(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
16 January 2025 (16.01.2025)

WIPO | PCT

(10) International Publication Number
WO 2025/015261 A1

(51) International Patent Classification:
C09K 8/05 (2006.01) *C01D 3/10* (2006.01)
B01J 20/04 (2006.01) *C09K 8/03* (2006.01)
B01J 20/20 (2006.01)

(21) International Application Number:
PCT/US2024/037764

(22) International Filing Date:
12 July 2024 (12.07.2024)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
63/526,280 12 July 2023 (12.07.2023) US

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(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CV, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IQ, IR, IS, IT, JM, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, MG, MK, MN, MU, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, WS, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, CV, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SC, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, ME, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:
— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*
— *as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))*

Published:
— *with international search report (Art. 21(3))*
— *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))*

(54) Title: SORBENTS FOR HIGH DENSITY AQUEOUS WELL FLUIDS

(57) Abstract: This invention provides aqueous fluids which comprise a halogen-containing sorbent comprising one or more halogens selected from fluorine, chlorine, bromine, and/or iodine, and one or more substrate materials, and a zinc-free aqueous brine.

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SORBENTS FOR HIGH DENSITY AQUEOUS WELL FLUIDS

RELATED APPLICATIONS

[0001] This application claims the benefit of United States Provisional Patent Application Serial No. 63/526,280, filed July 12, 2023, the disclosure of which is incorporated by reference herein in its entirety.

TECHNICAL FIELD

[0002] This invention relates to aqueous fluids comprising a halogen-containing sorbent and a zinc-free aqueous brine.

BACKGROUND

[0003] Conventional aqueous brine fluids, like calcium bromide, which can have densities up to about 14.2 pounds per gallon (1.70 kg/L), are widely used in oilfield production as clear completion fluids, drilling fluids, packer fluids, and so forth. For some wells, downhole pressures can reach 30,000 psi (2.1×10^8 Pa). Such high pressures occur downhole at least in the Gulf of Mexico, and temperatures at the mud line in the Gulf of Mexico can reach 40°F (4.4°C). As a general observation, each 10,000 pounds per square inch (6.9×10^7 Pa) increase in pressure can increase the crystallization temperature of an aqueous brine by about ten Fahrenheit degrees (about 5.6 Celsius degrees).

[0004] Typical aqueous brine fluids include calcium bromide having densities up to about 14.2 ppg (1.70 kg/L). A calcium bromide aqueous brine of about 14.2 ppg (1.70 kg/L) density has a true crystallization temperature of 10°F (−12.2°C). Calcium bromide aqueous brines having densities as high as 15 ppg (1.8 kg/L) can be made; however, these solutions have a true crystallization temperature of about 61°F (16.1°C). These higher density calcium bromide aqueous brines are not suitable for use in some downhole applications, such as conditions often found in the Gulf of Mexico, because precipitates will form in these higher density calcium bromide aqueous brines due to their relatively high true crystallization temperatures.

[0005] Zinc-containing calcium bromide aqueous brines of high density, *e.g.*, about 14.5 pounds per gallon (1.74 kg/L) or greater, are easily obtained by blending enough zinc bromide into the calcium bromide aqueous brine to reach the desired density value. Zinc-containing calcium bromide aqueous brines have true crystallization temperatures that are usually about

20°F (–6.7°C) or lower, making these zinc-containing brines more suitable for downhole use. However, inclusion of zinc necessitates increased reporting to government agencies for environmental reasons, resulting in more costly environmental mitigation measures. For example, zinc is regulated as a Priority Pollutant by the United States Environmental Protection Agency (EPA).

[0006] Co-produced water (often called produced water) from oil and gas drilling sometimes contains substances that are environmentally regulated, such as mercury. It is believed that these substances may originate in the hydrocarbons and migrate into the co-produced water. See in this connection Darrell L. Gallup, *Removal of Mercury from Water in the Petroleum Industry*, 21st International Petroleum Environmental Conference (IPEC), Houston, TX, October 14-16, 2014: The University of Tulsa, Continuing Education for Science and Engineering. The mercury may be present in multiple forms including elemental mercury, organic mercury compounds, and inorganic mercury compounds. Other substances, including halogenated organic compounds and/or other heavy elements, may also be present in the hydrocarbons and/or produced water.

[0007] It would be desirable to have another method for removing mercury, halogenated organic compounds, and/or other heavy elements from the hydrocarbons and/or produced water from oil and gas drilling.

SUMMARY OF THE INVENTION

[0008] This invention provides aqueous fluids comprising a halogen-containing sorbent and a zinc-free aqueous brine. These brines are suitable for use as wellbore fluids, such as 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. A benefit provided by this invention is a reduction in the amount of mercury, other heavy metals, and/or halogenated organic compounds in the hydrocarbons and/or produced water from oil and gas drilling. The halogen-containing sorbents used in the practice of this invention capture mercury in multiple forms including elemental mercury, organic mercury compounds, and inorganic mercury compounds; these halogen-containing sorbents can also capture halogenated organic compounds and other heavy elements.

[0009] An embodiment of this invention is a zinc-free aqueous well fluid. The zinc-free aqueous well fluid comprises:

I) a halogen-containing sorbent comprising one or more halogens selected from fluorine, chlorine, bromine, and/or iodine, and one or more substrate materials, and

II) a zinc-free aqueous brine having

A) a density of about 14.3 pounds per gallon or more, and a true crystallization temperature of about 20°F or less, which aqueous brine 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 about 10°F or less, when manganese(II) bromide is present, one or more other water-soluble inorganic salts are also present, or

B) a density of about 14.3 pounds per gallon to about 15.8 pounds per gallon, and a true crystallization temperature of about 20° F or less, which aqueous brine comprises water and calcium bromide and cesium bromide, or

C) having a density of about 12.3 pounds per gallon or more, which aqueous brine comprises sodium bromide,

wherein the halogen-containing sorbent is in an amount of about 0.1 wt% to about 30 wt%, relative to the combined amount of the halogen-containing sorbent and the zinc-free aqueous brine.

[0010] Another embodiment of this invention is a process for forming a zinc-free aqueous well fluid comprising a halogen-containing sorbent comprising one or more halogens selected from fluorine, chlorine, bromine, and/or iodine, and one or more substrate materials, and a zinc-free aqueous brine.

[0011] Other embodiments of the invention include a method of treating a wellbore, said method comprising introducing into the wellbore a zinc-free aqueous well fluid comprising a halogen-containing sorbent comprising one or more halogens selected from fluorine, chlorine, bromine, and/or iodine, and one or more substrate materials, and a zinc-free aqueous brine.

[0012] These and other embodiments and features of this invention will be still further apparent from the ensuing description and appended claims.

FURTHER DETAILED DESCRIPTION OF THE INVENTION

[0013] As used throughout this document, the phrase "halogenated sorbent" is sometimes used to refer to a halogen-containing sorbent used in this invention.

[0014] As used throughout this document, the phrase "zinc-free" means that except for adventitious impurities, neither zinc nor zinc compounds are present in, or introduced into, the well fluids or processes of this invention. Generally, there is about 25 ppm or less of zinc present in the aqueous brines of this invention.

[0015] The term ppm means parts per million (wt/wt), as used throughout this document, unless specifically stated otherwise herein. Throughout this document, both "ppg" and "lb/gal" are abbreviations for pounds per gallon as used throughout this document.

[0016] The abbreviation "TCT" stands for true crystallization temperature (or true crystallization point) as used throughout this document. True crystallization temperature is the temperature at which precipitate begins to form in the absence of supercooling. A method for determining true crystallization temperature is described hereinbelow.

[0017] The phrases "inorganic bromide salt", "inorganic bromide", and "bromide salt" are used interchangeably throughout this document.

[0018] As used throughout this document, the phrase "halogenated organic compounds" refers to halogenated organic compounds that are environmentally regulated.

[0019] To be suitable for use as well fluids, the aqueous brines have little or no precipitate formation over time (e.g., about one week) at ambient temperature and pressure (e.g., 17 to 25°C and 14 to 15 psi ($9.65x10^4$ to $1.03x10^5$ Pa)) or at elevated temperature (e.g., about 60°C) and ambient pressure.

