[0005] Hence, there is a need to develop high density aqueous brine fluids that are zinc-free, and that have true crystallization temperatures that are suitably low for downhole use.

SUMMARY OF THE INVENTION

[0006] This invention provides aqueous brines of high density and low crystallization temperature that are zinc-free. It has been discovered, for example, that a high density, zinc-free aqueous brine can be prepared from a combination of water and one or more inorganic bromide salts such as calcium bromide, manganese bromide ($MnBr_2$) tin bromide ($SnBr_2$ or $SnBr_4$), bismuth bromide, and/or indium bromide; calcium bromide is used in combination with one or more other water-soluble inorganic salts, preferably selected from an inorganic bromide salt, manganese(II) nitrate, and a water-soluble polytungstate salt; lithium bromide is used in combination with an alkali metal polytungstate salt; bismuth(III) bromide is used in combination with one or more other water-soluble inorganic salts, preferably selected from an inorganic bromide salt; when lithium bromide is present, calcium bromide is absent. Such brines can exhibit densities of about 15.0 ppg (1.78 kg/L) or greater, and have crystallization temperatures of about 20°F (−6.7°C) or less, often about 10°F (−12.2°C) or less. These brines are suitable for use as wellbore fluids, such as completion fluids, especially clear completion fluids, drilling fluids, packer fluids, workover fluids, and other fluids that employ aqueous brines, particularly aqueous brines of high density. The aqueous brines of this invention are well suited for offshore completion activities involving high pressure reservoirs, such as oil and gas fields located in the Gulf of Mexico.

[0007] An embodiment of this invention is a zinc-free aqueous brine composition. The composition has a density of about 14.3 pounds per gallon (1.71 kg/L) or more, and a true crystallization temperature of about 20°F (−6.7°C) or less, preferably about 10°F (−12.2°C) or less, and comprises water and one or more inorganic bromide salts, with the proviso that when calcium bromide is present, one or more other water-soluble inorganic salts is also present, preferably selected from an inorganic bromide salt, manganese(II) nitrate, and a water-soluble polytungstate salt; with the proviso that when bismuth(III) bromide is present, one or more other water-soluble inorganic salts is also present, preferably selected from an inorganic bromide salt, with the proviso that when lithium bromide is present, calcium bromide is absent, and with the proviso that for true crystallization temperatures of about −12.2°C (10°F) or less, when manganese(II) bromide is present,

to about 16.0 ppg (1.92 kg/L), and still more preferably about 15.1 ppg (1.81 kg/L) to about 15.6 ppg (1.87 kg/L). In other embodiments, preferred densities are about 14.6 ppg (1.75 kg/L) to about 15.0 ppg (1.80 kg/L), more preferably about 14.6 to about 14.8 ppg (1.77 kg/L). In still other embodiments, preferred densities are about 15.0 ppg (1.80 kg/L) to about 18.0 ppg (2.16 kg/L), more preferably about 15.5 ppg (1.86 kg/L) to about 17.75 ppg (2.13 kg/L). In yet other embodiments, especially when the inorganic bromide salt is calcium bromide and one other inorganic bromide salt selected from tin(IV) bromide, bismuth(III) bromide, or indium(III) bromide, preferred densities are about 16.0 ppg (1.92 kg/L) to about 17.5 ppg (2.10 kg/L), more preferably about 16.2 ppg (1.94 kg/L) to about 17.2 ppg (2.06 kg/L). In another embodiment, especially when the inorganic bromide salt is calcium bromide and manganese(II) nitrate is the other water-soluble inorganic salt, preferred densities are about 14.5 ppg (1.74 kg/L) to about 16.0 ppg (1.92 kg/L). In yet another embodiment, preferred densities are about 14.5 ppg (1.74 kg/L) to about 17.5 ppg (2.10 kg/L), more preferably about 14.5 ppg (1.74 kg/L) to about 16.5 ppg (1.98 kg/L), especially when the inorganic bromide salt is calcium bromide or manganese(II) bromide and the other water-soluble inorganic salt is a water-soluble polytungstate salt, or when the inorganic bromide salt is lithium bromide in combination with an alkali metal polytungstate salt.

[0027] For the compositions of the invention, the true crystallization temperatures are generally about 20°F (−6.7°C) or less, preferably about 10°F (−12.2°C) or less, more preferably about 8°F (−13.3°C) or less, and still more preferably about 7.5°F (−13.6°C) or less.

