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(57) Abstract: A wellbore fluid may include an aqueous base fluid; a mixture of metal bromides dispersed in the aqueous base fluid; and a plurality of nanoparticles suspended in the aqueous base fluid, where the metal bromides and the plurality of nanoparticles are present in the wellbore fluid in an amount to provide a fluid density of at least 14.5 ppg (1.74 kg/L) and a true crystallization temperature of the wellbore fluid below 40°F (4.4°C). A method for completing a wellbore may include pumping a wellbore fluid into the wellbore, the wellbore fluid may include an aqueous base fluid; a mixture of metal bromides dispersed in the aqueous base fluid; and a plurality of nanoparticles suspended in the aqueous base fluid, where the metal bromides and the plurality of nanoparticles are present in an amount to provide a fluid density of at least 14.5 ppg (1.74 kg/L) and a true crystallization temperature of the wellbore fluid below 40°F (4.4°C).



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HIGH DENSITY WELLBORE FLUID USING METAL HALIDE SALT AND METHODS THEREOF

BACKGROUND

[0001] This application claims priority to and the benefit of U.S. Provisional Application No. 62/623,305, filed January 29, 2018, the entire disclosure of which is hereby incorporated herein by reference.

[0002] During the drilling of a wellbore, various fluids are typically used in the well for a variety of functions. The fluids may be circulated through a drill pipe and drill bit into the wellbore, and then may subsequently flow upward through wellbore to the surface. During this circulation, a drilling fluid may act to remove drill cuttings from the bottom of the hole to the surface, to suspend cuttings and weighting material when circulation is interrupted, to control subsurface pressures, to maintain the integrity of the wellbore until the well section is cased and cemented, to isolate the fluids from the formation by providing sufficient hydrostatic pressure, to prevent the ingress of formation fluids into the wellbore, to cool and lubricate the drill string and bit, and/or to maximize penetration rate.

[0003] Once drilling operations have been completed, the well is prepared for the completion operations whereby the mud used for drilling is often displaced by a completion fluid. There are numerous methods of completing a well, amongst which are open-hole completions, pre-drilled, liner, and gravel packed screened systems. Completion fluids broadly refer to any fluid pumped down a well after drilling operations have been completed, including fluids introduced during acidizing, perforating, fracturing, workover operations, etc. A drill-in fluid is a specific type of drilling fluid that is designed to drill and complete the reservoir section of a well in an open hole, *i.e.*, the “producing” part of the formation. In particular, it is desirable to protect the formation from damage and fluid loss, and not impede future production. Most drill-in fluids contain several solid materials including viscosifiers, drill solids, and additives used as bridging agents to prevent lost circulation and a barite weighting material to control pressure formation.

[0004] Completion fluids are typically water-based clear fluids and are formulated to the same density as or slightly greater density than the mud used to drill the well in order to retain the hydraulic pressure on the well bore. The clear fluids are typically halide based brines or organic based brines such as the formate-based fluids. There are occasions when a completion fluid with density up to 19.0 lbm/gal is desired. Currently, there are two conventional choices commercially available in the oil industry that allow to reach such a density—zinc bromide and cesium formate. Each of these two candidates has limitations. For example, zinc bromide is a priority pollutant and, as a result, cannot be used in some applications. Because cesium is rare, the cost and availability of cesium formate are often prohibitive.

[0005] Upon completion of drilling, a filter cake and/or fluid loss pill may stabilize the wellbore during subsequent completion operations such as placement of a gravel pack in the wellbore. Additionally, during completion operations, when fluid loss is suspected, a fluid loss pill of natural polymers and/or bridging agents may be spotted into to reduce or prevent such fluid loss by injection of other completion fluids behind the fluid loss pill to a position within the wellbore which is immediately above a portion of the formation where fluid loss is suspected. Injection of fluids into the wellbore is then stopped, and fluid loss will then move the pill toward the fluid loss location.

SUMMARY

[0006] This summary is provided to introduce a selection of concepts that are further described below in the detailed description. This summary is not intended to identify key or essential features of the claimed subject matter, nor is it intended to be used as an aid in limiting the scope of the claimed subject matter.

[0007] In one aspect, embodiments disclosed herein relate to a wellbore fluid that includes an aqueous base fluid; a mixture of metal bromides dispersed in the aqueous base fluid; and a plurality of nanoparticles suspended in the aqueous base fluid, where the metal bromides and the plurality of nanoparticles are present in the wellbore fluid in an amount to provide a fluid

density of at least 14.5 ppg (1.74 kg/L) and a true crystallization temperature of the wellbore fluid below 40°F (4.4°C).

[0008] In another aspect, embodiments of the present disclosure relate to a method for completing a wellbore, the method including pumping a wellbore fluid into the wellbore, the wellbore fluid including an aqueous base fluid; a mixture of metal bromides dispersed in the aqueous base fluid; and a plurality of nanoparticles suspended in the aqueous base fluid, where the metal bromides and the plurality of nanoparticles are present in an amount to provide a fluid density of at least 14.5 ppg (1.74 kg/L) and a true crystallization temperature of the wellbore fluid below 40°F (4.4°C).

[0009] Other aspects and advantages of the claimed subject matter will be apparent from the following description and the appended claims.

DETAILED DESCRIPTION

[0010] Generally, embodiments disclosed herein relate to high density wellbore fluids and methods of using the same. More specifically, embodiments disclosed herein relate to wellbore fluids for downhole applications formed of an aqueous base fluid, a mixture of metal bromides dispersed in the aqueous base fluid and a plurality of colloidal particles such as nanoparticles suspended in the aqueous base fluid. The inventors of the present disclosure have found that wellbore fluids that include a mixture of metal bromides and a plurality of nanoparticles in a specific amount may exhibit high density and a low true crystallization temperature (TCT).