Halogen-Containing Sorbents

[0020] Halogen-containing sorbents are typically formed from one or more halogen-containing compounds and one or more substrate materials. Many substrate materials, especially activated carbons, are available or obtainable in a wide range of particle sizes, from nanometer to centimeter.

[0021] Substrate materials include carbonaceous materials and inorganic materials. Suitable carbonaceous materials that can be used as sorbents in the practice of this invention include,

for example, without limitation, activated carbon, carbon black, char, and coke. A preferred carbonaceous material is activated carbon, which can be used in many forms including, for example, without limitation, powdered, granular, microspherical, pelleted, or extruded; and high specific surface area.

[0022] Suitable inorganic materials include inorganic oxides such as alumina (amorphous and crystalline), silica, magnesia and titania; natural zeolites such as chabazite, clinoptilolite, and faujasite; synthetic zeolites such as synthetic chabazite, zeolites with high Si:Al ratios (such as ZSM-5, beta zeolites), zeolites with moderate Si:Al ratios (such as Y zeolites, mordenite), zeolites with low Si:Al ratio (such as A zeolites, X zeolites), silica alumina phosphate (SAPO) zeolites, ion exchanged zeolites, uncalcined zeolites with or without organic structure directing agents, aluminosilicates with ordered pore structures (such as MCM-41, MCM-48, SBA-15, HMS, MSU-X), clay minerals such as kaolin, kaolinite, bentonite, and montmorillonite; synthetic clays such as laponite, saponite, sauconite, stevensite, kaolinite, and hectorite; organo-clays such as montmorillonite that has been treated with a trimethyl stearyl ammonium salt, a dimethyl dialkyl (C_{14}-C_{18}) ammonium salt, a methyl dihydroxy ethyl ammonium salt and a hydrogenated tallow ammonium salt, and aminopropyltriethoxysilane and octadecylamine; bentonite, hectorite, and attapulgite that have been treated with a quaternary ammonium salt; and zeolites that have been treated with N,N,N-trimethyl-l-hexadecanaminium chloride; inorganic hydroxides such as iron hydroxide; mixed metal oxides such as hydrotalcites and metallated double layered clays; diatomaceous earth; cement dust; hydroprocessing catalysts including those on substrates comprising alumina, silica, and/or titania, inorganic carbonates, such as alkali metal carbonates (*e.g.*, sodium carbonate and potassium carbonate) and alkaline earth carbonates (e.g., calcium carbonate); and mixtures of any two or more of the foregoing. Preferred inorganic materials include inorganic oxides, especially silica, natural zeolites, especially chabazite, and clay minerals, especially kaolinite and bentonite; $CaCO_3$ is also a preferred substrate material.

[0023] The halogen element in the halogen-containing sorbent is fluorine, chlorine, bromine, iodine, or a mixture of any two or more of these halogens. Bromine and iodine are preferred halogens; bromine is a more preferred halogen. Suitable halogen-containing substances for forming a halogen-containing sorbent include, for example, without limitation, elemental iodine and/or iodine compounds, elemental bromine and/or bromine compounds, elemental chlorine and/or chlorine compounds, elemental fluorine and/or fluorine compounds, and other suitable halogen compounds, as will be known to those skilled in the art. Types of halogen-

containing compounds that are used include hydrohalic acids, alkali metal halides, alkaline earth halides, and ammonium halides. Mixtures of any two or more halogen-containing substances can be used; the mixtures may contain the same or different halogens.

[0024] Hydrohalic acids include hydrogen fluoride, hydrogen chloride, hydrogen bromide, and hydrogen iodide. Bromides and iodides are preferred halides; more preferred are bromides. Alkali metal halides include lithium halides, sodium halides, potassium halides, rubidium halides, and cesium halides; sodium halides and potassium halides are preferred, and include sodium fluoride,

sodium chloride, sodium bromide, sodium iodide, potassium fluoride, potassium chloride, potassium bromide, and potassium iodide; more preferred are sodium bromide, potassium bromide, and potassium iodide. Alkaline earth halides include magnesium halides, calcium halides, strontium halides, and barium halides; magnesium halides and calcium halides are preferred, and include magnesium fluoride, magnesium chloride, magnesium bromide, magnesium iodide, calcium fluoride, calcium chloride, calcium bromide, and calcium iodide; more preferred are magnesium bromide and calcium bromide. Ammonium halides include ammonium fluoride, ammonium chloride, ammonium bromide, and ammonium iodide; a preferred ammonium halide is ammonium bromide. More preferred halogen-containing substances include elemental bromine, hydrogen bromide, sodium chloride, sodium bromide, potassium bromide, potassium iodide, and calcium bromide. Bromine-containing compounds are preferred halogen-containing compounds; more preferred are hydrogen bromide and elemental bromine, especially elemental bromine.

[0025] Halogen-containing sorbents are often made from a substrate material and one or more halogen-containing substances, especially for bromine-containing sorbents, as described in U.S. Pat. Nos. 6,953,494 and 9,101,907, and in International Patent Pub. No. WO 2012/071206. In some embodiments, preferred halogen-containing sorbents are bromine-containing sorbents. In some embodiments, preferred halogen-containing sorbents are halogen-containing activated carbons. In other embodiments, preferred halogen-containing activated carbons are chlorine-containing activated carbons, bromine-containing activated carbons, and iodine-containing activated carbons. In preferred embodiments, the halogen-containing sorbents are iodine-containing activated carbons and bromine-containing activated carbons. In more preferred embodiments, the halogen-containing sorbents are bromine-containing activated carbons. Bromine-containing activated carbons are available commercially from Albemarle Corporation.

[0026] In other embodiments, preferred halogen-containing sorbents are chlorine-containing activated carbons and iodine-containing activated carbons. In still other embodiments, preferred halogen-containing sorbents are halogen-containing chabazites, halogen-containing bentonites, halogen-containing kaolinites, and halogen-containing silicas; more preferred halogen-containing sorbents are iodine-containing chabazites, bromine-containing chabazites, iodine-containing bentonites, bromine-containing bentonites, iodine-containing kaolinites, bromine-containing kaolinites, iodine-containing silicas, and bromine-containing silicas; still more preferred are bromine-containing silica, bromine-containing kaolinite, and bromine-containing bentonites.

[0027] In another embodiment, preferred halogen-containing sorbents include bromine-containing silica, bromine-containing kaolinite, and bromine-containing bentonite.

[0028] The amount of halogen (or halogen content) on the substrate material is typically equivalent to a total bromine content (or calculated as bromine) in the range of about 0.1 wt% to about 50 wt%, preferably equivalent to a total bromine content in the range of about 0.25 wt% to about 40 wt%, more preferably about 0.5 wt% to about 35 wt%, even more preferably about 1 wt% to about 20 wt%, still more preferably about 2 wt% to about 12 wt%, and yet more preferably about 3 wt% to about 8 wt%, based on the total weight of the halogen-containing sorbent.

[0029] As used throughout this document, the phrases "as bromine," "reported as bromine," "calculated as bromine" and analogous phrases for the halogens refer to the amount of halogen, where the numerical value is calculated for bromine, unless otherwise noted. For example, chlorine may be used, but the amount of halogen in the halogen-containing sorbent is stated as the value for bromine.

[0030] Halogen-containing activated carbons suitable for use in processes of this invention can have a wide range of particle sizes and distributions, from nanometer to centimeter; and can be formed from activated carbon forms including, for example, without limitation, powdered, granular, microspherical, pelleted, or extruded; high specific surface area, a variety of unique pore structures; and other features as will be familiar to those skilled in the art.

[0031] The amount of halogen-containing sorbent in the aqueous well fluid is about 0.1 wt% to about 30 wt%, relative to the combined amount of the halogen-containing sorbent and the zinc-free aqueous brine; when more than one halogen-containing sorbent is used, the amount refers to the total amount of halogen-containing sorbents. Preferred amounts of halogen-containing sorbent depend on the desired density of the aqueous well fluid, and there is

typically about 0.1 wt% to about 30 wt% halogen-containing sorbent in a mixture with a zinc-free aqueous brine, more often about 0.1 to about 15 wt%, preferably about 2 wt% to about 10 wt% halogen-containing sorbent. Mixtures of zinc-free aqueous brines and halogen-containing sorbents are sometimes suspensions or slurries.

