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(54) Title: DISINFECTING WATER USED IN A FRACTURING OPERATION

(57) Abstract: A process for disinfecting a treatment fluid is disclosed, including admixing an aqueous solution of a mixed disinfectant generated via electrolysis of a quaternary ammonium halide salt solution with a treatment fluid.

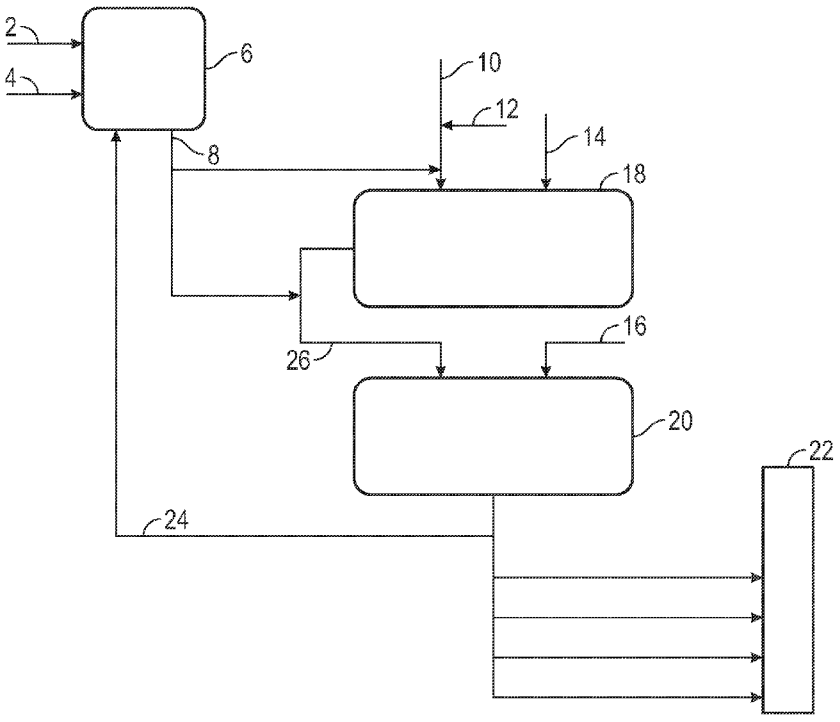


FIG. 1

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DISINFECTING WATER USED IN A FRACTURING OPERATION

BACKGROUND

[0001] Treatment fluids may be used in a variety of subterranean operations, including, but not limited to, stimulation treatments, damage removal, formation isolation, wellbore cleanout, scale removal, scale control, drilling operations, cementing, conformance treatments, water injection, steam injection, and sand control treatments. Treatment fluids may also be used in a variety of pipeline treatments. As used herein, the term "treatment," or "treating," refers to any operation that uses a fluid in conjunction with a desired function and/or for a desired purpose. The term "treatment," or "treating," does not imply any particular action by the fluid or any particular component thereof.

[0002] One common well production stimulation operation that employs a treatment fluid is hydraulic fracturing. Hydraulic fracturing operations generally involve pumping a treatment fluid (e.g., a fracturing fluid) into a well bore that penetrates a subterranean formation at a sufficient hydraulic pressure to create or enhance one or more cracks, or "fractures," in the subterranean formation. "Enhancing" one or more fractures in a subterranean formation, as that term is used herein, is defined to include the extension or enlargement of one or more natural or previously created fractures in the subterranean formation. The treatment fluid may comprise particulates, often referred to as "proppant particulates," that are deposited in the fractures. The proppant particulates, inter alia, may prevent the fractures from fully closing upon the release of hydraulic pressure, forming conductive channels through which fluids may flow to the well bore. The proppant particulates also may be coated with certain types of materials, including resins, tackifying agents, and the like, among other purposes, to enhance conductivity (e.g., fluid flow) through the fractures in which they reside. Once at least one fracture is created and the proppant particulates are substantially in place, the treatment fluid may be "broken" (i.e., the viscosity of the fluid is reduced), and the treatment fluid may be recovered from the formation.

[0003] Depending upon the source of the treatment fluid, or portions thereof, the treatment fluid may contain bacteria or other microorganisms that may attack downhole formations (e.g., growing downhole and plugging the formation), may attack polymers and other materials used as proppants, may attack treatment fluids

(e.g., affecting fluid properties and performance), or may attack well servicing equipment, including tanks and pipes, for example. In addition to restricting flow, bacteria may also produce unwanted gases downhole. The treatment fluid may contain organic material, either from the source water or from the chemicals and other materials added to the water that constitute a food source for the bacteria or other microorganisms and help promote their growth. The treatment fluid may also contain other chemical components that could be harmful to the performance of the treatment fluid or to the wellbore itself.

[0004] A wide variety of biocides have been used in these treatment fluids to control, limit, or eliminate the undesired effect of these microorganisms. For example bactericides may be used to control sulfate-reducing bacteria, slime-forming bacteria, iron-oxidizing bacteria and bacteria that attack polymers in fracture and secondary recovery fluids. Biocides may also include, among others, fungicides, and algaecides.

[0005] Biocides are, by their very nature, dangerous to handlers. Handlers typically avoid eye and skin contact and, when liquid biocides are utilized, avoid splashing or spilling the liquid biocide, as spilled biocides can contaminate potable water sources. As a result, regulators are becoming more stringent on the use of harsh biological agents, and on their introduction into the environment, either downhole or on the surface.

SUMMARY OF THE DISCLOSURE

[0006] It has been found that a mixed disinfectant produced via electrolysis of a salt solution may be used to effectively disinfect water and other fluids for use in well treatment fluids, including fracturing fluids. These mixed disinfectants may provide for a sufficient reduction in undesirable bacteria, spores, fungi, etc. They may also provide a reduction in the organic material that can provide a food source for the bacteria and other microorganisms, and provide a reduction in other harmful components, such as hydrogen sulfide gas. The mixed disinfectants are of low or no toxicity and additionally have a short half-life (less than 24 hours, for example) and may degrade rapidly to naturally occurring chemicals following use or contact with the downhole formation, minimizing the environmental impact post-use. Due to the rapid degradation, the sterilization provided by embodiments herein may be considered virtually chemical free. It has also been found that the mixed disinfectants

may be provided to a well site using a unique, transportable delivery system as will be described below.

[0007] In one aspect, embodiments disclosed herein relate to a process for disinfecting a treatment fluid, the process including admixing an aqueous solution comprising a mixed disinfectant generated via electrolysis of a quaternary ammonium halide salt solution with a treatment fluid.