[0011] According to the present embodiments, the wellbore fluids of the present disclosure incorporate a mixture of metal halides that can be dispersed or solubilized in a base fluid, such as an aqueous base fluid. The mixtures that have shown utility in the wellbore fluids of this disclosure are mixtures of metal bromides. In one or more embodiments, the metal bromides are stably solubilized in the aqueous base fluid for at least one month at 77°F (25°C). In the field, the wellbore fluids as described herein may be stable for at least 6 months and up to a year.

[0012] According to embodiments of the present disclosure, the mixtures of metal bromides may be selected from the group of alkaline earth metal bromides, Group VIIB metal bromides and mixtures of thereof. In one or more embodiments, the mixture of metal bromides may include at least two metal bromides. For example, in embodiments where a mixture of two metal bromides is used, one of the metal bromide (first metal bromide) is an alkaline earth metal bromide (such as CaBr_2), and the second metal bromide is a Group VIIB metal bromide (such as MnBr_2). In such embodiments, the molar ratio of the first metal bromide and the second metal bromide may range from about 1:1 to about 2:1, where the lower molar ratio can be any of 1:1, 1.4:1, 1.5:1 and the upper molar ratio can be any of 1.56:1, 1.94:1 or 2:1, where any lower molar ratio can be used with any upper molar ratio. It is also envisioned that the mixture of the metal bromides may include more than two metal bromides.

[0013] In one or more embodiments, the wellbore fluids as described herein may be zinc free for environmental benefit and cesium free for cost benefit. According to the present embodiments, the wellbore fluids of the present disclosure may also be free of tin bromides such as SnBr_2 and/or SnBr_4 which may form undesirable precipitates at pHs often used in the wellbore environment.

[0014] As noted above, the wellbore fluids of the present disclosure may incorporate a plurality of colloidal particles that may be dispersed or suspended in an aqueous base fluid. The colloidal particles that have shown utility in the present disclosure are selected from the group of nanoparticles. As defined herein, nanoparticles are defined as having at least one dimension of less than 1 micron. The nanoparticles of the present disclosure do not increase the viscosity of the wellbore fluid, as compared to wellbore fluids containing the same type of particles, but of larger size. Rather, the nanoparticles act as densification agents that may increase the density of the fluid into which they are dispersed or suspended without substantially increasing the plastic viscosity (PV) of the fluid and/or without substantial solid sagging (settling). In contrast, regular solids such as CaCO_3 /barite that may be used in wellbore fluids increase mud density and PV and settle without stirring. As it will be

described later in more detail, the wellbore fluids as described herein may exhibit a Newtonian low viscosity.

[0015] According to various embodiments, wellbore fluids as described herein may have an apparent kinetic viscosity at room temperature that ranges from about 5 cP to about 150 cP, where the lower limit can be any of 5 cP, 10 cP, 15 cP or 20 cP and the upper limit can be any of 120 cP, 130 cP, 140 cP or 150 cP, where any lower limit can be used with any upper limit.

[0016] According to the present embodiments, the nanoparticles may be present in the wellbore fluid in an amount that ranges from 4 wt% to 60 wt% of the total weight of the wellbore fluid, where the lower limit can be any of 4 wt%, 10 wt%, 15 wt%, 20 wt%, or 25 wt% and the upper limit can be any of 35 wt%, 40 wt%, 45 wt%, 50 wt%, 55 wt%, or 60 wt% where any lower limit can be used with any upper limit.

[0017] The resulting density of wellbore fluids as described herein is a function of the amount of the metal bromides and the nanoparticles suspended in the aqueous base fluid. Furthermore, due to their small size, nanoparticles do not damage or plug the producing formation and thus may be present in the production interval during completion operations for example. The wellbore fluids incorporating the mixture of metal bromides and nanoparticles of the present disclosure are stable and meet the desired rheology and filtration properties for application in completion operations such as completion brines, fluid loss pills, drilling fluids, or as gravel packing fluids.

[0018] As previously noted, it was found by the inventors of the present disclosure that the combination of a mixture of metal bromides with a plurality of nanoparticles as described herein, has a synergetic effect on the properties of a wellbore fluid by increasing its density while lowering the TCT. For example, wellbore fluids formulated with such components may exhibit high density and a low TCT. According to the present embodiments, wellbore fluids as described herein may be formulated with a salt density typically in a range from about 14.5 ppg (1.74 kg/L) to about 18.0 ppg (2.16 kg/L), depending on the particular use of the fluid and specific conditions. For example, in one or more embodiments, a wellbore fluid that includes an aqueous base fluid, a plurality of nanoparticles and a mixture of metal

bromides present in the wellbore fluid in a specific molar ratio, may exhibit a density of at least 14.5 ppg (1.74 kg/L) and a true crystallization temperature below 40°F (4.4°C). Without being bound by the theory, it is believed that the molar ratio of the metal bromides suspended in the aqueous base fluid dictates the density of the wellbore fluid and its TCT. For example, in one or more embodiments, the wellbore fluid may include a plurality of nanoparticles and a mixture of metal bromides that includes a first metal bromide and a second metal bromide. When the molar ratio of the first and the second metal bromide ranges from 1:1 to 2:1, the wellbore fluid may exhibit a density of at least 14.5 ppg (1.74 kg/L) and a true crystallization temperature of the wellbore fluid below 40°F (4.4°C).