Zinc-free Aqueous Brines

[0032] The zinc-free aqueous brines generally have a density about 14.3 ppg (1.71 kg/L) or more, and a true crystallization temperature of about 20 F° (−6.7 °C) or less.

[0033] The zinc-free aqueous brines are aqueous brine solutions comprising one or more inorganic bromide salts other than zinc bromide. In some embodiments, the aqueous brines may contain one or more other salts in addition to one or more inorganic bromide salts. Although it is convenient to refer to compounds of bromide salts and to metal cations and bromide anions, the species in the zinc-free aqueous brines may be complexed with water, or in some other form. Similarly, the other water-soluble inorganic salts which are comprised in the aqueous brine solutions that are referred to as salts or their respective cations and/or anions may be complexed with water, or in some other form.

Zinc-free Aqueous Brines – Group A

[0034] In the zinc-free aqueous brines of this group, the inorganic bromide salts are selected from calcium bromide, manganese(II) bromide, tin(II) bromide, tin(IV) bromide, bismuth(III) bromide, indium(III) bromide, and mixtures of any two or more of these; when calcium bromide is used, one or more other water-soluble inorganic salts is also used, and preferably is selected from an inorganic bromide salt, manganese(II) nitrate, and a water-soluble polytungstate salt; when bismuth(III) bromide is used, one or more other water-soluble inorganic salts is also used, and preferably is selected from an inorganic bromide salt. Manganese(II) bromide is preferably used in combination with one or more other water-soluble inorganic salts, especially when a brine with a true crystallization temperature of about 10°F (−12.2°C) or less is needed; in preferred embodiments, the other inorganic salt is preferably selected from an inorganic bromide salt, manganese(II) nitrate, and a water-soluble polytungstate salt, more preferably an inorganic bromide, which inorganic bromide is preferably calcium bromide or a combination of calcium bromide and one or more other inorganic bromide salts. In some embodiments, the inorganic bromide salt is lithium bromide in combination with an alkali metal polytungstate salt. Preferred inorganic bromide salts when

only one bromide salt is present include tin(IV) bromide and indium(III) bromide, especially tin(IV) bromide. When two bromide salts are used, they are preferably a combination of calcium bromide and manganese(II) bromide; when three bromide salts are used, they are preferably 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.

[0035] In some preferred embodiments, 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. In other preferred embodiments, the inorganic bromide salt is 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. In another preferred embodiment, the inorganic bromide salt is 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. In still another preferred embodiment, one inorganic bromide salt is present, and the inorganic bromide salt is tin(IV) bromide or indium(III) bromide.

[0036] When the other water-soluble inorganic salt is a water-soluble polytungstate salt, it can be an alkali metal polytungstate, an alkaline earth metal polytungstate, manganese polytungstate, and the like. Alkali metal polytungstates include lithium polytungstate, lithium metatungstate, sodium polytungstate, sodium metatungstate, potassium polytungstate, potassium metatungstate, and the like; preferred alkali metal polytungstates include sodium metatungstate and potassium metatungstate. Alkaline earth metal polytungstates include calcium polytungstate, magnesium polytungstate, and strontium polytungstate; preferred alkaline earth polytungstates include calcium polytungstate. The term "metatungstate" often refers to a hydrated form of a polytungstate salt.

[0037] For the combination of lithium bromide with an alkali metal polytungstate salt, the alkali metal polytungstate salts include lithium polytungstate, lithium metatungstate, sodium polytungstate, sodium metatungstate, potassium polytungstate, potassium metatungstate, and the like; preferred alkali metal polytungstates include lithium metatungstate and sodium metatungstate.

[0038] When the inorganic salts of the aqueous brine are comprised only of inorganic bromide salts, the total amount of inorganic bromide salt(s) in the aqueous brine is typically in the range of about 40 wt% to about 75 wt%, relative to the total weight of the aqueous brine.

Preferred total amounts of inorganic bromide salt(s) are from about 45 wt% to about 75 wt%, relative to the total weight of the aqueous brine.

[0039] In some embodiments, the total amount of inorganic bromide salt(s) in the aqueous brine is preferably in the range of about 45 wt% to about 65 wt%, more preferably about 55 wt% to about 65 wt%, relative to the total weight of the aqueous brine, especially when calcium bromide and one other inorganic bromide salt are used, and the other inorganic bromide salt is selected from tin(II) bromide, tin(IV) bromide, bismuth(III) bromide, and indium(III) bromide.

[0040] In other embodiments, the total amount of inorganic bromide salt(s) in the aqueous brine is preferably in the range of about 55 to about 70 wt%, relative to the total weight of the aqueous brine, especially when the inorganic bromide salts are calcium bromide and two other inorganic bromide salts, which other inorganic bromide salts are a combination of manganese(II) bromide and one other metal bromide selected from tin(II) bromide, tin(IV) bromide, bismuth(III) bromide, and indium(III) bromide.

[0041] When the inorganic salts of the aqueous brine are comprised of one or more inorganic bromide salts and one or more other water-soluble inorganic salts, the total amount of inorganic bromide salt(s) in the aqueous brine is typically in the range of about 15 wt% to about 60 wt%, preferably about 20 wt% to about 55 wt%, more preferably about 25 wt% to about 55 wt%, relative to the total weight of the aqueous brine. The total amount of the other water-soluble inorganic salt(s) varies, depending on the identity of the inorganic salt. For manganese(II) nitrate, the total amount in the aqueous brine is usually in the range of about 5 wt% to about 75 wt%, sometimes preferably about 35 wt% to about 70 wt%, sometimes preferably about 10 wt% to about 50 wt%, relative to the total weight of the aqueous brine; for water-soluble polytungstate salts, the total amount in the aqueous brine is typically in the range of about 5 wt% to about 40 wt%, preferably about 10 wt% to about 35 wt%, relative to the total weight of the aqueous brine.

[0042] The total amount of inorganic salts in an aqueous brine comprised of one or more inorganic bromide salts and one or more other water-soluble inorganic salts is in the range of about 60 wt% to about 85 wt%, sometimes preferably in the range of about 65 wt% to about 85 wt%, relative to the total weight of the aqueous brine when the other water-soluble inorganic salt is manganese(II) nitrate. When the other water-soluble inorganic salt is a water-soluble polytungstate, the total amount of inorganic salts in an aqueous brine comprised of one or more inorganic bromide salts and one or more other water-soluble inorganic salts is in the range of

about 50 wt% to about 75 wt%, preferably in the range of about 55 wt% to about 70 wt%, relative to the total weight of the aqueous brine.

[0043] The zinc-free aqueous brines have densities of about 14.3 pounds per gallon (1.71 kg/L) or more. Preferably, the aqueous brines have densities of about 14.6 ppg (1.75 kg/L) or more. In some embodiments, the aqueous brines preferably have densities of about 14.8 ppg (1.77 kg/L) or more, or preferably about 15.0 ppg (1.80 kg/L) or more, or more preferably about 15.1 ppg (1.81 kg/L) or more. In other embodiments, especially when the inorganic bromide salt is calcium bromide and one or more inorganic bromide salts selected from tin(IV) bromide, bismuth(III) bromide, or indium(III) bromide, the aqueous brines preferably have densities of about 16.0 ppg (1.92 kg/L) or more.

[0044] Density ranges for the zinc-free aqueous brines used in this invention are preferably about 14.3 ppg (1.71 kg/L) to about 19.0 ppg (2.28 kg/L), more preferably about 14.6 ppg (1.75 kg/L) to about 18.0 ppg (2.16 kg/L). In some embodiments, preferred densities are about 14.8 ppg (1.77 kg/L) to about 16.0 ppg (1.92 kg/L),more preferably about 15.0 ppg (1.80 kg/L) 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.

[0045] For the zinc-free aqueous brines, 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.

[0046] Aqueous brines 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.

[0047] 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.