[0028] Aqueous brine compositions of the invention preferred pH values are in the range of about 0 to about 7; more preferred are pH values in the range of about 1 to about 6; still more preferred are pH values in the range of about 1.5 to about 5, especially about 2.5 to about 5. Even more preferred are pH values in the range of about 3 to about 4.

[0029] As is known in the art, it is often useful to include one or more optional additives in an aqueous brine, and the inclusion of such additives is within the scope of this invention. Optional additives can include, for example, corrosion inhibitors, lubricants, pH control additives, surfactants, and/or solvents. Glycerol and formic acid are preferred optional additives.

CLAIMS

1. A composition which is a zinc-free aqueous brine having a density of 14.3 pounds per gallon (1.71 kg/L) or more, and a true crystallization temperature of 20°F (−6.7°C) or less, which composition comprises water and one or more inorganic bromide salts, with the provisos that:

when calcium bromide is present, one or more other water-soluble inorganic salts are also present, wherein the other water-soluble inorganic salt is selected from an inorganic bromide salt and manganese(II) nitrate,

when lithium bromide is present, calcium bromide is absent,

when bismuth(III) bromide is present, one or more other water-soluble inorganic salts are also present, and

for a true crystallization temperature of 10°F (−12.2°C) or less, when manganese(II) bromide is present, one or more other water-soluble inorganic salts are also present.

2. A composition as in Claim 1 wherein the inorganic bromide salt is:

manganese(II) bromide, tin(II) bromide, tin(IV) bromide, indium(III) bromide, or a mixture of any two or more of these; or

a combination of calcium bromide and one or more inorganic bromide salts selected from manganese(II) bromide, tin(II) bromide, tin(IV) bromide, bismuth(III) bromide, indium(III) bromide, or a mixture of any two or more of these; or

a combination of bismuth(III) bromide and one or more inorganic bromide salts selected from manganese(II) bromide, tin(II) bromide, tin(IV) bromide, indium(III) bromide, or a mixture of any two or more of these; or

wherein only one inorganic bromide salt is present, and the inorganic bromide salt is tin(IV) bromide or indium(III) bromide.

3. A composition as in Claim 2 wherein the inorganic bromide salt is a combination of calcium bromide and manganese(II) bromide, a combination of calcium bromide,

manganese(II) bromide, and tin(IV) bromide, or a combination of calcium bromide, manganese(II) bromide, and bismuth(III) bromide.

4. A composition as in Claim 1 wherein the other water-soluble inorganic salt present with bismuth(III) bromide is an inorganic bromide salt.

5. A composition as in Claim 1 wherein the inorganic bromide salt is manganese(II) bromide, wherein one or more other water-soluble inorganic salts is present, and wherein the one or more other water-soluble inorganic salts is manganese(II) nitrate or a water-soluble polytungstate salt.

6. A composition as in any of Claims 1-3 wherein the composition has a density of 14.6 pounds per gallon (1.75 kg/L) or more.

7. A composition as in any of Claims 1-3 wherein the composition has a density of 15.0 pounds per gallon (1.80 kg/L) or more.

8. A composition as in Claim 1 wherein:

the inorganic bromide salt is a combination of calcium bromide and manganese(II) bromide, and the composition has a density of 14.6 pounds per gallon (1.75 kg/L) or more, and a pH value in the range of 2.5 to 5; or

the inorganic bromide salt is a combination of calcium bromide, manganese(II) bromide, and tin(IV) bromide, and the composition has a density of 15.0 pounds per gallon (1.80 kg/L) or more; or

the inorganic bromide salt is a combination of calcium bromide, manganese(II) bromide, and bismuth(III) bromide, and the composition has a density of 16.0 pounds per gallon (1.92 kg/L) or more; or

the inorganic bromide salt is calcium bromide, and the other water-soluble inorganic salt is manganese(II) nitrate, and the composition has a density of 14.5 pounds per gallon (1.74 kg/L) or more; or

the inorganic bromide salt is manganese(II) bromide, and the other water-soluble inorganic salt is a water-soluble polytungstate salt, and the composition has a density of 14.5 pounds per gallon (1.74 kg/L) or more.

9. A composition as in any of Claims 5 or 8 wherein the water-soluble polytungstate salt is an alkali metal polytungstate, an alkaline earth metal polytungstate, or manganese polytungstate.