[0008] In another aspect, embodiments disclosed herein relate to a method of servicing a wellbore, the method including: transporting a portable tank containing a quantity of one or more quaternary ammonium halide salts to a well site to be serviced; generating a salt solution by admixing water with at least a portion of the quaternary ammonium halide salt; converting the salt solution to an aqueous solution comprising one or more disinfectants via electrolysis; contacting the aqueous solution with a treatment fluid to form a treated treatment fluid; and providing the treated treatment fluid for placement into the wellbore.

[0009] In another aspect, embodiments disclosed herein relate to a portable system for disinfecting water, including: a fluid connection for connecting to a water supply; a treatment system for conditioning the water supplied; a mixing device, such as a tank, mixing tee, or the like, for admixing at least a portion of the conditioned water with one or more quaternary ammonium halide salts or a solution comprising one or more quaternary ammonium halide salts to form a salt solution; an electrolytic disinfectant producing unit for converting at least a portion of the salt solution to an aqueous solution comprising mixed disinfectants; optionally one or more tanks for storing the aqueous solution; and a fluid connection for transporting the aqueous solution from the one or more tanks for storing a fluid to be disinfected. In some embodiments, the system is modular and/or contained.

[0010] In another aspect, embodiments disclosed herein relate to a method of disinfecting a fluid, including: disposing a quantity of one or more quaternary ammonium halide salts or a solution comprising one or more quaternary ammonium halide salts in a tank; receiving water from a water supply; treating the water received in a water treatment system to form a conditioned water stream; generating a salt solution by admixing a first portion of the conditioned water with a portion of the one or more quaternary ammonium halide salts or a solution comprising one or more

quaternary ammonium halide salts; combining the salt solution with a second portion of the conditioned water to form a diluted salt solution; feeding the diluted salt solution to an electrolytic disinfectant producing unit to convert the salt solution to an aqueous solution comprising one or more disinfectants via electrolysis; contacting the aqueous solution with a fluid to form a treated fluid.

[0011] In another aspect, embodiments disclosed herein relate to a method for disinfecting a treatment fluid, including: admixing an aqueous solution comprising quaternary ammonium hypohalouos acid generated from a quaternary ammonium halide salt solution with a treatment fluid.

[0012] In another aspect, embodiments disclosed herein relate to a method for forming a treatment fluid using an ammonia-containing water source, the method including: admixing an aqueous solution comprising quaternary ammonium hypohalouos acid generated from a quaternary ammonium halidesalt solution to the ammonia-containing water.

[0013] This summary is provided to introduce a selection of concepts that are further described below in the detailed description. This summary is not intended to identify key or essential features of the claimed subject matter, nor is it intended to be used as an aid in limiting the scope of the claimed subject matter.

[0014] Other aspects of the present disclosure will be apparent from the following description and the appended claims.

BRIEF DESCRIPTION OF DRAWINGS

[0015] FIG. 1 is a flow diagram of a process for disinfecting a treatment fluid according to embodiments disclosed herein.

[0016] FIG. 2 is a flow diagram of a process for disinfecting a treatment fluid according to other embodiments disclosed herein.

[0017] FIG. 3 is a flow diagram of a system for generating and delivering a disinfectant according to embodiments disclosed herein.

[0018] FIGs. 4A, 4B, 4C & 5 are flow diagrams of transportable systems according to embodiments disclosed herein.

[0019] FIG. 6 is flow diagram of a system for generating and delivering a disinfectant according to other embodiments disclosed herein.

[0020] FIG. 7 is a flow diagram of a system for generating and delivering a disinfectant according to yet other embodiments disclosed herein.

DETAILED DESCRIPTION

[0021] As used herein, the term "treatment fluid" is meant to include those fluids having oil field applications, such as any number of fluids suitable for pumping downhole to service or treat a wellbore. "Treatment fluid" may thus refer to a fluid used to drill, complete, enhance, work over, fracture, repair, or in any way prepare a wellbore for the recovery of materials residing in a subterranean formation penetrated by the wellbore, including water in ponds and pits, as well as fluids produced during drilling operations, such as flowback water and produced water that may contain residual polymers and dissolved metals in a non-oxidized state, such as Fe, Mn, and S, for example. It is to be understood that "subterranean formation" encompasses both areas below exposed earth and areas below earth covered by water, such as ocean or fresh water. Examples of treatment fluids may include, but are not limited to, cement slurries, drilling fluids or drilling muds, spacer fluids, packer fluids, fracturing fluids, steam or water injection fluids, or completion fluids, all of which are well known in the art. Without limitation, servicing the wellbore includes positioning the treatment fluid in the wellbore to isolate the subterranean formation from a portion of the wellbore; to support a conduit in the wellbore; to plug a void or crack in the conduit; to plug a void or crack in a cement sheath disposed in an annulus of the wellbore; to plug an opening between the cement sheath and the conduit; to prevent the loss of aqueous or non-aqueous drilling fluids into loss circulation zones such as a void, vugular zone, or fracture; to be used as a fluid in front of cement slurry in cementing operations; to seal an annulus between the wellbore and an expandable pipe or pipe string; to fracture a formation; to flood a formation to improve hydrocarbon recovery, to work over the wellbore to remove scale, bacteria or other accumulations or blockages; or combinations thereof.

[0022] In one aspect, embodiments disclosed herein relate to disinfecting wellbore treatment fluids to reduce biological contamination of the fluid prior to placement of the treatment fluid into the wellbore and use of the treatment fluid downhole. More specifically, embodiments disclosed herein relate to disinfecting treatment fluids using a mixed disinfectant generated at a well site.

[0023] Any number of the treatment fluids noted above may be formed using water or other fluids contaminated with various microorganisms, including sulfate-reducing bacteria, slime-forming bacteria, iron-oxidizing bacteria and/or bacteria that attack polymers in fracture and secondary recovery fluids, as well as fungi and/or algae and organic food sources or other components that can be treated according to embodiments disclosed herein. Prior to use of the contaminated fluids to form the desired treatment fluids, or concurrent with the formation of the treatment fluids with the contaminated fluid, it is desirable to disinfect the water or treatment fluid to minimize the impact the microorganisms may have on drilling, completion, fracturing, and/or production.