[0048] In some preferred zinc-free aqueous brines, only water, inorganic bromide salts, one or more other water-soluble inorganic salts, and species derived from these components are present in the zinc-free aqueous brine; in some of these preferred embodiments, one of the inorganic bromide salts is calcium bromide. In some of these preferred embodiments, the other water-soluble inorganic salts are selected from manganese(II) nitrate, and a water-soluble polytungstate salt, and more preferably, one of the inorganic bromide salts is calcium bromide.

[0049] In other preferred zinc-free aqueous brines, only water, inorganic bromide salts, and species derived from these components are present in the zinc-free aqueous brine; in some of these preferred embodiments, one of the inorganic bromide salts is calcium bromide. In other preferred zinc-free aqueous brines, only water, tin(IV) bromide, and species derived from these components are present in the zinc-free aqueous brine.

[0050] Preferred zinc-free aqueous brines in the practice of this invention include zinc-free aqueous brines which comprise water; calcium bromide; and one or more other inorganic bromide salts, preferably selected from manganese(II) bromide, tin(II) bromide, tin(IV) bromide, bismuth(III) bromide, indium(III) bromide, and mixtures of any two or more of these; wherein the -free aqueous brine has a density of about 14.3 ppg (1.71 kg/L) or more, preferably about 14.6 ppg (1.75 kg/L) or more, more preferably about 15.0 ppg (1.80 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, more preferably about 8°F (–13.3°C) or less. In these calcium bromide-containing zinc-free aqueous brines, the inorganic bromide salt(s) other than calcium bromide is preferably in an amount of about 3.0 wt% to about 40 wt%, relative to the total weight of the

zinc-free aqueous brine; preferably, these calcium bromide-containing zinc-free aqueous brines have a pH in the range of about 0 to about 8, more preferably about 1 to 7.

[0051] Additional preferred zinc-free aqueous brines in the practice of this invention include zinc-free aqueous brines which comprise water and one inorganic bromide salt selected from tin(IV) bromide and indium(III) bromide; more preferably tin(IV) bromide; wherein the zinc-free aqueous brine has a density of about 15.0 ppg (1.80 kg/L) or more, preferably about 16.0 ppg (1.92 kg/L) or more, more preferably about 18.0 ppg (2.16 kg/L) or more.

[0052] In a preferred embodiment, the inorganic bromide salts are calcium bromide and manganese(II) bromide, and the zinc-free aqueous brine has a density of about 14.6 ppg (1.75 kg/L) or more and a true crystallization temperature at atmospheric pressure of about 20°F (–6.7°C) or less, preferably about 10°F (–12.2°C) or less. Particularly preferred are zinc-free aqueous brines containing calcium bromide and manganese(II) bromide which have densities of about 15 lb/gal (1.8 kg/L) or more, and true crystallization temperatures at atmospheric pressure of about 8°F (–13.3°C) or less. Preferably, these zinc-free aqueous brines containing calcium bromide and manganese(II) bromide have pH values in the range of about 2.5 to 5, more preferably about 3 to 4.

[0053] In some preferred embodiments, the inorganic bromide salts are calcium bromide and manganese(II) bromide in combination with another inorganic bromide salt selected from tin(IV) bromide, tin(II) bromide, bismuth(III) bromide, and indium(III) bromide.

[0054] In another preferred embodiment, the inorganic bromide salts are calcium bromide, manganese(II) bromide, and tin(IV) bromide, and the zinc-free aqueous brine has a density of about 15.0 ppg (1.80 kg/L) or more. Particularly preferred zinc-free aqueous brines containing calcium bromide, manganese(II) bromide, and tin(IV) bromide as the inorganic bromide salts have densities of about 16.0 ppg (1.92 kg/L) or more, more preferably densities of about 16.5 ppg (1.98 kg/L) or more.

[0055] In still another preferred embodiment, the inorganic bromide salts are calcium bromide, manganese(II) bromide, and bismuth(III) bromide, and the zinc-free aqueous brine has a density of about 16.0 ppg (1.92 kg/L) or more. Particularly preferred zinc-free aqueous brines containing calcium bromide, manganese(II) bromide, and bismuth(III) bromide as the inorganic bromide salts have densities of about 16.3 ppg (1.95 kg/L) or more.

[0056] In another preferred embodiment, the inorganic bromide salt is calcium bromide, and manganese(II) nitrate is present; preferably, the zinc-free aqueous brine has a density of about 14.5 ppg (1.74 kg/L) or more, more preferably about 14.8 ppg (1.77 kg/L) or more.

[0057] In yet another preferred embodiment, the inorganic bromide salt is calcium bromide or manganese(II) bromide, and a water-soluble polytungstate, preferably an alkali metal polytungstate, more preferably sodium metatungstate, is present; more preferably, the zinc-free aqueous brine has a density of about 14.5 ppg (1.74 kg/L) or more, more preferably about 14.8 ppg (1.77 kg/L) or more.

[0058] In a further preferred embodiment, the inorganic bromide salt is lithium bromide in combination with an alkali metal polytungstate salt; more preferably the alkali metal polytungstate salt is lithium metatungstate or sodium metatungstate; more preferably, the zinc-free aqueous brine has a density of about 14.5 ppg (1.74 kg/L) or more, more preferably about 14.8 ppg (1.77 kg/L) or more.

[0059] Zinc-free aqueous brines used in this invention having 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 are typically formed by processes as described in International Patent Pub. No. WO 2016/025137. Preferences for salts, combinations of salts, and densities are as described above.

[0060] Under storage conditions, aqueous brines having a density of about 15.0 ppg (1.80 kg/L) or greater often form a precipitate. Stabilization of these dense aqueous brines can be achieved by adjusting the pH of the aqueous brine. Adjustment of the pH value is accomplished by adding an inorganic hydroxide and/or oxide and/or by adding an acid, preferably hydrogen bromide, usually to a value in the range of about 1 to about 7, more preferably about 1 to about 6; still more preferably about 2.5 to about 5.

Zinc-free Aqueous Brines – Group B

[0061] In the zinc-free aqueous brines of this group, the inorganic bromide salts are selected from calcium bromide and cesium bromide. One or more other water-soluble inorganic salts can be used, and preferably are selected from an inorganic bromide salt.

[0062] When the inorganic salts of the aqueous brine are comprised only of inorganic bromide salts, the total amount of inorganic bromide salts in the aqueous brine is typically in the range of about 50 wt% to about 60 wt%, relative to the total weight of the zinc-free aqueous brine. Preferred total amounts of inorganic bromide salts are from about 53 wt% to about 58 wt%, relative to the total weight of the zinc-free aqueous brine.

[0063] Zinc-free aqueous brines of this group have densities of about 14.3 pounds per gallon (1.71 kg/L) to about 15.8 pounds per gallon (1.89 kg/L). Preferably, the zinc-free aqueous brines have densities of about 14.6 ppg (1.75 kg/L) or more. In some embodiments, the zinc-

free aqueous brines preferably have densities of about 14.8 ppg (1.77 kg/L) or more, or preferably about 15.0 ppg (1.80 kg/L) or more, or more preferably about 15.1 ppg (1.81 kg/L) or more.

[0064] Density ranges for the zinc-free aqueous brines of this group are preferably about 14.3 ppg (1.71 kg/L) to about 15.8 ppg (1.89 kg/L), more preferably about 14.6 ppg (1.75 kg/L) to about 15.6 ppg (1.87 kg/L). In some embodiments, preferred densities are about 14.8 ppg (1.77 kg/L) to about 15.4 ppg (1.85 kg/L), more preferably about 15.0 ppg (1.80 kg/L) to about 15.6 ppg (1.87 kg/L).

[0065] For the zinc-free aqueous brines of this group, the true crystallization temperatures are generally about 20°F (–6.7°C) or less, preferably about 15°F (–9.4°C) or less, more preferably about 10°F (–12.2°C) or less, and still more preferably about 5°F (–15.0°C) or less.

[0066] Zinc-free aqueous brines of this group normally have pH values of about 2 or more, preferably about 4 or more, and can range from about 2 to about 10. Preferred pH values are in the range of about 4 to about 8; more preferred are pH values in the range of about 6 to about 8.

[0067] 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.

[0068] In some preferred zinc-free aqueous brines, only water, inorganic bromide salts, one or more other water-soluble inorganic salts, and species derived from these components are present in the zinc-free aqueous brine; in these preferred embodiments, the inorganic bromide salts include calcium bromide and cesium bromide.

