or salt thereof, e.g. hydrochloric acid or an organic acid or salt thereof, e.g. acetic acid, or other acid, to solubilize the bridging and formation particles, such as calcium carbonate, hematite, ilmenite, and barite. Bridging particles composed of manganese tetroxide (in one non-limiting embodiment) may be treated with the multiple phase composition, providing the acid is an organic acid in one non-limiting embodiment. It has been found that PACAs perform relatively better in an alkaline environment as the salt of these acids, which further differentiates them from the more common acidic acids and salts thereof.

[0040] For instance a salt of PACA dissociates barium sulfate from the calcium carbonate treated; the PACA takes on the cation. In a non-limiting example, a Na or K salt of PACA when contacting calcium carbonate contacts and dissolves the barium salt through cationic exchange. The salt form of PACAs performs relatively better than the plain acid form, but the non-salt acid

form still performs the functions and achieves the desired results of the methods herein. The plain acid form works somewhat better at relatively low pH.

[0041] In the non-limiting embodiment where the multiple phase composition contains at least one chelating agent, the chelating agent should be capable of solubilizing or dissolving the bridging particles that make up the filter cake. The chelating agent may be an inorganic acid or salt thereof including, but not necessarily limited to, hydrochloric acid, sulfuric acid, and/or an organic acids including, but not necessarily limited to, an organic agent or salt thereof, e.g. acetic acid, formic acid and mixtures thereof. In one non-limiting embodiment, the acid may be only one mineral acid or only one organic acid.

[0042] In most embodiments, the multiple phase composition may contain a chelating agent that is a polyamino carboxylic acid (PACA) or a salt of PACA. Suitable PACAs include, but are not necessarily limited to, nitrilotriacetic acid (NTA), ethylenediamine tetraacetic acid (EDTA), trans-1,2-diaminocyclohexane-N,N,N',N',-tetraacetic acid monohydrate (CDTA), diethylenetriamine pentaacetic acid (DTPA), dioxaoctamethylene dinitrilo tetraacetic acid (DOCTA), hydroxyethylethylenediamine triacetic acid (HEDTA), triethylenetetramine hexaacetic acid (TTHA), trans-1,2-diaminocyclohexane tetraacetic acid (DCTA), and mixtures thereof.

[0043] The net effect of such a treatment system will improve an operator's chance of injecting water in a reservoir to maintain reservoir pressure (for example, for injection wells), and improve production rates in producing wells. In either case, skin (filter cake) alteration is accomplished by circulating and placing the broken multiple phase composition and additive across the injection production interval. The multiple phase composition may be used for open hole expandable and non-expandable screen applications or other various open hole operations.

[0044] The concentration of chelating agent in the multiple phase composition has a lower limit of about 1 vol % independently, alternatively of about 5 vol %, and an upper limit of about 30 vol %, alternatively about 20 vol %, and in another non-restrictive embodiment up to about 15 vol %. There are

various ways by which the chelating agent may be delivered. The chelating agent may be an additive within the multiple phase composition and released onto the filter cake once the multiple phase composition is broken; or may be added after the broken multiple phase composition has contacted the filter cake; or may be added to the broken multiple phase composition once it is in place before removing the majority of the OBM filter cake, or invert emulsion, and combinations thereof.

[0045] With the optional employment of a filtration control additive, also called an additive for delay herein, the skin removal rate may be controlled for operational flexibility. In brief, one non-limiting embodiment OBM or invert emulsion filter cake clean up technology utilizes the in situ emulsion formed and optional chelating agent techniques and optional filtration control additives in a single blend to change the OBM or invert emulsion filter cake to a microemulsion and simultaneously decompose its acid soluble components. Altering the filter cake using the in situ emulsion facilitates solubilization of solids by preventing a sludge that could form between the chelating agent and OBM or invert emulsion cake and making soluble particles unavailable to unspent chelating agent.