[0024] It has been found that a mixed disinfectant may be used to control the growth of the microorganisms. The mixed disinfectant may be generated in some embodiments by the electrolysis of a brine or salt solution, such as a solution of one or more salts in water. The one or more salts may include at least one of an alkali metal halide, an alkaline earth metal halide, and a transition metal halide, where the halide may include fluorine, chlorine, bromine, or iodine, for example. In particular embodiments, the salt may be sodium chloride, sodium bromide, potassium bromide or a mixture including sodium chloride, sodium bromide, or potassium bromide, among others. Electrolysis of the salt solution may produce a mixture of disinfectant, including two or more of ozone, hydrogen peroxide, hypohalite (e.g., hypochlorite), hypohalous acid (e.g., hypochlorous acid or hypobromous acid), halogen oxides (e.g., chlorine dioxide, bromine dioxide), and halogen (e.g., chlorine, bromine), and other halo-oxygen (e.g., chlor-oxygen) species, for example. However, it should be understood that the term "mixed disinfectant" as used herein may also include a solution of at least one disinfectant except where defined otherwise, and may include oxidants and non-oxidative disinfectants.

[0025] In other embodiments, the mixed disinfectant may be generated by the electrolysis of a solution containing one or more quaternary ammonium salt. The one or more quaternary ammonium salts include compounds having the general structure NR_4X, where N is a nitrogen atom, R denotes an organic hydrocarbon functional group, and X represents a halide (Cl^-, Br^-, or I^-). Examples of quaternary ammonium halides that may be used include, among others: Examples of quaternary ammonium

compounds that could be utilized in this process include, but are not limited to, benzalkonium chloride, didecyldimethylammonium chloride, cetyltrimethylammonium chloride, octyltrimethylammonium chloride, tetramethylammonium chloride, tetraethylammonium chloride, tetrapropylammonium chloride, tetrabutylammonium chloride, cetylpyridinium chloride, benzalkonium bromide, didecyldimethylammonium bromide, cetyltrimethylammonium bromide, octyltrimethylammonium bromide, tetramethylammonium bromide, tetraethylammonium bromide, tetrapropylammonium bromide, tetrabutylammonium bromide, cetylpyridinium bromide, benzalkonium iodide, didecyldimethylammonium iodide, cetyltrimethylammonium iodide, octyltrimethylammonium iodide, tetramethylammonium iodide, tetraethylammonium iodide, tetrapropylammonium iodide, tetrabutylammonium iodide, and cetylpyridinium iodide. Polymeric quaternary ammonium compounds, for example, but not limited to, the polyquaternium polymers, can also be used as the quaternary ammonium halide source in these reactions. Electrolysis of a solution containing the quaternary ammonium salts may result in a mixed disinfectant solution including at least one of hypohalous acid and quaternary ammonium hypohalite.

[0026] In other embodiments, the mixed disinfectant may be generated from the electrolysis of a solution containing a combination of one or more salts and one or more quaternary ammonium salts. The one or more salts and one or more quaternary ammonium salts may include those compounds as described above. Electrolysis of the mixed solution may produce a mixed disinfectant, including two or more of quaternary ammonium hypohalite, ozone, hydrogen peroxide, hypohalite (e.g., hypochlorite), hypohalous acid (e.g., hypochlorous acid or hypobromous acid), halogen oxides (e.g., chlorine dioxide, bromine dioxide), and halogen (e.g., chlorine, bromine), and other halo-oxygen (e.g., chlor-oxygen) species, for example.

[0027] In some embodiments, a mixed disinfectant may be generated by separate electrolysis of a salt solution and a quaternary ammonium halide salt solution, the mixed disinfectant generated in each being combined to form a combined mixed disinfectant solution.

[0028] In other embodiments, the mixed disinfectant may be generated from the electrolysis of a solution containing a combination of one or more salts, where the

resulting mixture is combined with one or more quaternary ammonium salts to produce a quaternary ammonium hypohalite solution.

[0029] In addition to the above described salts and quaternary ammonium halide salts, other compounds that may be admixed with the solution to be electrolyzed may include, but are not limited to, ammonia, ammonia salts (such as ammonium chloride, ammonium sulfate, ammonium bromide, ammonium iodide, etc.), and dissolved oxygen. Mixed disinfectant solutions produced with such compounds may thus also include haloamines, halogen dioxides, and hydrogen peroxide, among other compounds noted above. In some embodiments, ammonia may be added to the mixed disinfectant solution (after electrolysis of the quaternary ammonium halide salt solution).

[0030] When quaternary ammonium halide salts are used in admixture with other halide salts, such as sodium chloride, the quaternary ammonium halide salts may be present at a ratio to the halide salt in the range from about 1:40 to about 1: 1, such as from about 1:30 to about 1:5 in other embodiments, and from about 1:20 to about 1:10 in yet other embodiments. Likewise, when a mixed disinfectant is generated separately via electrolysis and mixed, the resulting mixed disinfectant may be admixed at similar ratios, based on particular mixed disinfectant concentrations.

[0031] The combination of disinfecting compounds, such as oxidants and halide compounds in a water-based solution, produced via electrolysis of salt or quaternary ammonium salt solutions discussed above, may enhance the potential of the disinfecting formulation and create an unexpected synergistic effect for substantially increasing rates of disinfection as compared to disinfectants, such as ozone, utilized alone. In some embodiments, for example, the mixed disinfectant system may result in a reduction of bacterial concentration in water by a 6 log reduction or more. The reduction in bacteria concentration may be realized by contacting the fluid to be treated with the aqueous solution comprising the mixed disinfectant for a time period of up to about 2 weeks, such as in the range from about 1 second to about 2 hours in some embodiments; in the range from about 1 minute to about 30 minutes in other embodiments; and in the range from about 2 minutes to about 10 minutes, such as about 5 minutes, in yet other embodiments.

[0032] In addition to treatment fluids mentioned above, a mixed disinfectant generated according to embodiments disclosed herein may also be useful for treating other oilfield waters, such as tanks, ponds, recycled waters, discharged waters, flow back waters, and recycling of water used in steam injection. The treatment may be used for all fresh or recycled water (flow back, produced, water from drilling fluids, in frac tanks, water produced during air drilling, stagnant ponds, etc.), water and steam injection (enhanced recovery), packer fluids, oilfield pipelines, disposal wells, workovers, production (replace biocides, remove slime), and other applications in the downstream areas.