[0069] In other preferred zinc-free aqueous brines, only water, inorganic bromide salts, and species derived from these components are present in the aqueous brine; the inorganic bromide salts include calcium bromide and cesium bromide.

[0070] Preferred zinc-free aqueous brines of this group comprise water, calcium bromide, and cesium bromide; wherein the zinc-free aqueous brine has a density of about 14.3 ppg (1.71 kg/L) or more, preferably about 14.6 ppg (1.75 kg/L) or more, more preferably about 15.0 ppg (1.80 kg/L) or more; and a true crystallization temperature of about 20°F (–6.7°C) or less, preferably about 15°F (–9.4°C) or less, more preferably about 10°F (–12.2°C) or less. In these zinc-free aqueous brines, the calcium bromide is preferably in an amount of about 45 wt% to about 60 wt%, relative to the total weight of the zinc-free aqueous brine. The cesium bromide

in these zinc-free aqueous brines is preferably in an amount of about 3.0 wt% to about 15 wt%, preferably about 3 wt% to about 12 wt%, relative to the total weight of the zinc-free aqueous brine; preferably, these zinc-free aqueous brines have a pH in the range of about 4 to about 8, more preferably about 6 to 8.

[0071] In a preferred embodiment, the inorganic bromide salts are calcium bromide and cesium bromide, and the zinc-free aqueous brine has a density of about 14.6 ppg (1.75 kg/L) or more and a true crystallization temperature at atmospheric pressure of about 20°F (–6.7°C) or less, preferably about 15°F (–9.4°C) or less. Particularly preferred are zinc-free aqueous brines containing calcium bromide and cesium bromide which have densities of about 15 lb/gal (1.8 kg/L) to 15.6 ppg (1.87 kg/L), and true crystallization temperatures at atmospheric pressure of about 15°F (–9.4°C) or less, more preferably about 10°F (–12.2°C) or less. Preferably, these zinc-free aqueous brines containing calcium bromide and cesium bromide have pH values in the range of about 4 to 8, more preferably about 6 to 8.

[0072] The zinc-free aqueous brines used in this invention having 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 and comprising calcium bromide and cesium bromide are typically formed by processes as described in U.S. Pat. No. 10,759,985. Preferences for salts, combinations of salts, and densities are as described above.

[0073] Under storage conditions, zinc-free aqueous brines having a density of about 15.0 ppg (1.80 kg/L) or greater often form a precipitate. Stabilization of these dense aqueous brines can be achieved by adjusting the pH of the aqueous brine. Adjustment of the pH value is accomplished by adding an inorganic hydroxide and/or oxide and/or by adding an acid, preferably hydrogen bromide, usually to a value in the range of about –2 to about 10, more preferably about 4 to about 8; still more preferably about 6 to about 8.

Zinc-free Aqueous Brines – Group C

[0074] In the zinc-free aqueous brines of this group, the inorganic bromide salt is sodium bromide. Zinc-free aqueous brines of this group have densities of about 12.3 pounds per gallon (1.47 kg/L) or more. Preferably, the zinc-free aqueous brines have densities of about 12.5 pounds per gallon (1.50 kg/L) or more. In some embodiments, the zinc-free aqueous brines preferably have densities of about 14.2 pounds per gallon (1.70 kg/L) or more. In other embodiments, density ranges for the zinc-free aqueous brines of this group are preferably about 12.3 ppg (1.47 kg/L) to about 12.5 pounds per gallon (1.50 kg/L).

[0075] 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.

[0076] In some preferred zinc-free aqueous brines of this group, only water, sodium bromide, and species derived from these components are present in the zinc-free aqueous brine.

[0077] Preferred zinc-free aqueous brines of this group comprise water and sodium bromide; wherein the zinc-free aqueous brine has a density of about 12.3 pounds per gallon (1.47 kg/L) or more, preferably about 12.3 pounds per gallon (1.47 kg/L) to about 12.5 pounds per gallon (1.50 kg/L) or more, or preferably about 14.2 pounds per gallon (1.70 kg/L) or more.

Formation of aqueous well fluids

[0078] When forming an aqueous well fluid of the invention comprising a halogen-containing sorbent and a zinc-free aqueous brine, the process comprises contacting the zinc-free aqueous brine and the halogen-containing sorbent in any order. For example, a zinc-free aqueous brine and the halogen-containing sorbent can be added sequentially, or they can be introduced to a vessel or location simultaneously. In these processes, the halogen-containing sorbent is in an amount of about 0.1 wt% to about 30 wt%, relative to the combined amount of the halogen-containing sorbent and the zinc-free aqueous brine; when more than one halogen-containing sorbent is used, the amount refers to the total amount of halogen-containing sorbents. Preferred amounts of halogen-containing sorbent in the zinc-free aqueous brine depend on the desired density of the aqueous well fluid, and there is typically about 0.1 wt% to about 30 wt% halogen-containing sorbent, more often about 0.1 to about 15 wt%, preferably about 2 wt% to about 10 wt% halogen-containing sorbent relative to the combined amount of the halogen-containing sorbent and the zinc-free aqueous brine.

[0079] Any optional additives that are included can be combined with the halogen-containing sorbent and/or the zinc-free aqueous brine in any convenient manner. When the halogen-containing sorbent is in a mixture with a zinc-free aqueous brine, optional additives can be added before, during, and/or after formation of the mixture of a zinc-free aqueous brine and the halogen-containing sorbent.

[0080] The halogen-containing sorbents can be combined with the well fluid alone or in admixture with one or more other additives and/or in a mixture with a zinc-free aqueous brine.

[0081] Further embodiments of the invention include, without limitation:

[0082] a) An aqueous well fluid which comprises

I) a halogen-containing sorbent comprising one or more halogens selected from fluorine, chlorine, bromine, and/or iodine, and one or more substrate materials, and

II) a zinc-free aqueous brine having

A) a density of about 14.3 pounds per gallon or more, and a true crystallization temperature of about 20°F or less, which aqueous brine 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 about 10°F or less, when manganese(II) bromide is present, one or more other water-soluble inorganic salts are also present, or

B) a density of about 14.3 pounds per gallon to about 15.8 pounds per gallon, and a true crystallization temperature of about 20° F or less, which aqueous brine comprises water and calcium bromide and cesium bromide, or

C) having a density of about 12.3 pounds per gallon or more, which aqueous brine comprises sodium bromide,

wherein the halogen-containing sorbent is in an amount of about 0.1 wt% to about 30 wt%, relative to the combined amount of the halogen-containing sorbent and the zinc-free aqueous brine.

[0083] b) An aqueous well fluid according to a) wherein the halogen-containing sorbent comprises a substrate material selected from one or more carbonaceous materials and/or selected from one or more inorganic materials.

[0084] c) An aqueous well fluid according to b) wherein the carbonaceous material is activated carbon, and/or wherein the inorganic material is selected from inorganic oxides, natural zeolites, inorganic carbonates, and clay minerals.

[0085] d) An aqueous well fluid according to any of b)-c) wherein the inorganic material is selected from chabazite, silica, kaolinite, and bentonite.

[0086] e) An aqueous well fluid according to any of a)-d) wherein the halogen-containing sorbent is a bromine-containing sorbent.

[0087] f) An aqueous well fluid according to a) wherein the halogen-containing sorbent is a halogen-containing activated carbon sorbent.

[0088] g) An aqueous well fluid according to a) wherein the halogen-containing sorbent is a bromine-containing activated carbon sorbent.

[0089] h) An aqueous well fluid according to any of a)-g) wherein the halogen-containing sorbent has a halogen content of about 0.1 wt% to about 50 wt% calculated as bromine and based on the total weight of the halogen-containing sorbent.

[0090] i) An aqueous well fluid as in any of a)-g) wherein the zinc-free aqueous brine has the features of A).

[0091] j) An aqueous well fluid as in h) 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.

[0092] k) An aqueous well fluid as in b) 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.

[0093] l) An aqueous well fluid as in i) wherein the other water-soluble inorganic salt present with bismuth(III) bromide is an inorganic bromide salt.