[0019] As described herein, the term completion fluid refers to fluids present in the wellbore and/or used during a wellbore operation to complete a well. A completion brine is a high-density fluid which is substantially free of solids and may be used as a completion fluid in the wellbore or may be used as a base to which other additives may be added for specific completion purposes (such as gravel packing, fluid loss pills or drilling fluids). While a completion brine is conventionally solids free, the present fluid may still be used, because of the small size of the nanoparticles incorporated therein. Their presence may be tolerated in certain proportions while still imparting an improvement in the density of the wellbore fluid and in lowering the freezing temperature of the wellbore fluid.

[0020] As noted above, the nanoparticles may be added, along with the mixture of metal bromides, with the purpose of increasing the density of the fluid into which they are dispersed or suspended while decreasing the true crystallization temperature, TCT, of the fluid. The nanoparticles used for the formulation of wellbore fluids of the present disclosure may exhibit the following properties: a) do not or minimally interact with the base fluid and other components of the wellbore fluid; b) form a stable dispersion; and c) do not settle.

[0021] According to various embodiments, the nanoparticles of the present disclosure may be coated or uncoated. As used herein, the term coated refers to any chemical or physical modification applied to the surface of the nanoparticles with the purpose of improving the dispersibility and/or the suspendability of the nanoparticles, as well as to modify their physical and/or chemical properties. Thus, for example, in the context of silica

nanoparticles, the particles may have a hydrous oxide (such as alumina) or silane coating provided thereon, or optionally in combination with an overlay reacted upon the base coating.

[0022] The nanoparticles that have shown utility in the wellbore fluids of the present disclosure are selected from the group of silica, iron carbonate, iron oxide, titanium oxide, tungsten oxide, zirconium oxide, zirconium silicate nanoparticles which may be suspended or dispersed in an aqueous base fluid.

[0023] In embodiments where silica nanoparticles are used, such nanoparticles may be provided as colloidal silica nanoparticles. In such embodiments, the amount of pure silica contained in the colloidal silica products may range from 5 wt% to 50 wt%, where the lower limit can be any of 5 wt%, 10 wt%, 15 wt%, or 20 wt% and the upper limit can be any of 35 wt%, 40 wt%, 45 wt%, or 50 wt% where any lower limit can be used with any upper limit. One example of such a solution is commercially available from NYACOL NANO TECHNOLOGIES (Ashland, MA) under the name of DP9717. DP9717 contains surface modified SiO₂ in water. Such a silica product is stable in a pH range from 2.5 to 10.5. In various embodiments, the silica nanoparticles may be provided as a solution of nano-sized precipitated silica which is formed from a controlled neutralization of sodium silicate with the formation of a nano-sized solid material that can be concentrated in the solution. Such solid suspensions, depending on the method of manufacture, can be closer to neutral pH, and can be engineered to be very stable in high hardness solutions.

[0024] The size of the nanoparticles used for the formulation of the wellbore fluids as described herein may prevent or reduce the particles from sagging or settling. In addition, the size of the nanoparticles may determine the optical properties of the fluid. For example, it is well known that small particles are very efficient at scattering shorter light wavelengths.

[0025] Light scattering and absorption of light are major physical processes that contribute to the visible appearance of most objects or media. Surfaces or media described as white owe their appearance to multiple scattering of light by internal or surface inhomogeneities in the media or object. Spectral absorption, defined as the selective absorption of certain light wavelengths, determines the color of most objects, with some modification by elastic

scattering. Light scattering which can also create color without absorption, often shades of blue, as with the sky, for example, can be classified as Rayleigh and Mie scattering.

[0026] According to the Rayleigh light scatter equation, the scattering intensity, I , by a particle is described by equation (1),

$$I=I_0 [(1+\cos^2\theta)/2R^2] [2\pi/\lambda]^4 [(n^2-1)/(n^2+2)]^2 (d/2)^6 \quad (1)$$

where R represents the distance to the particle, θ is the scattering angle, n is the refractive index of the particle, d is the diameter of the particle, λ is the wavelength of the incident light, and I_0 is the intensity of the incident light. There are numerous factors that contribute to the scattering intensity, such as the particle size, distance to the particle, the scattering angle, and the refractive index of the particle. However, nanoparticles scattering is highly dependent on wavelength with shorter wavelengths such as ultraviolet or blue light, which are scattered much more intensely than longer wavelengths (red light). According to embodiments of the present disclosure, the wellbore fluids as described herein may have a clear appearance, or a semi-transparent appearance, and may also have a light blue hazy look. As described herein, the term appearance is a qualitative description of the wellbore formulation. In one or more embodiments, the size of the nanoparticles is selected in such a manner that the wellbore fluid does not scatter light above 400 nm. In various embodiments, the nanoparticles may have an average size of less than 1 micron, 0.75 microns, 0.5 microns, or 0.4 microns. According to various embodiments, wellbore fluids formulated as described herein may be filtered using filter paper with pore size less than 1 micron in order to remove larger particles that may have a deleterious effect on the wellbore operation, but wherein such a filtration process preserves the presence of the nanoparticles with the desired size in the fluid formulation. By using such nanoparticles, the scattering of the light by the wellbore fluid at lower wavelengths is avoided or reduced.