[0033] Referring now to FIG. 1, a flow diagram of a process for contacting a mixed disinfectant with a treatment fluid according to embodiments disclosed herein is illustrated. Water 2 and one or more salts and/or quaternary ammonium salts 4, and optionally ammonia, ammonia salts, or oxygen, are admixed to form a salt solution, which may undergo electrolysis in mixed disinfectant generating system 6, which includes an electrolytic disinfectant producing unit (not shown), to form an aqueous solution comprising mixed disinfectant 8.

[0034] A treatment fluid may be formed by admixing a base fluid 10 with one or more additives 12, 14, 16 in one or more mixing devices or tanks 18, 20. For example, a base fluid 10, such as water or brine, may be mixed with additives 12, 14, 16, such as proppants, weighting agents, etc., in tanks 18 and 20, which may include a precision continuous mixer (PCM) and/or a programmable optimum density blender (POD) to form a treatment fluid.

[0035] The fluid to be treated may be contacted with mixed disinfectant 8 to disinfect the treatment fluid prior to placement of the treatment fluid into the wellbore 22, such as at varying positions along the length of the missile. Contact of the treatment fluid with the mixed disinfectant may be initiated in the mixers, blenders, pumps, or associated piping, and may be initiated at one or more locations so as to provide a sufficient residence time for obtaining the desired reduction in biological contamination. For example, as illustrated, a first portion of the mixed disinfectant 8 may be combined with the treatment fluid upstream of tank 18, and a second portion of the mixed disinfectant 8 may be combined with the treatment fluid upstream of tank 20, prior to delivery of the disinfected fluid downhole to wellbore 22.

[0036] The effectiveness of the mixed disinfectant treatment may be monitored or controlled using one or more analyzers to measure or determine residual halogen content, such as free available chlorine (FAC), free available bromine (FAB), residual disinfectant content, oxidation reduction potential (ORP), pH, microorganism concentrations, or other relevant indicators known to one skilled in the art. For example, for a mixed disinfectant produced using chlorine salts, a sample of the treated fluid may be analyzed for residual chlorine content, which may provide a measure of the effectiveness of the biological reduction as well as an indication as to the excess or shortage of the dosage provided. A residual chlorine content of about 2 ppm, for example, may indicate that the treatment fluid has been sufficiently disinfected. Higher residuals may also be targeted to ensure that the treatment water has been sufficiently disinfected and/or to ensure that little or no bacteria is present in the flowback water. Higher residuals may also be targeted to provide some treatment capacity for the fluid flowing downhole, which may aid in the treatment, removal and/or prevention of biofilm buildup and other biological contamination of one or more of the mixing tanks 18, 20, associated piping, the wellbore, and rock formations that may come into contact with the treatment fluid during the treatment process.

[0037] As illustrated and by way of example only, a sample of the treated treatment fluid may be obtained via flow line 24 and analyzed for residual disinfectant levels via measurement of oxidation reduction potential (ORP) using an appropriate analyzer (not shown), which may be located in mixed disinfectant generating system 6 (feed back control loop). Samples may be obtained from the tanks 18 and 20, i.e., PCM or POD, or the transfer line 26 between the PCM and POD (feed back control). If desired, a sample of the fluid to be treated may be taken from flow line 10 upstream of tank 18 (feed forward control loop). A combination of feed back and feed forward control may also be used. The volumetric ratio of mixed disinfectant solution to treatment fluid (dosage ratio) may then be adjusted or controlled based upon the analyses from the various samples. Additionally, the point of contact or a throughput rate may be adjusted or controlled to vary the contact time provided before use of the treated fluid downhole.

[0038] As another example, the effectiveness of the mixed disinfectant treatment may be monitored or controlled using one or more sample points measuring free available

chlorine and oxidative reduction potential. Due to chemical species that may be present in the water used to generate the treatment fluid or in the chemicals and additives added to the water, contact with the mixed disinfectant may result in reactions that form chemical species that may mask the actual effect achieved. For example, ammonia may react with hypochlorous acid to form monochloramines (NH_2Cl), dichloramines ($NHCl_2$), and trichloramines (NCl_3), which may be detected when measuring residual chlorine levels, but may be accounted for by additionally measuring oxidative reduction potential. Thus, in some embodiments, use of multiple analytical techniques may provide an indication of the true effectiveness of the mixed disinfectant treatment, enhancing the control of the mixed disinfectant treatment (dosage rates, etc.). Real time or near real time measurement of ORP, FAC, pH or other properties of the treated treatment fluid may thus provide for fully integrated control of the system to ensure disinfection dose rates are suitable to achieved the desired disinfection, and may allow for optimal dosage rates to be used, preventing under dosing or excess dosing of the treatment fluid with the mixed disinfectants.

[0039] Depending upon the concentration of salt in the salt solution and the electrolysis results, the mixed disinfectant solution may contain 100 ppm to 10,000 ppm disinfectants, such as about 2000 ppm to about 8000 ppm disinfectants in some embodiments, or from about 3000 ppm to about 6000 ppm disinfectants in other embodiments, such as about 4000 ppm to about 5000 ppm (by weight). To achieve the desired reduction in biological microorganisms, the mixed disinfectants solution may be used in some embodiments at a volume ratio in the range from about 1 gallon mixed disinfectant solution per 10 barrels treatment fluid to about 1 gallon mixed disinfectant solution per 500 barrels treatment fluid (1 gallon : 10 barrels to 1 gallon : 500 barrels). In other embodiments, the volume ration may be in the range from about 1 gallon to 20 barrels to about 1 gallon to 100 barrels; from about 1 gallon to 30 barrels to about 1 gallon to 50 barrels in yet other embodiments.

[0040] Electrolysis of the salt solution may be performed using an electrolytic disinfectant producing unit. Such units are disclosed or referenced in, for example, U.S. Patent Publication No. 20120228149 and U.S. Patent Nos. 7,922,890, 5,853,579, 7,429,556, and 6,524,475, among others. Electrolytic disinfectant producing units are available from MIOX Corporation (Albuquerque, New Mexico), for example.

[0041] The electrolytic disinfectant producing units may be sensitive to various metals and other components that may be present in the water supplied via flow line 2. One of the major failure mechanisms of undivided electrolytic cells is the buildup of unwanted films and scaling on the surfaces of the electrodes. The source of these contaminants is typically either from the feed water to the on-site generation process or contaminants in the salt(s) that may be used to produce the brine solution feeding the electrolytic system. As such, it may be desirable or necessary to treat the water supplied via flow line 2 to reduce, regulate, or control the total dissolved solids (TDS) of the water to be less than about 5000 mg/L in some embodiments; less than about 3000 mg/L in other embodiments; and less than about 1000 mg/L in yet other embodiments. To minimize unwanted contaminants, the water fed to the system may be processed through one or more filtration systems and/or a water softening system. Further, the quality of the salt provided may be specified to minimize the incidence of electrolytic cell cleaning operations.