[0094] m) An aqueous well fluid as in i) 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.

[0095] n) An aqueous well fluid as in any of i)-k) wherein the aqueous brine has a density of about 14.6 pounds per gallon or more.

[0096] o) An aqueous well fluid as in any of i)-k) wherein the aqueous brine has a density of about 15.0 pounds per gallon or more.

[0097] p) An aqueous well fluid as in i) wherein:

the inorganic bromide salt is a combination of calcium bromide and manganese(II) bromide, and the aqueous brine has a density of about 14.6 pounds per gallon or more, and a pH value in the range of about 2.5 to 5; or

the inorganic bromide salt is a combination of calcium bromide, manganese(II) bromide, and tin(IV) bromide, and the aqueous brine has a density of about 15.0 pounds per gallon or more; or

the inorganic bromide salt is a combination of calcium bromide, manganese(II) bromide, and bismuth(III) bromide, and the aqueous brine has a density of about 16.0 pounds per gallon or more; or

the inorganic bromide salt is calcium bromide, and the other water-soluble inorganic salt is manganese(II) nitrate, and the aqueous brine has a density of about 14.5 pounds per gallon 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 aqueous brine has a density of about 14.5 pounds per gallon or more.

[0098] q) An aqueous well fluid as in any of m) or p) wherein the water-soluble polytungstate salt is an alkali metal polytungstate, an alkaline earth metal polytungstate, or manganese polytungstate.

[0099] r) An aqueous well fluid in any of a)-h) wherein the zinc-free aqueous brine has the features of B).

[00100] s) An aqueous well fluid as in r) wherein the inorganic bromide salts are in a total amount of about 50 wt% to about 60 wt%, relative to the total weight of the aqueous brine.

[00101] t) An aqueous well fluid as in any of r)-s) wherein the calcium bromide is in an amount of about 45 wt% to about 60 wt% relative to the total weight of the aqueous brine.

[00102] u) An aqueous well fluid as in any of r)-s) wherein the cesium bromide is in an amount of about 3.0 wt% to about 15 wt% relative to the total weight of the aqueous brine.

[00103] w) An aqueous well fluid as in q) wherein the aqueous brine has a density of about 14.6 pounds per gallon or more, and a pH value in the range of about 4 to about 8.

[00104] x) An aqueous well fluid as in any of r)-w) wherein the aqueous brine has a true crystallization temperature of about 15°F or less.

[00105] y) An aqueous well fluid in any of a)-h) wherein the zinc-free aqueous brine has the features of C).

[00106] z) An aqueous well fluid as in y) wherein the zinc-free aqueous brine has a density of about 12.5 pounds per gallon or more.

[00107] aa) An aqueous well fluid as in y) wherein the zinc-free aqueous brine has a density of about 14.2 pounds per gallon or more.

[00108] ab) A process for forming an aqueous well fluid, which process comprises contacting

I) a halogen-containing sorbent comprising one or more halogens selected from fluorine, chlorine, bromine, and/or iodine, and one or more substrate materials, and

II) a zinc-free aqueous brine having

A) a density of about 14.3 pounds per gallon or more, and a true crystallization temperature of about 20°F or less, which aqueous brine 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 about 10°F or less, when manganese(II) bromide is present, one or more other water-soluble inorganic salts are also present, or

B) a density of about 14.3 pounds per gallon to about 15.8 pounds per gallon, and a true crystallization temperature of about 20° F or less, which aqueous brine comprises water and calcium bromide and cesium bromide, or

C) having a density of about 12.3 pounds per gallon or more, which aqueous brine comprises sodium bromide,

wherein the halogen-containing sorbent is in an amount of about 0.1 wt% to about 30 wt%, relative to the combined amount of the halogen-containing sorbent and the zinc-free aqueous brine.

[00109] ac) A process according to ab) wherein the halogen-containing sorbent comprises a substrate material selected from one or more carbonaceous materials and/or selected from one or more inorganic materials.

[00110] ad) A process according to ac) wherein the carbonaceous material is activated carbon, and/or wherein the inorganic material is selected from inorganic oxides, natural zeolites, inorganic carbonates, and clay minerals.

[00111] ae) A process according to any of ac)-ad) wherein the inorganic material is selected from chabazite, silica, kaolinite, and bentonite.

[00112] af) A process according to any of ab)-ae) wherein the halogen-containing sorbent is a bromine-containing sorbent.

[00113] ag) A process according to ab) wherein the halogen-containing sorbent is a halogen-containing activated carbon sorbent.

[00114] ah) A process according to ab) wherein the halogen-containing sorbent is a bromine-containing activated carbon sorbent.

[00115] ai) A process according to any of ab)-ah) wherein the halogen-containing sorbent has a halogen content of about 0.1 wt% to about 50 wt% calculated as bromine and based on the total weight of the halogen-containing sorbent.

[00116] aj) A process as in any of ab)-ah) wherein the zinc-free aqueous brine has the features of A).

[00117] ak) A process as in aj) 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.

[00118] al) A process as in aj) 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.

[00119] am) A process as in aj) wherein when the inorganic bromide salt is bismuth(III) bromide, the other water-soluble inorganic salt is an inorganic bromide salt.

[00120] an) A process as in ak) 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.

[00121] ao) A process as in an) wherein the water-soluble polytungstate salt is an alkali metal polytungstate, an alkaline earth metal polytungstate, or manganese polytungstate.

[00122] ap) A process as in any of aj)-al) wherein the aqueous brine has a density of about 14.6 pounds per gallon or more, and/or wherein the inorganic bromide salt is in a total amount of about 40 wt% to about 75 wt%, relative to the total weight of the aqueous brine.

[00123] aq) A process as in any of ai)-ap) wherein the aqueous brine has a true crystallization temperature of about 10°F or less.

[00124] ar) A process as in any of ab)-ai) wherein the zinc-free aqueous brine has the features of B).

[00125] as) A process as in ar) wherein the aqueous brine has a density of about 14.6 pounds per gallon or more, and/or wherein the inorganic bromide salts are in a total amount of about 50 wt% to about 60 wt%, relative to the total weight of the aqueous brine.

[00126] at) A process as in ar) wherein the aqueous brine has calcium bromide in an amount of about 45 wt% to about 60 wt% relative to the total weight of the aqueous brine.

[00127] au) A process as in ar) wherein the aqueous brine has cesium bromide in an amount of about 3.0 wt% to about 15 wt% relative to the total weight of the aqueous brine.

[00128] av) A process as in any of ar)-au) wherein the aqueous brine has a true crystallization temperature of about 15°F or less.

[00129] aw) A process as in any of ab)-ai) wherein the zinc-free aqueous brine has the features of C).

[00130] ax) A process as in aw) wherein the zinc-free aqueous brine has a density of about 12.5 pounds per gallon or more.

[00131] ay) A process as in aw) wherein the zinc-free aqueous brine has a density of about 14.2 pounds per gallon or more.

[00132] az) A method of treating a wellbore, said method comprising introducing into the wellbore an aqueous well fluid as in any of a)-aa).

[00133] ba) A method as in az) wherein the fluid is a completion fluid, drilling fluid, packer fluid, or workover fluid.

[00134] bb) A method as in az) wherein the wellbore is connected to a high pressure reservoir.

[00135] Components referred to by chemical name or formula anywhere in the specification or claims hereof, whether referred to in the singular or plural, are identified as they exist prior to coming into contact with another substance referred to by chemical name or chemical type (*e.g.*, another component, a solvent, or *etc.*). It matters not what chemical changes, transformations and/or reactions, if any, take place in the resulting mixture or solution as such changes, transformations, and/or reactions are the natural result of bringing the specified components together under the conditions called for pursuant to this disclosure. Thus the components are identified as ingredients to be brought together in connection with performing a desired operation or in forming a desired composition. Also, even though the claims hereinafter may refer to substances, components and/or ingredients in the present tense ("comprises", "is", *etc.*), the reference is to the substance, component or ingredient as it existed at the time just before it was first contacted, blended or mixed with one or more other substances, components and/or ingredients in accordance with the present disclosure. The fact that a substance, component or ingredient may have lost its original identity through a chemical reaction or transformation during the course of contacting, blending or mixing operations, if conducted in accordance with this disclosure and with ordinary skill of a chemist, is thus of no practical concern.