[0027] As used herein, turbidity (or haze) is the cloudiness or haziness of a wellbore fluid caused by colloidal particles (such as nanoparticles) and other contributing factors that may be generally invisible to the naked eye. As described herein, “clear and colorless” with respect to a brine or a completion fluid means that the fluid has an “NTU” (nephelometric turbidity unit) less than about 20. For example, a pure CaBr_2 brine (when is filtered and

clean) has an NTU less than 20. NTU is an American Petroleum Institute accepted unit related to the suspended solids in a brine (higher NTU=more suspended solids), based on how much light is scattered by a sample. The procedure for determining NTU is described in API RP 13J and is a procedure well known to those of ordinary skill in the art. According to the present embodiments, the turbidity of wellbore fluids of the present disclosure may range from about 5 to about 300 NTU, where the lower limit can be any of 5 NTU, 10 NTU, 15 NTU, 20 NTU, 25 NTU, and 50 NTU and the upper limit can be any of 50 NTU, 100 NTU, 200 NTU, 250 NTU, 280 NTU or 300 NTU where any lower limit can be used with any upper limit.

[0028] The aqueous base fluid of the present disclosure may generally be any water based fluid phase. In one or more embodiments, the aqueous base fluid forms the continuous phase of the fluid and may be selected from: fresh water, sea water, brines, mixtures of water or brine and water soluble organic compounds and mixtures thereof. In those embodiments of the disclosure where the aqueous medium is a brine, the brine is water comprising an inorganic salt or organic salt. The salt may serve to provide a portion of the fluid's density (to balance against the formation pressures), and may also reduce the effect of the water based fluid on hydratable clays and shales encountered during completion. In various embodiments of the wellbore fluid disclosed herein, the brine may include seawater, aqueous solutions wherein the salt concentration is less than that of sea water, or aqueous solutions wherein the salt concentration is greater than that of sea water. Salts that may be found in seawater include, but are not limited to, sodium, calcium, aluminum, magnesium, potassium, strontium, and lithium, salts of chlorides, bromides, carbonates, iodides, chlorates, bromates, nitrates, oxides, sulfates, silicates, phosphates and fluorides. Salts that may be incorporated in a brine include any one or more of those present in natural seawater or any other organic or inorganic dissolved salts. The brines that have shown utility in the wellbore fluids of this disclosure are halide brines. According to embodiments of the present disclosure, the halide brines may be selected from the group of alkaline earth metal bromides, Group VIIB metal bromides and mixtures of thereof.

[0029] A first characteristic of a wellbore fluid is the density of the fluid. Moreover, as the brine may contain one or more salts dissolved in a base fluid, the crystallization temperature of the brine is another parameter to be considered. For example, it is well known that the use of brines for low temperature applications in cold climates and/or deep wells presents a problem of brine crystallization. At temperatures at or below the crystallization temperature of the brine, the precipitation of crystallizing solids (e.g., salts) can change the density of the brine fluid through the wellbore column and as a result, deteriorate the ability of the fluid to maintain pressure control. Further crystallization may also lead to crystallized solids plugging the subterranean well. For example, CaBr_2 is a brine useful to formulate wellbore fluids with a density ranging up to 15.3 lb/gal (1.84 kg/L), but from 14.5 lb/gal (1.74 kg/L) to above, its true crystallization temperature (TCT) and the PCT (crystallization under pressure) are too high for deep water applications. In the case when nanosilica is used, the density is 15.4 ppg (1.85 kg/L), while the TCT is about 30°F (-1.11°C). However, silica nanoparticles cannot be used by themselves as a brine because an increase in their amount may trigger an increased in the density, TCT, as well as the viscosity of the fluid.

[0030] The crystallization temperature of a brine is commonly measured in accordance to a standardized test method described in ANSI/APS Recommended Practice 13J. To characterize the crystallization profile of the brine, as described in API Recommended Practice 13J, an apparatus is used to alternately cool and heat a sample of brine fluid for measuring three different crystallization temperatures. During testing, the sample is slowly and continuously cooled until a temperature is reached at which visible crystals start to form in the sample and the temperature is recorded as the First Crystal to Appear (FCTA) temperature. During cooling, the FCTA temperature corresponds to a minimum inflection point in a plot of temperature versus time, the minimum inflection point being generally the result of a super-cooling effect. Upon reaching the FCTA temperature, the cooling temperature is held constant while the exothermic brine crystallization process proceeds. Heat is released during the brine crystallization process and the maximum temperature, or maximum inflection point, reached immediately following the FCTA temperature is recorded as the True Crystallization Temperature (TCT). The TCT corresponds to the actual true crystallization temperature of the brine. In one or more embodiments of the disclosure, a

mixture of metal bromides and nanoparticles present in the wellbore fluid in a specific amount may reduce the TCT of the brine below 40°F (4.4°C).

[0031] One of the optional components of the wellbore fluids of this disclosure is a polymeric crystallization temperature agent which may be added to the mixture of aqueous base fluid, mixture of metal bromides and the plurality of nanoparticles in order to regulate the true crystallization temperature (TCT) of the brine. Such a polymer may be fully dispersible in the halide brine. To control the formation of the foam formed upon mixing the polymer with the brine, a silicone defoamer may be added to the formulation. The polymers that have shown utility in the completion fluids of this disclosure are selected from the group of pyrrolidones based polymers. In one or more embodiments, the polymeric crystallization temperature agent is polyvinylpyrrolidone (PVP). The role of the crystallization temperature agent is to lower the true crystallization temperature (TCT), especially the crystallization temperature of the brine under pressure (PCT). According to various embodiments, the amount of PVP added to the wellbore fluid may range from 0.5 to 1.5 v%.