[0042] Operation of the electrolytic cells may also be sensitive to the temperature and pressure of the salt and quaternary ammonium halide salt solutions. As native water supplies (streams, rivers, lakes, etc.) and other water supplies (wells, public water supply, etc.) may be provided at varying temperatures and pressures, it may be necessary to boost or reduce the supply pressure and/or to increase or reduce the temperature of the water or salt solution. In some embodiments, the temperature of the water supplied may be adjusted to be within the range from about 45°F to about 100°F; in the range from about 50°F to about 90°F in other embodiments; and in the range from about 55°F to about 80°F in yet other embodiments. In some embodiments, the pressure of the water supplied may be adjusted to be within the range from about 20 to about 200 psi; in the range from about 40 to about 150 psi in other embodiments; and in the range from about 60 to about 110 psi in yet other embodiments. Depending upon the design of the electrolytic cells, other temperatures and pressures may also be used.

[0043] Referring now to FIG. 2, a flow diagram of a process for contacting a mixed disinfectant with a treatment fluid according to embodiments disclosed herein is illustrated, where like numerals represent like parts. Water 2 and one or more salts and/or quaternary ammonium salts 4, and optionally ammonia, ammonia salts, or

oxygen, are admixed to form a salt solution, which then undergoes electrolysis in mixed disinfectant generating system 6, which includes an electrolytic disinfectant producing unit (not shown), to form an aqueous solution comprising mixed disinfectant 8.

[0044] In this embodiment, the treatment fluid may be formed by admixing one or more portions (a, b, c) of a base fluid 10 with one or more additives 14, 16 in one or more mixing devices or tanks 18, 20, with the admixture being combined with additional base fluid for pumping of the treatment fluid downhole (i.e., a split line frac system, limiting the overall amount of base fluid being pumped through mixing vessels). For example, a first portion 10a of base fluid 10, such as water or brine, may be mixed with additives 14, 16, such as proppants, weighting agents, etc., in tanks 18, 20, such as a precision continuous mixer (PCM) and/or a programmable optimum density blender (POD), to form a treatment fluid 21. If desired, a second portion 10b may be added to the tank 20.

[0045] The mixed disinfectant 8 may be contacted with the treatment fluid 21, or a treatment fluid precursor, such as base fluid 10 or a portion thereof or an admixture within or an effluent from tanks 18, 20, to disinfect the treatment fluid prior to placement of the treatment fluid into the wellbore 22, such as at varying positions along the length of the wellbore 22. Contact of the treatment fluid with the mixed disinfectant may be initiated in the mixers, blenders, pumps, or associated piping, and may be initiated at one or more locations so as to provide a sufficient residence time for obtaining the desired reduction in biological contamination. For example, as illustrated, a first portion of the mixed disinfectant solution may be combined with the base fluid portion 10a upstream of tank 18, a second portion of the mixed disinfectant solution may be combined with the effluent from tank 18 upstream of tank 20, and a third portion of the mixed disinfectant may be contacted with the remaining base fluid portion 10c prior to delivery of the disinfected fluid downhole to wellbore 22 via high pressure pump 27. A sample of the treated treatment fluid may be obtained via flow line 24 upstream of pump 27 (i.e., on the low pressure side of the pump) for analyses as described above, including one or more of residual disinfectant content, a pH, a free available halogen content, and an oxidation reduction potential, among others.

[0046] Control of the flow of mixed disinfectant may be based on the specific needs of the various streams. For example, the bulk of the base fluid may be contained in portion 10c, with which more or less oxidation may occur, depending upon the supply. In contrast, the lower flow of base fluid through tanks 18, 20 may exhibit less treatment (lower base fluid flow) or possibly more treatment (possibly due to chemical injection / additive mixing or stagnant areas within the mixing tanks and associated piping, if any, allowing for growth of biological contaminants). The multiple injection points for the mixed disinfectant solution may thus be controlled to meet the specific needs of the particular mixing system and additives used, resulting in a properly treated fluid injected downhole.

[0047] Referring now to FIG. 3, a flow diagram of a mixed disinfectant generating system 6 according to embodiments disclosed herein is illustrated, where like numerals represent like parts. Pumps, flow control valves, pressure control valves, block valves, and other related equipment are not illustrated for simplicity of illustration. Water 2 may be supplied via a flow line and fed to a water treatment system 30. In water treatment system 30, the water may be filtered, softened, and heat exchanged to result in a conditioned water stream 32 having a desired temperature and TDS content.

[0048] A first portion 33 of the conditioned water may then be combined with one or more salts and/or quaternary ammonium salts 4, and optionally ammonia, ammonia salts, or oxygen, in salt solution generation system 34. For example, a quantity of salt may be disposed in a tank, and the salt solution may be generated by passing the first portion 33 of the conditioned water through the tank to dissolve a portion of the salt. The resulting salt solution, recovered via flow line 36, will be saturated or close to saturation with salt. Furthermore, a salt solution or a quaternary ammonium salt solution, optionally containing ammonia, ammonia salts, and/or oxygen, may be disposed in a feed system 35 and fed via solution flow line 37 for admixture with conditioned water 32, 38.

[0049] The salt solutions 36 and/or 37 may then be combined with a second portion 38 of the conditioned water (or the conditioned water where system 34 is not used) to form a diluted salt solution 40 for feed to an electrolytic disinfectant producing unit 42. The diluted salt solution should be at the desired feed temperature, such as

between about 55°F and 80°F, and may have a dissolved salt content in the range from about 0.01% to 5% by weight, such as in the range from about 0.1% to about 3% by weight. Electrolysis of the dissolved salt solution in electrolytic disinfectant producing unit 42 may result in various disinfectant compounds, including ozone, hydrogen peroxide, hypohalite (e.g., hypochlorite), hypohalous acid (e.g., hypochlorous acid), quaternary ammonium hypohalite, halogen oxides (e.g., chlorine dioxide), and halogen (e.g., chlorine), and other halo-oxygen (e.g., chlor-oxygen) species, for example. The mixed disinfectant solution may then be recovered from unit 42 via flow line 44 and fed, optionally to one or more storage vessels 46, via flow line 8 for contact with a fluid to be disinfected. Electrolytic cells useful in electrolytic disinfectant producing unit 42 may vary in size / capacity, and some embodiments of systems disclosed herein may include two or more electrolytic disinfectant producing units 42.