[00136] The invention may comprise, consist, or consist essentially of the materials and/or procedures recited herein.

[00137] As used herein, the term "about" modifying the quantity of an ingredient in the compositions of the invention or employed in the methods of the invention refers to variation in the numerical quantity that can occur, for example, through typical measuring and liquid handling procedures used for making concentrates or use solutions in the real world; through inadvertent error in these procedures; through differences in the manufacture, source, or purity of the ingredients employed to make the compositions or carry out the methods; and the like. The term about also encompasses amounts that differ due to different equilibrium conditions for a composition resulting from a particular initial mixture. Whether or not modified by the term "about", the claims include equivalents to the quantities.

[00138] Except as may be expressly otherwise indicated, the article "a" or "an" if and as used herein is not intended to limit, and should not be construed as limiting, the description or a claim to a single element to which the article refers. Rather, the article "a" or "an" if and as used herein is intended to cover one or more such elements, unless the text expressly indicates otherwise.

[00139] This invention is susceptible to considerable variation in its practice. Therefore the foregoing description is not intended to limit, and should not be construed as limiting, the invention to the particular exemplifications presented hereinabove.

THAT WHICH IS CLAIMED IS:

1. An aqueous well fluid which comprises

I) a halogen-containing sorbent comprising one or more halogens selected from fluorine, chlorine, bromine, and/or iodine, and one or more substrate materials, and

II) a zinc-free aqueous brine having

A) a density of about 14.3 pounds per gallon or more, and a true crystallization temperature of about 20°F or less, which aqueous brine 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 about 10°F or less, when manganese(II) bromide is present, one or more other water-soluble inorganic salts are also present, or

B) a density of about 14.3 pounds per gallon to about 15.8 pounds per gallon, and a true crystallization temperature of about 20° F or less, which aqueous brine comprises water and calcium bromide and cesium bromide, or

C) having a density of about 12.3 pounds per gallon or more, which aqueous brine comprises sodium bromide,

wherein the halogen-containing sorbent is in an amount of about 0.1 wt% to about 30 wt%, relative to the combined amount of the halogen-containing sorbent and the zinc-free aqueous brine.

2. An aqueous well fluid according to Claim 1 wherein the halogen-containing sorbent comprises a substrate material selected from one or more carbonaceous materials and/or selected from one or more inorganic materials.

3. An aqueous well fluid according to Claim 2 wherein the carbonaceous material is activated carbon, and/or wherein the inorganic material is selected from inorganic oxides, natural zeolites, inorganic carbonates, and clay minerals.

4. An aqueous well fluid according to any of Claims 2-3 wherein the inorganic material is selected from chabazite, silica, kaolinite, and bentonite.

5. An aqueous well fluid according to any of Claims 1-4 wherein the halogen-containing sorbent is a bromine-containing sorbent.

6. An aqueous well fluid according to Claim 1 wherein the halogen-containing sorbent is a halogen-containing activated carbon sorbent.

7. An aqueous well fluid according to Claim 1 wherein the halogen-containing sorbent is a bromine-containing activated carbon sorbent.

8. An aqueous well fluid according to any of Claims 1-7 wherein the halogen-containing sorbent has a halogen content of about 0.1 wt% to about 50 wt% calculated as bromine and based on the total weight of the halogen-containing sorbent.

9. An aqueous well fluid as in any of Claims 1-7 wherein the zinc-free aqueous brine has the features of A).

10. An aqueous well fluid as in Claim 8 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.

11. An aqueous well fluid 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.

12. An aqueous well fluid as in Claim 9 wherein the other water-soluble inorganic salt present with bismuth(III) bromide is an inorganic bromide salt.

13. An aqueous well fluid as in Claim 9 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.

14. An aqueous well fluid as in any of Claims 9-11 wherein the aqueous brine has a density of about 14.6 pounds per gallon or more.

15. An aqueous well fluid as in any of Claims 9-11 wherein the aqueous brine has a density of about 15.0 pounds per gallon or more.

16. An aqueous well fluid as in Claim 9 wherein:

the inorganic bromide salt is a combination of calcium bromide and manganese(II) bromide, and the aqueous brine has a density of about 14.6 pounds per gallon or more, and a pH value in the range of about 2.5 to 5; or

the inorganic bromide salt is a combination of calcium bromide, manganese(II) bromide, and tin(IV) bromide, and the aqueous brine has a density of about 15.0 pounds per gallon or more; or

the inorganic bromide salt is a combination of calcium bromide, manganese(II) bromide, and bismuth(III) bromide, and the aqueous brine has a density of about 16.0 pounds per gallon or more; or

the inorganic bromide salt is calcium bromide, and the other water-soluble inorganic salt is manganese(II) nitrate, and the aqueous brine has a density of about 14.5 pounds per gallon 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 aqueous brine has a density of about 14.5 pounds per gallon or more.

17. An aqueous well fluid as in any of Claims 13 or 16 wherein the water-soluble polytungstate salt is an alkali metal polytungstate, an alkaline earth metal polytungstate, or manganese polytungstate.

18. An aqueous well fluid in any of Claims 1-8 wherein the zinc-free aqueous brine has the features of B).

19. An aqueous well fluid as in Claim 18 wherein the inorganic bromide salts are in a total amount of about 50 wt% to about 60 wt%, relative to the total weight of the aqueous brine.

20. An aqueous well fluid as in any of Claims 18-19 wherein the calcium bromide is in an amount of about 45 wt% to about 60 wt% relative to the total weight of the aqueous brine.

21. An aqueous well fluid as in any of Claims 18-19 wherein the cesium bromide is in an amount of about 3.0 wt% to about 15 wt% relative to the total weight of the aqueous brine.

22. An aqueous well fluid as in any of Claims 18-19 wherein the aqueous brine has a pH in the range of about 2 to about 10.

23. An aqueous well fluid as in Claim 17 wherein the aqueous brine has a density of about 14.6 pounds per gallon or more, and a pH value in the range of about 4 to about 8.

24. An aqueous well fluid as in any of Claims 18-23 wherein the aqueous brine has a true crystallization temperature of about 15°F or less.

25. An aqueous well fluid in any of Claims 1-8 wherein the zinc-free aqueous brine has the features of C).

26. An aqueous well fluid as in Claim 25 wherein the zinc-free aqueous brine has a density of about 12.5 pounds per gallon or more.

27. An aqueous well fluid as in Claim 25 wherein the zinc-free aqueous brine has a density of about 14.2 pounds per gallon or more.

28. A process for forming an aqueous well fluid, which process comprises contacting

I) a halogen-containing sorbent comprising one or more halogens selected from fluorine, chlorine, bromine, and/or iodine, and one or more substrate materials, and

II) a zinc-free aqueous brine having

A) a density of about 14.3 pounds per gallon or more, and a true crystallization temperature of about 20°F or less, which aqueous brine 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 about 10°F or less, when manganese(II) bromide is present, one or more other water-soluble inorganic salts are also present, or

B) a density of about 14.3 pounds per gallon to about 15.8 pounds per gallon, and a true crystallization temperature of about 20° F or less, which aqueous brine comprises water and calcium bromide and cesium bromide, or

C) having a density of about 12.3 pounds per gallon or more, which aqueous brine comprises sodium bromide,

wherein the halogen-containing sorbent is in an amount of about 0.1 wt% to about 30 wt%, relative to the combined amount of the halogen-containing sorbent and the zinc-free aqueous brine.

29. A process according to Claim 28 wherein the halogen-containing sorbent comprises a substrate material selected from one or more carbonaceous materials and/or selected from one or more inorganic materials.

30. A process according to Claim 29 wherein the carbonaceous material is activated carbon, and/or wherein the inorganic material is selected from inorganic oxides, natural zeolites, inorganic carbonates, and clay minerals.

31. A process according to any of Claims 29-30 wherein the inorganic material is selected from chabazite, silica, kaolinite, and bentonite.

32. A process according to any of Claims 28-31 wherein the halogen-containing sorbent is a bromine-containing sorbent.

33. A process according to Claim 28 wherein the halogen-containing sorbent is a halogen-containing activated carbon sorbent.