10. A process for forming a zinc-free aqueous brine composition having a density of 14.3 pounds per gallon (1.71 kg/L) or more, and a true crystallization temperature of 20°F (−6.7°C) or less, which process comprises combining, in any order, components comprising water and one or more inorganic bromide salts, with the provisos that:

when the inorganic bromide salt is calcium bromide, one or more other water-soluble inorganic salts is also included, wherein the other water-soluble inorganic salt is selected from an inorganic bromide salt and manganese(II) nitrate,

when the inorganic bromide salt is lithium bromide, calcium bromide is not used,

when the inorganic bromide salt is bismuth(III) bromide, one or more other water-soluble inorganic salts is also included, and

for a true crystallization temperature of 10°F (−12.2°C) or less, when the inorganic bromide is manganese(II) bromide, one or more other water-soluble inorganic salts is also included.

11. A process as in Claim 10 wherein one or more inorganic bromide salts are formed during the process from (i) an inorganic oxide and/or hydroxide and (ii) hydrogen bromide and/or bromine.

12. A process as in Claim 11 wherein the inorganic oxide and/or hydroxide is

one or more oxides and/or hydroxides of calcium, manganese(II), tin(II), tin(IV), indium(III), or a mixture of any two or more of the foregoing; or

one or more oxides and/or hydroxides of manganese(II), tin(IV), and/or bismuth(III) in combination with calcium bromide and/or oxides and/or hydroxides of calcium.

13. A process as in any of Claims 10-12 wherein the inorganic bromide salt is

manganese(II) bromide, tin(II) bromide, tin(IV) bromide, indium(III) bromide, or a mixture of any two or more of these; or

a combination of calcium bromide and manganese(II) bromide, tin(II) bromide, tin(IV) bromide, bismuth(III) bromide, indium(III) bromide, or a mixture of any two or more of these; or

a combination of bismuth(III) bromide and manganese(II) bromide, tin(II) bromide, tin(IV) bromide, indium(III) bromide, or a mixture of any two or more of these; or

wherein only one inorganic bromide salt is present, and the inorganic bromide salt is tin(IV) bromide or indium(III) bromide.

14. A process as in Claim 13 wherein the inorganic bromide salt is a combination of calcium bromide and manganese(II) bromide, a combination of calcium bromide, manganese(II) bromide, and tin(IV) bromide, or a combination of calcium bromide, manganese(II) bromide, and bismuth(III) bromide.

15. A process as in Claim 10 wherein when the inorganic bromide salt is bismuth(III) bromide, the other water-soluble inorganic salt is an inorganic bromide salt.

16. A process as in Claim 10 wherein the inorganic bromide salt is manganese(II) bromide, wherein one or more other water-soluble inorganic salts is used, and wherein the one or more other water-soluble inorganic salts is manganese(II) nitrate or a water-soluble polytungstate salt.

17. A process as in Claim 16 wherein the water-soluble polytungstate salt is an alkali metal polytungstate, an alkaline earth metal polytungstate, or manganese polytungstate.

18. A process as in any of Claims 10-14 wherein the composition has a density of 14.6 pounds per gallon (1.75 kg/L) or more, and/or wherein the inorganic bromide salt is in a total amount of 40 wt% to 75 wt%, relative to the total weight of the composition.

19. A process as in any of Claims 10-14 which further comprises heating during and/or after the combining.

20. A process as in any of Claims 10-18 wherein the composition formed has a true crystallization temperature of 10°F (−12.2°C) or less.

21. A method of treating a wellbore, said method comprising:
introducing into the wellbore a fluid which is a zinc-free aqueous brine having a density of 14.3 pounds per gallon (1.71 kg/L) or more, and a true crystallization temperature of 20°F (−6.7°C) or less, which fluid comprises water and one or more inorganic bromide salts, with the provisos that:

when calcium bromide is present, one or more other water-soluble inorganic salts are also present,

when lithium bromide is present, calcium bromide is absent,

when bismuth(III) bromide is present, one or more other water-soluble inorganic salts are also present, and

for a true crystallization temperature of 10°F (−12.2°C) or less, when manganese(II) bromide is present, one or more other water-soluble inorganic salts are also present.

22. A method as in Claim 21 wherein the fluid is a completion fluid, drilling fluid, packer fluid, or workover fluid.

23. A method as in Claim 21 wherein the fluid is a clear completion fluid.

24. A method as in Claim 21 wherein the wellbore is connected to a high pressure reservoir.