[0032] In one or more embodiments of the present disclosure, the wellbore fluids as described herein may be prepared using metal bromides as dry salts. It is also envisioned that the metal bromides may be provided as a brine. In yet another embodiment, one of the metal bromide may be provided as a dry salt, while another metal bromide may be provided as a brine. In such embodiments, when two metal bromides are used (such as a first metal bromide and a second metal bromide), the first metal bromide is provided as a brine, while the second metal bromide may be provided as a dry salt or as a brine. In such embodiments, the wellbore fluid that includes a mixture of two metal bromides may be prepared by first adjusting the pH of the solution containing the second metal bromide (e.g. MnBr_2) to a specific pH, namely pH_1 . In one or more embodiments, pH_1 may range from about 4 to about 5. Next, a first metal bromide (e.g. CaBr_2) is provided as a stock brine, followed by the addition of a solution containing a plurality of silica nanoparticles with the formation of a premix fluid. In such embodiments, mixing the solution containing the plurality of the silica nanoparticles with the brine may be performed at a pH ranging from about 2 to about 10.

According to the present embodiments, the density of the stock brine may vary from about 2 to about 5. For example, in one embodiment, the density of the stock solution may be 14.2 ppg (1.70 kg/L). Afterwards, the water may be removed from the premix fluid to form a wellbore fluid with a desired density.

[0033] In one or more embodiments, the water may be removed by heating the premix fluid with the formation of a wellbore fluid with a desired density. It is also envisioned that the water may be removed by mixing the premix fluid with dry salts with the formation of a wellbore fluid with a desired density. For example, in one or more embodiments, the wellbore fluid may be manufactured by removing water from a pre-mix fluid having a density of d_1 to form a wellbore fluid with a density of d_2 . In such embodiments, the nanoparticles may be precipitated by neutralizing sodium silicate in an aqueous fluid. According to one or more embodiments, removing water may be performed by a vapor evaporation process.

[0034] In yet another embodiment, the wellbore fluid may be manufactured by mixing, at a pH ranging from about 2 to about 10, a first aqueous fluid comprising a plurality of nanoparticles with a second aqueous fluid comprising a mixture of metal bromides in a specific molar ratio to form a premix fluid having a density d_1 . Afterwards, the water is removed from the premix fluid having a density d_1 to form a wellbore fluid with a density d_2 . In such embodiments, $d_1 < d_2$. The wellbore fluid having a density d_2 may be further mixed with water or a third mixed metal bromide fluid in a specific molar ratio to form a wellbore fluid having a desired density d_3 . In such embodiments, the second and third aqueous fluids are selected from the group of metal bromides. As noted above, removing water may be performed by a vapor evaporation process. As described herein, the metal bromide salts may be selected from the group of alkaline earth metal bromides, Group VIIB metal bromides and mixtures of thereof.

[0035] As noted above, the brines are formulated in such a manner that the density of the resulted wellbore fluids ranges from 14.5 ppg (1.74 kg/L) to 18 ppg (2.16 kg/L), where the lower limit can be any of 14.5 ppg (1.74 kg/L), 14.7 ppg (1.76 kg/L), 15.0 ppg (1.80 kg/L), 15.4 ppg (1.85 kg/L) or 16.0 ppg (1.92 kg/L), and the upper limit can be any of 16.0 ppg

(1.92 kg/L), 16.4 ppg (1.97 kg/L), 16.5 ppg (1.98 kg/L), 17 ppg (2.04 kg/L), or 18 ppg (2.16 kg/L), where any lower limit can be used with any upper limit. According to the present embodiments, the wellbore fluids as described herein may have a pH ranging from about 3 to about 7, where the lower limit can be any of 3, 4 or 5 and the upper limit can be any of 6 or 7, where any lower limit can be used with any upper limit. For example, in one or more embodiments, the pH may be adjusted to about 5. Compounds that may be used to adjust the pH may include, but are not limited to lime.

[0036] Upon mixing, the fluids of the present embodiments may be used in wellbore operations, such as base brines in drilling fluids and fluid loss treatment (when the fluids as described herein may further include a gelling agent and a plurality of salt or mineral particulates), gravel packing operations when gravel may be used, or completion operations. It is also envisioned that the wellbore fluids as described herein may be used as an internal phase of an invert emulsion drilling fluid, or an invert emulsion gravel packing carrier fluid which may further include gravel. Such operations are known to persons skilled in the art and involve pumping a wellbore fluid into a wellbore through an earthen formation and performing at least one wellbore operation while the wellbore fluid is in the wellbore.

[0037] One embodiment of the present disclosure involves a method for completing a wellbore. In one such an illustrative embodiment, the method involves pumping a wellbore fluid into a wellbore and performing at least one completion operation while the wellbore fluid is in the wellbore. In such embodiments, the wellbore fluid includes an aqueous base fluid, a mixture of metal bromides dispersed in the aqueous base fluid and a plurality of nanoparticles suspended in the aqueous base fluid. As noted above, the metal bromides and the plurality of nanoparticles are present in an amount to provide a fluid density of at least 14.5 ppg (1.74 kg/L) and a true crystallization temperature of the wellbore fluid below 40°F (4.4°C).

[0038] In one or more embodiments, the fluids formulated according to this disclosure may be used as fluid loss pills when fluid loss to the formation is experienced during a completion operation. In one embodiment, the fluid loss pill may be prepared using high density base brines as described herein. The brine may be pre-saturated with a selected salt

or mineral particulates thereby rendering any further salt or particulates as substantially insoluble in the pre-saturated base brine. In yet another embodiment, when the wellbore fluid is a fluid loss pill, the fluid may further include a gelling agent which can be added to the formulation in a concentration as rheologically and functionally determined by wellbore conditions. Suitable gelling agents or viscosifiers further include various organic and/or inorganic polymeric species including polymer viscosifiers, especially metal-crosslinked polymers. Suitable polymers for making the metal-crosslinked polymer viscosifiers include, for example, polysaccharides e.g., substituted galactomannans, such as guar gums, high-molecular weight polysaccharides composed of mannose and galactose sugars, or guar derivatives such as hydroxypropyl guar (HPG), carboxymethylhydroxypropyl guar (CMHPG) and carboxymethyl guar (CMG), hydrophobically modified guar, guar-containing compounds, and synthetic polymers. Crosslinking agents which include boron, titanium, zirconium and/or aluminum complexes are used to increase the effective molecular weight of the polymer and make them better suited for use as viscosity increasing agents, especially in high-temperature wells.