34. A process according to Claim 28 wherein the halogen-containing sorbent is a bromine-containing activated carbon sorbent.

35. A process according to any of Claims 28-34 wherein the halogen-containing sorbent has a halogen content of about 0.1 wt% to about 50 wt% calculated as bromine and based on the total weight of the halogen-containing sorbent.

36. A process as in any of Claims 28-34 wherein the zinc-free aqueous brine has the features of A).

37. A process as in Claim 36 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.

38. A process as in Claim 36 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.

39. A process as in Claim 36 wherein when the inorganic bromide salt is bismuth(III) bromide, the other water-soluble inorganic salt is an inorganic bromide salt.

40. A process as in Claim 36 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.

41. A process as in Claim 40 wherein the water-soluble polytungstate salt is an alkali metal polytungstate, an alkaline earth metal polytungstate, or manganese polytungstate.

42. A process as in any of Claims 36-38 wherein the aqueous brine has a density of about 14.6 pounds per gallon or more, and/or wherein the inorganic bromide salt is in a total amount of about 40 wt% to about 75 wt%, relative to the total weight of the aqueous brine.

43. A process as in any of Claims 35-42 wherein the aqueous brine has a true crystallization temperature of about 10°F or less.

44. A process as in any of Claims 28-35 wherein the zinc-free aqueous brine has the features of B).

45. A process as in Claim 44 wherein the aqueous brine has a density of about 14.6 pounds per gallon or more, and/or wherein the inorganic bromide salts are in a total amount of about 50 wt% to about 60 wt%, relative to the total weight of the aqueous brine.

46. A process as in Claim 44 wherein the aqueous brine has calcium bromide in an amount of about 45 wt% to about 60 wt% relative to the total weight of the aqueous brine.

47. A process as in Claim 44 wherein the aqueous brine has cesium bromide in an amount of about 3.0 wt% to about 15 wt% relative to the total weight of the aqueous brine.

48. A process as in any of Claims 44-47 wherein the aqueous brine has a true crystallization temperature of about 15°F or less.

49. A process as in any of Claims 28-35 wherein the zinc-free aqueous brine has the features of C).

50. A process as in Claim 49 wherein the zinc-free aqueous brine has a density of about 12.5 pounds per gallon or more.

51. A process as in Claim 49 wherein the zinc-free aqueous brine has a density of about 14.2 pounds per gallon or more.

52. A method of treating a wellbore, said method comprising introducing into the wellbore an aqueous well fluid as in any of Claims 1-27.

53. A method as in Claim 52 wherein the fluid is a completion fluid, drilling fluid, packer fluid, or workover fluid.

54. A method as in Claim 52 wherein the wellbore is connected to a high pressure reservoir.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2024/037764

A. CLASSIFICATION OF SUBJECT MATTER

IPC: ***C09K 8/05*** (2024.01); ***B01J 20/04*** (2024.01); ***B01J 20/20*** (2024.01); ***C01D 3/10*** (2024.01); ***C09K 8/03*** (2024.01)

CPC: ***C09K 8/05; B01J 20/046; B01J 20/20; C01D 3/10; C09K 8/032;*** *B01D 2257/602*

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)

See Search History Document

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

See Search History Document

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

See Search History Document

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2020/0181471 A1 (ALBEMARLE CORPORATION) 11 June 2020 (11.06.2020) entire document	1-4, 6, 7, 11
A	US 2004/0059054 A1 (LOPEZ et al.) 25 March 2004 (25.03.2004) entire document	1-4, 6, 7, 11
A	US 2021/0170332 A1 (MIDWEST ENERGY EMISSIONS CORP) 10 June 2021 (10.06.2021) entire document	1-4, 6, 7, 11
A	US 2020/0255715 A1 (TETRA TECHNOLOGIES INC.) 13 August 2020 (13.08.2020) entire document	1-4, 6, 7, 11

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"D" document cited by the applicant in the international application
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"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

Date of the actual completion of the international search	Date of mailing of the international search report
11 September 2024 (11.09.2024)	**22 November 2024 (22.11.2024)**

Name and mailing address of the ISA/US	Authorized officer
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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2024/037764

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☑ Claims Nos.: **5, 8-10, 12-27, 32, 35-54**
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

This application contains the following inventions or groups of inventions which are not so linked as to form a single general inventive concept under PCT Rule 13.1. In order for all inventions to be examined, the appropriate additional examination fees need to be paid.

Group I: claims 1-4, 6, 7, and 11 are drawn to aqueous well fluids.

Group II: claims 28-31, 33, and 34 are drawn to processes for forming an aqueous well fluid.

The inventions listed in Groups I and II do not relate to a single general inventive concept under PCT Rule 13.1, because under PCT Rule 13.2 they lack the same or corresponding special technical features for the following reasons:

The special technical features of Group I, aqueous well fluids, are not present in Group II; and the special technical features of Group II, processes for forming an aqueous well fluid, are not present in Group I.

Additionally, even if Groups I and II were considered to share the technical features of an aqueous well fluid which comprises I) a halogen-containing sorbent comprising one or more halogens selected from fluorine, chlorine, bromine, and/or iodine, and one or more substrate materials, and II) a zinc-free aqueous brine having A) a density of about 14.3 pounds per gallon or more, and a true crystallization temperature of about 200 F or less, which aqueous brine 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 about 100F or less, when manganese(II) bromide is present, one or more other water-soluble inorganic salts are also present, or B) a density of about 14.3 pounds per gallon to about 15.8 pounds per gallon, and a true crystallization temperature of about 200 F or less, which aqueous brine comprises water and calcium bromide and cesium bromide, or C) having a density of about 12.3 pounds per gallon or more, which aqueous brine comprises sodium bromide, wherein the halogen-containing sorbent is in an amount of about 0.1 wt% to about 30 wt%, relative to the combined amount of the halogen-containing sorbent and the zinc-free aqueous brine, these shared technical features do not represent a contribution over the prior art as disclosed by US 2020/0181471 A1 to Albemarle Corporation (hereinafter, "Albemarle"), US 2021/0170332 A1 to Midwest Energy Emissions Corp. (hereinafter, "MEEC"), and US 2004/0059054 A1 to Lopez et al. (hereinafter, "Lopez").

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2024/037764

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

Albemarle teaches an aqueous well fluid (para [0002]) and II) a zinc-free aqueous brine (para [0008] a zinc–free aqueous brine composition) having A) a density of about 14.3 pounds per gallon or more (para [0008] 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 or less (para [0008] a true crystallization temperature of about 20 F. (- 6.7 C.) or less), which aqueous brine comprises water and one or more inorganic bromide salts (para [0008] 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 (para [0008] with the proviso that when calcium bromide is present , one or more other water-soluble inorganic salts is also present), wherein the other water-soluble inorganic salt is selected from an inorganic bromide salt and manganese(II) nitrate (para [0008] preferably selected from an inorganic bromide salt , manganese (II) nitrate…), when lithium bromide is present, calcium bromide is absent (para [0008] 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 (para [0008] when bismuth (III) bromide is present, one or more other water-soluble inorganic salts is also present), and for a true crystallization temperature of about 10 F or less, when manganese(II) bromide is present, one or more other water-soluble inorganic salts are also present (para [0008] for true crystallization temperatures of about 10 F. or less, when manganese(II) bromide is present, one or more other water soluble inorganic salts are also present.).

MEEC teaches a halogen-containing sorbent (Abstract) comprising one or more halogens selected from fluorine, chlorine, bromine, and/or iodine (para [0063] a molecular bromine molecule…), and one or more substrate materials (para [0063] forms a complex with the surface of the base sorbent).

Lopez teaches a well fluid comprising an aqueous brine (Abstract) wherein the sorbent is in an amount of about 0.1 wt% to about 30 wt%, relative to the combined amount of the sorbent and the aqueous brine (para [0050] 0.05 to 20% by weight of water-superabsorbent polymer; 0 to 99.95% by weight of water and/or brine containing inorganic or organic salts).

The inventions listed in Groups I and II therefore lack unity under Rule 13 because they do not share a same or corresponding special technical feature.

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☑ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.: **1-4, 6, 7, 11**

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.