[0046] In one non-limiting embodiment, the methods herein utilize a filtration control additive (fluid loss control additive), such as a polymer and/or solid particulates such as sized salts, to convert an OBM cake to a water-based filter cake. The benefits of such conversions are several. When an OBM filter cake is oil wet and poses compatibility problems for certain completion operations, such as water injection and gravel packing, a water-based filter cake is naturally compatible with injection water and brine-based gravel pack carrier fluids. Additionally, a water-based filter cake is ideal for damage remediation (filter cake destruction) when mineral acids, organic acids, oxidizing agents, water soluble enzymes (catalysts) and in situ acid generators are spotted in a wellbore after (or during) the filter cake reversal process. This non-restrictive method may use a polymeric filtration control additive, such as but not limited to a non-ionic starch or other cellulosic additives, such as, but not limited to HEC (hydroxyethyl cellulose). When one of these fluid loss control additives is pre-

solubilized in the water phase of a multiple phase composition, the fluid loss control additive retards the disintegration of the filter cake that happens when the oil is solubilized. The filter cake becomes water-wet, but maintains a compact consistency for a longer time when compared to the treatment without a fluid loss additive in the multiple phase composition. The solid particulates that once comprised the OBM filter cake, such as sized calcium carbonate and barite, or any other particulates, are still in place after the conversion. The fluid loss control additive found in the multiple phase composition is deposited in and around pre-existing particulates to redevelop a waterbased filter cake. It should be recognized that this process, reversal of an oil wettability (OBM) to water-based wettability, including the deposition of the water-based fluid loss control additive occurs in a single step.

[0047] As the OBM filter cake is converted with the aforementioned water-based filtration control additive, the internal phase may also contain acids, barite dissolvers (chelants) or other precursor additives that can dissolve the acid-soluble particles or dissolve the barite and break down the fluid loss additive (polymeric or otherwise). The value of such a conversion using a multiple phase composition to delay the forming of an in situ emulsion is that more of the OBM filter cake may be converted to a water-based filter cake containing dissolvable particulates that may be removed in a single operational step compared to an emulsion formed at the surface and lowered downhole.

[0048] Modified starches and/or biopolymers may be used to increase the viscosity and/or other rheological properties of the multiple emulsion, which also helps to control or delay the release of the additives from the multiple phase emulsion by increasing the viscosity and/or rheology of the multiple phase emulsion. Typical modified starches used are known by those skilled in the art. However, a modified starch usually refers to a carboxymethylated starch, although the starch may be modified in other ways. One or more carboxymethyl groups may be grafted on to a simple starch to give it additional temperature stability as well as improved rheological properties. Starches may also be crosslinked, such as with agents including, but not necessarily limited

to, epichlorohydrin, polyvinyl alcohol, boric acid, glyoxal, succinic acid, urea/formaldehyde, and combinations thereof.

[0049] In one non-limiting embodiment, the proportion of filtration control additive in the multiple phase composition ranges from about 0.1 lb/bbl (about 0.285 kg/m³) independently to about 10 lb/bbl (about 28.5 kg/m³). Alternatively, the upper proportion range of the filtration control additive may be about 2.0 lb/bbl (about 5.7 kg/m³). The exact or desired proportion of filtration control additive in the multiple phase composition will depend upon a number of interrelated factors, including, but not necessarily limited to, the type of filtration control additive, the desired in situ emulsion to be formed and type and proportion of components therein, as well as the nature of the OBM filter cake being contacted. In another non-limiting embodiment, the salts suitable for use in creating the brine include, but are not necessarily limited to, sodium chloride, potassium chloride, calcium chloride, sodium bromide, calcium bromide, sodium formate, potassium formate, cesium formate and combinations thereof. The density of the brines may range from about 8.4 lb/gal (about 1006.5 kg/m³) independently to about 15 lb/gal (1797.3 kg/m³), although other densities may be given elsewhere herein.

[0050] It will be appreciated that it is not necessary for all of the particles to be removed from a filter cake for the methods to be considered successful. Success is obtained if more particles are removed using the multiple phase composition than if it is not used, as compared to the case where no multiple phase composition is used. Alternatively, the methods herein are considered successful if a majority of the OBM filter cake is removed. In general, of course, it is desirable to remove as much of the OBM or invert emulsion and corresponding filter cake as possible. One non-restrictive goal is to remove filter cake particles to obtain 90% injection or production permeability.

[0051] The methods herein have the advantages of reduced formation skin damage to the wellbore, and consequently increased hydrocarbon recovery, and/or increased water injection rate, as compared with an otherwise identical method absent the delivery of a multiple phase composition that is broken for release of an additive in order to form an in situ emulsion downhole.