[0039] Other suitable classes of water-soluble polymers effective as viscosifiers include polyvinyl alcohols at various levels of hydrolysis, polyvinyl polymers, polymethacrylamides, cellulose ethers, lignosulfonates, and ammonium, alkali metal, and alkaline earth salts thereof. More specific examples of other typical water soluble polymers are acrylic acid-acrylamide copolymers, acrylic acid-methacrylamide copolymers, polyacrylamides, partially hydrolyzed polyacrylamides, partially hydrolyzed polymethacrylamides, polyvinyl alcohol, polyalkyleneoxides, other galactomannans, heteropolysaccharides obtained by the fermentation of starch-derived sugar and ammonium and alkali metal salts thereof.

[0040] In embodiments disclosed herein, cellulose derivatives are used, including hydroxyethylcellulose (HEC), hydroxypropylcellulose (HPC), carboxymethylhydroxyethylcellulose (CMHEC), and/or carboxymethylcellulose (CMC), with or without crosslinkers. Xanthan, diutan, and scleroglucan are also used.

[0041] In addition to cross-linked polymers, linear polymer systems may be used. Boron crosslinked polymers systems may be used including guar and substituted guar crosslinked

with boric acid, sodium tetraborate, and encapsulated borates; borate crosslinkers may be used with buffers and pH control agents such as sodium hydroxide, magnesium oxide, sodium sesquicarbonate, and sodium carbonate, amines (such as hydroxyalkyl amines, anilines, pyridines, pyrimidines, quinolines, and pyrrolidines, and carboxylates such as acetates and oxalates) and with delay agents such as sorbitol, aldehydes, and sodium gluconate. Suitable zirconium crosslinked polymer systems include polymers crosslinked with zirconium lactates (for example sodium zirconium lactate), triethanolamines, 2,2'-iminodiethanol, and with mixtures of these ligands, including when adjusted with bicarbonate. Suitable titanates include by non-limiting example, lactates and triethanolamines, and mixtures, for example delayed with hydroxyacetic acid.

[0042] To prevent fluid loss during well treatment, solid bridging materials may be used. Bridging materials may be insoluble, sparingly soluble, or slowly soluble in the wellbore fluid. Bridging materials may also have a particular shape and hardness such that they may be malleable, and/or round to non-spherical. Bridging materials may include various organic and inorganic salts, oxides, and the like in various insoluble physical forms, whether crystalline or amorphous, including powder, granules, beads, paste, fibers, and/or the like. These fluid loss additives are subsequently incorporated as filter cake components upon dehydration of the fluid loss pill when a differential pressure is applied on a porous medium. The bridging solid particles of the present disclosure may include inorganic compounds, such as salts and/or oxides. In one or more embodiments, the bridging solids may be carbonates such as calcium carbonates, barium carbonates, and the like.

[0043] The bridging solid particles may have an average size of about 0.5 to about 5,000 micrometers (μm) as determined according to methods known in the art. Within this range, the average size of the bridging solid particles may be greater than or equal to about 1 μm , greater than or equal to about 10 μm , or greater than or equal to about 100 μm . Also within this range, the average size of the bridging solid particles may be less than or equal to about 2,000 μm , less than or equal to about 1,000 μm , or less than or equal to about 500 μm . The bridging solid particles may be present within the fluid loss pill at about 1 wt %, to about 90 wt %, based on the total weight of the fluid loss pill. Within this range, the concentration of

the bridging solid particles may be greater than or equal to about 10 wt %, greater than or equal to about 20 wt %, or greater than or equal to about 30 wt %. Also within this range, the concentration of the bridging solid particles may be less than or equal to about 80 wt %, less than or equal to about 70 wt %, or less than or equal to about 60 wt %. The wellbore fluids of the present disclosure, which are prepared using an aqueous base fluid, a mixture of metal bromides dispersed in a specific amount in the aqueous base fluid and a plurality of nanoparticles, exhibit stability and wellbore performance, as well as high density and a low TCT.

[0044] EXAMPLES

[0045] The following examples are presented to further illustrate the preparation and properties of the wellbore fluids of the present disclosure and should not be construed to limit the scope of the disclosure, unless otherwise expressly indicated in the appended claims.

[0046] In order to find the proper formulation of a wellbore fluid exhibiting high density and a low crystallization temperature, several formulations were prepared. The TCT and the density of these formulations were compared with the ones of a pure CaBr_2 brine, which can reach 15.3 ppg (1.84 kg/L) as the highest density, while the TCT is about 70°F (21.1°C). As seen in Table 1, below, the addition of the silica nanoparticles (where silica nanoparticles refer to nano-sized silica in the colloidal silica) to a CaBr_2 brine may increase the density to 16.0 ppg (1.92 kg/L) while decreasing the TCT to 68°F (20°C). It is also observed that the addition of silica nanoparticles to a mixture of CaBr_2 and MnBr_2 further increases the density, while decreasing the TCT. As seen in Table 1, the addition of silica nanoparticles to a mixture of CaBr_2 and MnBr_2 may increase the density to 15.8 ppg (1.89 kg/L), while the TCT may be lowered to less than -10°F (-23.3°C).