[0050] Disinfection of the treatment fluids may not be desired during the entire drilling process, and may be desired, for example, during fracturing of a well with a fracturing fluid. In such instances, it would be desirable to have a mixed disinfectant delivery system arrive at the drill site for the time needed to disinfect the treatment fluid during the desired drill site operation.

[0051] To facilitate the temporary need at a drill site, the mixed disinfectant generating system may be transportable in some embodiments disclosed herein, where the mixed disinfectant system may be containerized and may be modular using two or more containerized modules. In some embodiments, the mixed disinfectant generating system may be contained within one module that is no greater in size than one forty-foot equivalent unit (FEU). In other embodiments, the mixed disinfectant generating system may be contained within two modules, where the first and second modules are no greater in size than one FEU. In yet other embodiments the mixed disinfectant generating system may be contained within two modules, where the first module is no greater in size than one twenty-foot equivalent unit (TEU), and the second module is no greater in size than two TEU. As used herein, one FEU is defined as being similar in size to that of a typical transport container 40 feet long by 8 feet wide by 9.5 feet tall (12.2 m x 2.4 m x 2.9 m) (approximately 3040 cu ft or 87 m^3), and one TEU is defined as being similar in size to that of a typical transport container 20 feet long by

8 feet wide by 9.5 feet tall (6.1 m x 2.4 m x 2.9 m) (approximately 1520 cu ft or 43 m^3). For example, as illustrated in FIG. 3, a first module 50 may contain water treatment system 30 and salt solution generation system 34, among other components (not illustrated), and a second module 52 may contain the electrolytic disinfectant producing unit 42 and one or more mixed disinfectant storage tanks 46. In this manner, the system for generating and delivering a mixed disinfectant may be modular, contained, easy to transport, and easy to set up at or remove from the well site. For example, to facilitate setup at the drill site, the modular system may be outfitted with fluid connections to quickly connect water supply line 2 to a water supply, to connect a stream carrying mixed disinfectant 8 to fluid conduits for transporting the mixed disinfectant for admixture with the treatment fluid, and to connect various lines between the modules 50, 52, including rinse lines, process returns lines, and other lines not shown.

[0052] Drill sites may be space constrained, and delivery or storage of chemicals may not always be possible or even desired due to potential for spillage and other handling issues. For example, delivery, storage, and handling of biocides at a drill site is generally not desirable, but is often tolerated for the short duration of a fracturing operation.

[0053] To avoid or minimize the handling of salts, quaternary ammonium salts, and other components, transportable systems for generating a mixed disinfectant according to embodiments disclosed herein may arrive at the drill site containing components and chemicals, including salts and quaternary ammonium salts for forming the salt solution and acid or other compounds used for cleaning the electrolytic cells. For example, salt solution generating system 34 may include a tank (not shown). A quantity of salt may be disposed in the tank at a remote location. The tank may then be transported to the drill site to be serviced and used to generate a salt solution by passing water through the transported tank. Likewise, feed system 35 may include a tank (not shown), where a salt solution or quaternary ammonium salt solution may be disposed in the tank at a remote location prior to transport to the drill site. Similarly, an acid storage tank may be provided in the module(s) for containing acid to be used for cleaning the electrolytic cells. In this manner, the salts and acids do not have to be shipped separately to the drill site and loaded into the tanks, thereby

minimizing the need for delivery, storage, and handling of these compounds at the drill site, and simultaneously minimizing possible spillage and exposure.

[0054] FIGs. 4 (4A, 4B, and 4C) and 5 illustrate flow diagrams for possible embodiments of modules 50 and 52, respectively, where like numerals represent like parts. As shown, the equipment in module 50 may be arranged and sized to fit in one TEU, and the equipment in module 52 may be arranged and sized to fit in one FEU.

[0055] Referring now to Figure 4A, module 50 may include a water treatment system 30, a salt solution generating system 34, a sampling system 60, and a process returns treatment system 62. As described above, water connection 64 may be connected to a water supply at the drill site. The water may then be pumped via conduit 66 to water treatment system 30, which may include one or more filtration systems 68, and one or more water softening systems 70. Filtration system 68 may include bag filters, cartridge filters, and the like. Water treatment system 30 may also include one or more heat exchangers 72, the location of which may depend upon whether it is desired to heat or cool the water before, intermediate, or after filtration and softening.

[0056] The water in conduit 66 passes through the one or more filters 68 to result in a filtered water stream 74, a portion of which is fed via flow line 76 to water softening systems 70. Conditioned water (i.e., filtered and softened, and optionally heated / cooled) may be recovered via flow line 80. A first portion of the conditioned water may then be forwarded to salt solution generation system 34 via flow line 82, and a second portion of the conditioned water may be recovered via flow stream 84.

[0057] Salt solution generating system 34 may include one or more tanks 90 that may be loaded with a quantity of one or more salts 92 over a bed of granular material that prevents the salt from flowing as a solid into conduit 96. As noted above, the salt may be loaded at the drill site or may be pre-loaded at a remote location, such as via an inlet 98 located on an upper portion of the tank 90. The conditioned water may be passed through the tank, dissolving a portion of the salt, and a salt solution may be recovered via flow line 96. Filter 99 may be provided to protect downstream equipment from any solids that may happen to pass out of tank 90. The salt solution 97 is then pressurized and pumped to connection 101.

[0058] As illustrated, the filtered water in conduit 74 is divided into three fractions, fraction 76 being described above. Additionally, a portion of the filtered water may

be used occasionally during routine operation of the system or for cleaning of the system, and may be routed to rinse water connection 102, or may be fed via flow line 104 to purge the process returns treatment system 62. Conditioned water stream 84 may similarly serve as a softened water rinse supply, being fed to softened water rinse connection 106. Conditioned water stream 84 is also fed to a booster pump 108 for feed to boost water connection 110.

[0059] Period regeneration may occur with water softening system 70, which may be performed using the salt solution generated in system 34. During regeneration of the softening system 70, a portion of the salt solution in conduit 96 is routed via flow line 112 to water softening system 70. The discharge is then fed via flow line 114 to process returns system 62.

[0060] Sampling system 60 may include one or more sample valves / diverters 116, each associated with one or more analyzers 118 for measuring residual chlorine content, conductivity, or other properties of the treatment fluid following contact with the mixed disinfectant solution. The samples may be transported from various points in the drilling or completion system, routed to module 50 via connections 120, 122.