[0052] Once the multiple phase composition has been broken, and the internal phase or additive released, the released additive/internal phase and the broken multiple phase composition may contact the filter cake, so that an in situ emulsion forms downhole, such as a microemulsion, miniemulsion, nanoemulsion, or mixtures thereof; i.e. for purposes of wellbore cleanup. In a non-limiting embodiment, additives that may aid in forming the in situ emulsion include structural stabilizers, surfactants, co-surfactants, viscosifiers, chelating agents, filtration control additives, suspending agents, dispersants, wetting agents, solvents, co-solvents, acids, and mixtures thereof.

[0053] Microemulsions are thermodynamically stable, macroscopically homogeneous mixtures of at least three components: a polar phase and a nonpolar phase (usually, but not limited to, water and organic phase) and a surfactant. Microemulsions form spontaneously and differ markedly from the thermodynamically unstable macroemulsions, which depend upon intense mixing energy for their formation. Microemulsions are well known in the art, and attention is respectfully directed to S. Ezrahi, A. Aserin and N. Garti, "Chapter 7: Aggregation Behavior in One-Phase (Winsor IV) Microemulsion Systems", in P. Kumar and K. L. Mittal, ed., Handbook of Microemulsion Science and Technology, Marcel Dekker, Inc., New York, 1999, pp. 185-246.

[0054] A miniemulsion may form by having two immiscible liquid phases mixed together, such as a surfactant and a co-surfactant, via high shear mixing. Droplets of about 50 nm to about 500 nm may form. A nanoemulsion has an inner phase that may act as an emulsifier, such that the inner state disperses into nano-size droplets within the outer phase. These types of emulsions may form spontaneously.

[0055] In the foregoing specification, the method has been described with reference to specific embodiments thereof, and has been suggested as effective in providing a method for forming and using a multiple emulsion for purposes of delaying the removal of a majority of an oil-based mud (OBM) filter cake from a hydrocarbon reservoir wellbore. The method may include delivering a multiple phase composition downhole and breaking the multiple phase composition for release of an additive or internal phase to delay the

forming of in situ emulsion, e.g. a microemulsion, a miniemulsion, a nanoemulsion, or mixtures thereof, where the delivered additive is utilized to form the in situ emulsion, for wellbore cleanup for purposes of contacting the OBM filter cake particles to remove the filter cake.

[0056] The multiple phase composition allows for controlled release in space and time to form the in situ emulsion. However, it will be evident that various modifications and changes can be made thereto without departing from the broader 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 phases, agents, additives, surface active material bilayers, structural stabilizers, etc. and proportions thereof falling within the claimed parameters, but not specifically identified or tried in a particular method to improve the delivery of agents and components herein, are anticipated to be within the scope of this application.

[0057] The present application may suitably comprise, consist or consist essentially of the elements disclosed and may be practiced in the absence of an element not disclosed. For instance, the method may consist of or consist essentially of a method for removing a majority of an oil-based mud (OBM) filter cake from a hydrocarbon reservoir wellbore by delivering a multiple phase composition comprising an additive into the wellbore; subsequently breaking the multiple phase composition thereby releasing the additive; and then contacting the OBM filter cake particles with the broken multiple phase composition and the released additive to form an in situ emulsion downhole. This in situ emulsion may be a nanoemulsion, a miniemulsion, a microemulsion, or mixtures thereof. Finally, the method consists of or consists essentially of incorporating a majority of the external oil from the OBM filter cake and into the in situ emulsion.

[0058] The words “comprising” and “comprises” as used throughout the claims, are to be interpreted to mean “including but not limited to” and “includes but not limited to”, respectively.

CLAIMS

What is claimed is:

1. A method for removing a majority of an oil-based mud (OBM) filter cake from a hydrocarbon reservoir wellbore comprising:

breaking a multiple phase composition after delivery of the multiple phase composition into a wellbore thereby releasing the additive, wherein the multiple phase composition comprises an internal phase and a second phase; wherein the additive is dispersed within the internal phase, the second phase, and combinations thereof; wherein the additive is released from the multiple phase composition; and wherein the at least one internal phase component is selected from the group consisting of structural stabilizers, surfactants, viscosifiers, chelating agents, filtration control additives, suspending agents, dispersants, wetting agents, and mixtures thereof;

contacting OBM filter cake particles with the broken multiple phase composition and the released internal phase component to form an in situ emulsion downhole, wherein the in situ emulsion is selected from the group consisting of a nanoemulsion, a miniemulsion, a microemulsion, and mixtures thereof; and

incorporating a majority of the external oil from the OBM filter cake into the in situ emulsion.