[0047] Without being bound by the theory, the inventors of the present disclosure have found that the density and the TCT of the wellbore fluid may be tailored based on the molar ratio of the two metal bromides. Thus, the molar ratio of the two bromides may be used as a tool to reach a density of 16.0 ppg (1.92 kg/L), while the TCT may be adjusted in the range of 30°F (-1.11°C) to 70°F (21.11°C).

Table 1.

TCT	Composition			
	CaBr ₂ +silica nanoparticles	CaBr ₂ +MnBr ₂ (vendor sample)	CaBr ₂ +MnBr ₂ Ca:Mn molar ratio=1.5:1	CaBr ₂ +MnBr ₂ +silica nanoparticles
TCT at 17.0 ppg (2.04 kg/L)	too high to measure	too high to measure	>60°F (>15.55°C)	<40°F (<4.44°C)
TCT at 16.5 ppg (1.98 kg/L)	too high to measure	65°F (18.33°C)	42°F (5.56°C)	10°F (-12.22°C)
TCT at 16.0 ppg (1.92 kg/L)	68°F (20.0°C)	56°F (13.33°C)	33°F (0.56°C)	3.3°F (-15.94°C)
TCT at 15.8 ppg (1.89 kg/L)	60°F (15.55°C)	50°F (10.0°C)	19°F (-7.22°C)	<-10°F (-23.33°C)

[0048] To study the effect of the molar ratio of the two metal bromides on the density and the TCT of the wellbore fluid, few formulations containing CaBr₂ and MnBr₂ were prepared. As a general procedure, a 14.2 ppg (1.70 kg/L) CaBr₂ brine was mixed with a MnBr₂ brine with the formation of a premix fluid. Next, the premix fluid was concentrated to about 17.0 ppg (2.04 kg/L), and afterwards diluted with water to the desired density. As seen below in Table 2, good results in terms of high density and low TCT may be obtained when the molar ratio of Ca:Mn is 1.56:1.

Table 2.

Density	Molar ratio Ca:Mn			
	1.56:1	1.94:1	1.43:1	2.12:1
	TCT			
16 ppg (1.92 kg/L)	32.77°F (0.43°C)	40.6°F (4.78°C)	-	-
15.87 ppg (1.90 kg/L)	-	-	16.6°F (-8.56°C)	33.6°F (0.89°C)
15.8 ppg (1.89 kg/L)	19.13°F (-7.15°C)	33.3°F (0.72°C)	-	-
15.55 ppg (1.87 kg/L)	-	-	27°F (-2.78°C)	19.5°F (-6.94°C)
15.4 ppg (1.85 kg/L)	4.19°F (-15.45°C)	15.6°F (-9.11°C)	-	-
15.35 ppg (1.84 kg/L)	-	-	12°F (-11.11°C)	10.8°F (-11.78°C)
15.0 ppg (1.80 kg/L)	-15°F (-26.11°C)	-7.2°F (-21.78°C)	-	-

[0049] The formulations presented in Tables 1 and 2 may be used as completion brines, as they exhibit minimal formation damage, good stability at both low and high temperature, low viscosity and low corrosivity. These fluids may be further built into fluid loss control pills, screen running fluids, gravel pack fluids, and drilling fluids after the addition of specific viscosifiers and emulsifiers.

[0050] Embodiments of the present disclosure provide wellbore fluids and methods for completing a wellbore with such fluids that include an aqueous base fluid, a mixture of metal bromides and colloidal particles such as nanoparticles suspended in the aqueous base fluid in a specific amount. As noted above, the synergism of the metal bromides and the plurality of nanoparticles has an effect on increasing the density of the wellbore fluid, while decreasing the TCT. The wellbore fluids as described herein exhibit good stability at both low and high

temperature, as well as low viscosity. Another aspect of the present disclosure is that the wellbore fluids as described herein have low corrosive effects upon metals such as iron, steel (including carbon steel) and other ferrous metals which typically come into contact with the brines during wellbore operations. In addition, the disclosed wellbore fluids have a low potential for formation damage. For example, the wellbore fluids as described herein do not form an emulsion with crude oils and do not precipitate with formation fluids. Furthermore, the wellbore fluids of the present disclosure may provide reduced environmental risks, as they can replace zinc containing brines for offshore and land drilling and completion activity. In addition, the wellbore fluids as described herein may provide a cost-effective alternative to cesium formate brines.

[0051] Although only a few example embodiments have been described in detail above, those skilled in the art will readily appreciate that many modifications are possible in the example embodiments without materially departing from this invention. Accordingly, all such modifications are intended to be included within the scope of this disclosure as defined in the following claims. In the claims, means-plus-function clauses are intended to cover the structures described herein as performing the recited function and not only structural equivalents, but also equivalent structures. Thus, although a nail and a screw may not be structural equivalents in that a nail employs a cylindrical surface to secure wooden parts together, whereas a screw employs a helical surface, in the environment of fastening wooden parts, a nail and a screw may be equivalent structures. It is the express intention of the applicant not to invoke 35 U.S.C. § 112, paragraph 6 for any limitations of any of the claims herein, except for those in which the claim expressly uses the words ‘means for’ together with an associated function.