[0061] Process returns treatment system 62 may include a storage tank 123 to accumulate materials from various streams and vessels during operation of the system, including process returns generated during startup of the electrolysis unit, sampling, water softening agent regeneration, and cleaning of the electrolytic cells, among others. Process returns from cleaning of the electrolytic cells may be routed to module 50 via connection 124 and conduit 126, for example.

[0062] The fluids accumulated in storage tank 123 may include water, treatment fluid samples, discharge from regeneration, and spent acid from electrolytic cell cleaning. As acid cleaning is performed when needed, it may not be necessary to clean the cells at each well site or even during the disinfecting process. The process returns fluids generated during the operation of the mixed disinfectant generation system may thus be fed via conduit 130 to connection 132 for fluid communication to other well site processes or storage tanks. For example, the process returns fluids or a portion thereof may be used to form at least a portion of the treatment fluid. In this manner, the process returns are effectively used to form a product, and all liquid "process returns" generated from the system may be consumed during other well site

operations, resulting in negligible waste production as a result of the disinfecting process (other than solid wastes collected, such as filter cartridges, etc.).

[0063] Referring now to FIG. 4B, where like numerals represent like parts, a module 50 is illustrated including a solution feed system 35, which may include a tank 91 containing a pre-mixed salt solution 93 such as a salt solution, a quaternary ammonium halide salt solution, or a combination thereof. Solution 93 may then be fed via flow line 95 and combined with conditioned water 82 to form a diluted feed salt solution 97. Valves, pumps, and metering systems may be included, as well as agitation or circulation systems (not shown) to keep the solution in tank 91 evenly mixed.

[0064] Referring now to FIG. 4C, where like numerals represent like parts, a module 50 is illustrated including a salt solution generating system 34 and a solution feed system 35, which may include a tank 91 containing a pre-mixed salt solution 93 such as a salt solution, a quaternary ammonium halide salt solution, or a combination thereof. Solution 93 may then be fed via flow line 95 and combined with salt solution 96 to form a diluted feed salt solution 97. Valves, pumps, and metering systems may be included, as well as agitation or circulation systems (not shown) to keep the solution in tank 91 evenly mixed.

[0065] Referring now to FIG. 5, module 52 may include mixed disinfectant solution storage system 46, electrolytic disinfectant producing unit 42, and acid wash system 136. Salt solution provided via connection 101 and conduit 138 and boost water provided via connection 110 and conduit 140, if needed, are fed to the electrolytic disinfectant producing unit 42. The flow rates and pressure of the boost water and salt solution are controlled such that a diluted salt solution 142 is provided to the electrolytic cells in chambers 144, 146, producing an effluent comprising a mixed disinfectant recovered via flow line 148. The mixed disinfectant is then fed, optionally via flow line 44 to mixed disinfectant storage system 46 when storage is provided and/or desired, via flow lines 8 to connections 149 for fluid transport of the mixed disinfectant solution for contact with the treatment fluid.

[0066] Mixed disinfectant storage system 46 may include one or more vessels 150, each having a size of at least 500 gallons. For example, as illustrated, module 52 may

include three storage vessels 150 each holding approximately 800 gallons, for a total reserve volume of about 2400 gallons.

[0067] The mixed disinfectant produced in electrolytic disinfectant producing unit 42 may be stable for a period of about 24 hours. As such, it is not desirable to produce mixed disinfectant solution until needed. The vessels 150, when used, may provide a buffer for storage of mixed disinfectant solution in the event of a power failure, such as where the power to electrolytic disinfectant producing unit 42 is inadvertently or temporarily cut off. As it is desired to continue feed of the mixed disinfectant solution for the disinfecting process, even in the event of a power loss to the remainder of the system, module 52 may also be provided with a power generator (not shown) to operate pumps 154 and the associated control valves, so as to maintain continuity of the disinfecting during the fracturing operation.

[0068] A byproduct of electrolytic disinfectant producing unit 42 is hydrogen, which may accumulate in vessels 150. To prevent excessive accumulation of hydrogen, and to maintain the hydrogen concentration well below flammability or explosion limits, a blower 160 may circulate air or nitrogen through the head space of vessels 150, venting a hydrogen-containing vapor stream via flow line 162, which may then be vented to the atmosphere, fed to a flare, or otherwise disposed of safely. A degassing column (not shown) may be used upstream of the vessels 150 to separate hydrogen.

[0069] As noted above, the electrolytic cells may be periodically cleaned due to film formation on the electrodes. Acid wash system 136 may include a tank containing an acid suitable to clean the electrodes, such as muriatic acid or hydrochloric acid. The acid may then be diluted with rinse water, if necessary, and circulated through chambers 144, 146 to clean the electrodes. The process returns generated during the cleaning operation may then be routed to the process returns tank 123, or may be managed as an individual process returns stream. Cleaning operations and routine operation of the unit may be monitored, for example, using one or more analyzers 180. In some embodiments, the cleaning may be performed using acid generated on site using an acid generating electrolytic cell, such as described in U.S. Patent No. 7,922,890, for example.

[0070] Cleaning water for flushing or purging components in module 52 may be supplied as described for FIG. 4, where module 52 includes connections for mating

with the flow line connections in module 50. These are similarly labeled in FIG. 5, with an (a) or (b) indicating that the flow may be split to different units following the mating connection between the two modules.

[0071] An amount of particulates (sand, dust) may be present in the air at the drill site, especially during fracturing operations due to transport of the proppant. To prevent damage to electrolytic disinfectant producing unit 42, the unit may be located in an enclosure 168 having a filtered air cooling system 170, thus providing for circulation of filtered air through the enclosure, removing heat generated or given off during the electrolysis process and protecting the equipment from exposure to conditions normally encountered at a well site during fracturing operations.

[0072] When the modular system arrives at a well site, the system may be set up and operational in a matter of hours (such as less than 8 hours). Connections may be made for fluid communication between the modules (connections 102, 106, 124, where each may be split in the modules into one or more fractions (a), (b)), for fluid communication with a water supply (connection 64), for transport of the boost water and salt solution to the electrolytic disinfectant producing unit 42 (connections 101, 110), and for transport of the mixed disinfectant solution via one or more flow lines 8 (connections 149). The remaining needs of the system are a power supply for the electrolytic cells, and communication conduits (hard or wireless) for communicating the treatment fluid flow rate, compositions, analyses, time to completion, time to start, and/or other information and process data to a control system 200, where the control system may use the communicated information to control or adjust the flow rate of the mixed disinfectant solution for contact with the treatment fluid based on the analyses and measured flow rates, among other possible variables. In this manner, the control system for the mixed disinfectant systems disclosed herein may communicate with internal and/or external sources to control the supply of mixed disinfectant solution to the treatment fluid.