2. The method of claim 1, further comprising delivering a multiple phase composition comprising an additive into the wellbore prior to breaking the multiple phase composition.

3. The method of claim 1 or 2, wherein the proportion of the internal phase in the multiple phase composition ranges from 1 vol. % to 90 vol. %.

4. The method of claim 1 or 2, wherein the internal phase comprises vesicles ranging in size from 0.01 micrometers to 1000 micrometers.
5. The method of claim 1 or 2, wherein the surfactant is selected from the group consisting of non-ionic surfactants, anionic surfactant, cationic surfactants, amphoteric, zwitterionic surfactants, extended surfactants, and combinations thereof.
6. The method of claim 1 or 2, wherein the proportion of the structural stabilizer based on the total of the internal phase and the second phase, prior to injection into the third phase for transport, ranges from 0.1 vol.% to 90 vol.%.
7. The method of claim 1 or 2 further comprising drilling a wellbore in a hydrocarbon reservoir with an OBM prior to delivering the multiple phase composition into the wellbore.
8. The method of claim 1 or 2 further comprising forming an OBM filter cake over at least part of the wellbore prior to breaking the multiple phase composition for release of an additive.
9. The method of claim 1 or 2 where incorporating a majority of the oil from the OBM filter cake into the in situ emulsion creates a characteristic selected from the group consisting of where formation skin damage to the wellbore is reduced, where subsequent hydrocarbon recovery is increased, where subsequent water injection rate into the reservoir is increased, and combinations thereof as compared with an otherwise identical method absent the in situ emulsion formed downhole.
10. The method of claim 1 or 2, wherein the in situ emulsion comprises a non-polar liquid selected from the group consisting of synthetic base and mineral oils, ester fluids, paraffins, isomerized olefins, and mixtures thereof.

11. The method of claim 1, wherein a chelating agent has been added to the multiple phase composition according to a procedure selected from the group consisting of:

- adding the chelating agent to a phase of the multiple phase composition;
- adding the chelating agent directly to the OBM after the multiple phase composition has been broken;
- adding the chelating agent to the broken multiple phase composition;
- and
- a combination thereof;

where the chelating agent improves the incorporating of the external oil from the OBM filter cake into the in situ emulsion as compared to an identical in situ emulsion absent the chelating agent.

12. The method of claim 11, wherein the chelating agent comprises an acid selected from the group of inorganic acids consisting of hydrochloric acid, sulfuric acid, and organic acids consisting of acetic acid, formic acid and salts thereof, and mixtures thereof.

13. The method of claim 11 or 12, wherein the chelating agent is a polyamino carboxylic acid selected from the group consisting of nitrilotriacetic acid (NTA), ethylenediamine tetraacetic acid (EDTA), trans-1,2-diaminocyclohexane- N,N,N', N',-tetraacetic acid monohydrate (CDTA), diethylenetriamine pentaacetic acid (DTPA), dioxaoctamethylene dinitrilo tetraacetic acid (DOCTA), hydroxy-ethylethylenediamine triacetic acid (HEDTA), triethylenetetramine hexaacetic acid (TTHA), trans-1,2diaminocyclohexane tetraacetic acid (DCTA), and salts thereof, and mixtures thereof.

14. The method of claim 11 or 12, wherein the concentration of the chelating agent in the multiple phase composition ranges from 1 to 30 vol%.

15. The method of claim 1 or 2, wherein the multiple phase composition further comprises a water-soluble filtration control additive selected from the group consisting of modified starch, polymers, and mixtures thereof.

16. The method of claim 15, wherein the proportion of the water-soluble filtration control additive in the multiple phase composition ranges from 0.1 lb/bbl (about 0.285 kg/m³) to 10 lb/bbl (about 28.5 kg/m³).

17. The method of claim 1 or 2, wherein the filter cake particles are selected from the group consisting of calcium carbonate, hematite, ilmenite, manganese tetroxide, manganous oxide, iron carbonate, magnesium oxide, barium sulfate, and mixtures thereof.