CLAIMS

What is claimed:

1. A wellbore fluid, comprising:
 - an aqueous base fluid;
 - a mixture of metal bromides dispersed in the aqueous base fluid; and
 - a plurality of nanoparticles suspended in the aqueous base fluid,wherein the metal bromides and the plurality of nanoparticles are present in the wellbore fluid in an amount to provide a fluid density of at least 14.5 ppg (1.74 kg/L) and a true crystallization temperature of the wellbore fluid below 40°F (4.4°C).
2. The wellbore fluid of claim 1, wherein the mixture of metal bromides is selected from the group of alkaline earth metal bromides, Group VIIB metal bromides and mixtures of thereof.
3. The wellbore fluid of claim 1, wherein the mixture of metal bromides is a mixture of calcium bromide and manganese bromide.
4. The wellbore fluid of claim 3, wherein a molar ratio of the calcium bromide and manganese bromide ranges from 1:1 to 2:1.
5. The wellbore fluid of claim 1, wherein the nanoparticles are selected from the group of colloidal silica nanoparticles and nano-sized precipitated silica.
6. The wellbore fluid of claim 1, wherein the wellbore fluid has a pH ranging from 3 to 7.
7. The wellbore fluid of claim 1, wherein the wellbore fluid has a density ranging from about 14.5 ppg (1.74 kg/L) to about 18 ppg (2.16 kg/L).
8. The wellbore fluid of claim 1, wherein the wellbore fluid is a drilling fluid and further comprises a gelling agent and a plurality of salt or mineral particulates.

9. The wellbore fluid of claim 1, wherein the wellbore fluid is a fluid loss pill and further comprises a gelling agent and a plurality of salt or mineral particulates.
10. The wellbore fluid of claim 1, wherein the wellbore fluid is a gravel packing carrier fluid further comprising gravel.
11. The wellbore fluid of claim 1, wherein the wellbore fluid is an internal phase of an invert emulsion gravel packing carrier fluid further comprising gravel.
12. The wellbore fluid of claim 1, wherein the wellbore fluid is an internal phase of an invert emulsion drilling fluid.
13. The wellbore fluid of claim 1, wherein the wellbore fluid is free of tin bromide.
14. The wellbore fluid of claim 1, wherein the metal bromides are stably solubilized in the aqueous base fluid for at least one month at 77°F (25°C).
15. A method for completing a wellbore, the method comprising:
 - pumping a wellbore fluid into the wellbore, the wellbore fluid comprising:
 - an aqueous base fluid;
 - a mixture of metal bromides dispersed in the aqueous base fluid; and
 - a plurality of nanoparticles suspended in the aqueous base fluid,
 - wherein the metal bromides and the plurality of nanoparticles are present in an amount to provide a fluid density of at least 14.5 ppg (1.74 kg/L) and a true crystallization temperature of the wellbore fluid below 40°F (4.4°C).
16. The method of claim 15, wherein the mixture of metal bromides is selected from the group of alkaline earth metal bromides, Group VIIB metal bromides and mixtures of thereof.
17. The method of claim 15, wherein the mixture of metal bromides is a mixture of calcium bromide and manganese bromide.
18. The method of claim 17, wherein a molar ratio of the calcium bromide and manganese bromide ranges from 1:1 to 2:1.

19. The method of claim 15, wherein the nanoparticles are selected from the group of colloidal silica nanoparticles and nano-sized precipitated silica.
20. The method of claim 15, wherein the wellbore fluid has a pH ranging from 3 to 7.
21. The method of claim 15, wherein the wellbore fluid has a density in the range of about 14.5 ppg (1.74 kg/L) to about 18 ppg (2.16 kg/L).
22. The method of claim 15, wherein the wellbore fluid is a drilling fluid and further comprises a gelling agent and a plurality of salt or mineral particulates.
23. The method of claim 15, wherein the wellbore fluid is a fluid loss pill and further comprises a gelling agent and a plurality of salt or mineral particulates.
24. The method of claim 15, wherein the wellbore fluid is a gravel packing carrier fluid further comprising gravel.
25. The method of claim 15, wherein the wellbore fluid is an internal phase of an invert emulsion gravel packing carrier fluid further comprising gravel.
26. The method of claim 15, wherein the wellbore fluid is an internal phase of an invert emulsion drilling fluid.
27. The method of claim 15, wherein the wellbore fluid is free of tin bromide.
28. The method of claim 15, wherein the metal bromides are stably solubilized in the aqueous base fluid for at least one month at 77°F (25°C).
29. The method of claim 15, wherein the method further comprises performing at least one completion operation while the wellbore fluid is in the wellbore.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 2019/015509

A. CLASSIFICATION OF SUBJECT MATTER

C09K 8/04 (2006.01)
C09K 8/36 (2006.01)
C09K 8/48 (2006.01)
C09K 8/565 (2006.01)
C09K 8/57 (2006.01)
E21B 33/138 (2006.01)

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C09K,E21B

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

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

PatSearch (RUPTO internal), Espacenet, DWPI, PAJ, USPTO, CIPO

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No
X	WO 2016/196332 A1 (M-I L.L.C.) 08.12.2016, claims 1, 3, 9, 13-16, [0022]-[0026], [0046], examples	1, 2, 5-16, 19-29
Y		3, 4, 17, 18
Y	WO 2016/075052 A1 (LAMBERTI SPA) 19.05.2016, abstract, p. 9, lines 12-17	3, 4, 17, 18
Y	SU 1709075 A1 (ВСЕСОЮЗНЫЙ НАУЧНО-ИССЛЕДОВАТЕЛЬСКИЙ И ПРОЕКТИРОВАТЕЛЬСКИЙ ИНСТИТУТ ПО КРЕПЛЕНИЮ СКВАЖИН И БУРОВЫМ РАСТВОРАМ) 30.01.1992, column 1, line 19 –column 3, line 3, column 6, lines 22-30, tables	3, 4, 17, 18



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:

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

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

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

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

“&” document member of the same patent family

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