[0073] For example, the external control system of fracturing operation may communicate the flow rate of a fracturing fluid or one or more components of a fracturing fluid to a well so that dosage of mixed disinfectant solution added may be controlled to match the changes in the flow rate and/or composition through the cycles of a fracturing operation. As another example, the communication may

provide an indication of when to start or stop feeding of the aqueous solution, such as for when fracturing operations are to be concluded or to avoid mixing of the aqueous solution during an acid spear, commonly used at the beginning of a fracturing operation, or when other potentially incompatible fracturing fluid additives may be used. As yet another example, the communication may provide an indication of a property or composition of the fluid to be disinfected, so as to properly adjust a flow rate of the mixed disinfectant, such as when a treatment fluid additive type or relative amount of a treatment fluid additive is changed.

[0074] As a specific control example, it may be common during a fracturing operation to change from an acrylamide based polymeric additive to guar. Communications may be received by the control system indicating that the composition of the polymeric additive is changing, and the control system may then adjust the flow rate of the mixed disinfectant to account for an increase in disinfectant demand due to the change in additives. Similarly, fracturing operations may switch from a non-coated proppant to a resin coated proppant, resulting in an increase in mixed disinfectant demand. Further, when live breakers (e.g., non-encapsulated ammonium persulfate) are used, it may be desirable to decrease mixed disinfectant feed rates to avoid potential reactions that may affect performance of breaker.

[0075] By further example, embodiments of the control process may include one or more of: **(a)** Receiving a signal indicating the flow rate of one or more components of a treatment fluid. The flow rate signals may be volumetric, mass, or weight flow rates and may provide the identity of the component. The signal may be provided by the external control system of a fracturing operation, and the signal may be received by the control system. **(b)** Calculating a flow rate (also referred to as a dose rate) of the aqueous solution comprising disinfectants from the component flow rate based on a predetermined disinfectant demand per volumetric, mass, or weight unit of the component. **(c)** Selecting the predetermined disinfectant demand for the dosing rate calculation when the signal indicates the component corresponding to the demand is present in treatment fluid from a group of disinfectant demands stored in the control system. **(d)** Calculating an aggregate dose rate of the aqueous solution based on the sum of the calculated dose rates for two or more components of the treatment fluid. **(e)** Admixing the aqueous solution to the treatment fluid at or in response to the

calculated dose rate or aggregate dose rate. **(f)** Using the calculated dose rate (or aggregate dose rate) as the rate of admixing of the aqueous solution to the treatment fluid for a predetermined period of time, and then controlling, based on a signal indicating at least one of a residual disinfectant content, a pH, a free available halogen content, and an oxidation reduction potential of the treated fluid. This may be done during the initial stages of a fracturing operation, e.g. until the operator has confidence that residual disinfectant levels in the treatment fluid are relatively steady. **(g)** Using the calculated dose rate (or aggregate dose rate) as the rate of admixing of the aqueous solution to the treatment fluid until a signal indicating at least one of a residual disinfectant content, a pH, a free available halogen content, and an oxidation reduction potential of the treated fluid is not changing at more than a pre-set rate (i.e. is steady). **(h)** Switching from the rate of admixing controlling based on a signal indicating at least one of a residual disinfectant content, a pH, a free available halogen content, and an oxidation reduction potential of the treated fluid to using the calculated dose rate as set point for the rate of admixing during an ongoing fracturing operation when the calculated dose rate changes for a predetermined period of time or until at least one of a residual disinfectant content, a pH, a free available halogen content, and an oxidation reduction potential of the treated fluid is steady. **(i)** Increasing the dose rate of the aqueous solution in response to the signal indicating the composition of the treatment fluid changing during a fracturing operation such that flow rate of an acrylamide-based polymeric additive decreases and the flow rate of a guar additive increases. **(j)** Decreasing the dose rate of the aqueous solution in response to the signal indicating the composition of the treatment fluid changing during a fracturing operation such that flow rate of a guar additive decreases and the flow rate of an acrylamide-based polymeric additive increases. **(k)** Increasing the dose rate of the aqueous solution in response to the signal indicating the composition of the treatment fluid changing during a fracturing operation such that flow rate of non-coated proppant decreases and the flow rate of resin coated proppant increases. **(l)** Decreasing the dose rate of the aqueous solution in response to the signal indicating the composition of the treatment fluid changing during a fracturing operation such that flow rate of resin coated proppant decreases and the flow rate of non-coated proppant increases. **(m)** Decreasing the dose rate of the aqueous solution

in response to the signal indicating the composition of the treatment fluid during a fracturing operation changing such that the flow rate of a live breaker increases.

[0076] Thus, embodiments of control systems herein may determine a mixed disinfectant demand, as well as control or adjust a flow rate of the mixed disinfectant, based on information provided by the local or remote communications conduits. Such control may include feedback control, such as based on sample analyses or on-line measurement of residual halogen content or ORP, feedforward control, such as based on flow rates, compositional analyses or other information that may be provided with respect to the treatment fluid upstream from the mixed disinfectant injection location(s).

[0077] Control systems herein may also generate a treatment report that can be provided to the operator of the drilling operations. The report may include process operations history, presented in the form of charts, graphs, or raw data, for example, to summarize the performance of the disinfecting process during the fracturing operation. For example, data may include mixed disinfectant type, mixed disinfectant flow rates, measured ORP, measured pH, measured residual free available or total halogen concentration or other disinfectant concentration, and other data available from the control system for monitoring and operating the disinfecting process. In some embodiments, the control system may integrate disinfecting process operations data with information received from the remote source, such as fracturing fluid additive types, compositions, flow rates, etc., so as to provide an integrated or overall operations report, inclusive of data related to the treatment fluid or fracturing fluid provided by the remote communications.

[0078] In other embodiments, the control system for the mixed disinfectant systems disclosed herein may rely on the sample analyses to control the process, such as where external communications are not available. Contained modules may include such communication conduits, and control systems of contained or non-contained processes disclosed herein may operate in the presence or absence of such communications, thus providing flexibility to meet the needs of the various wellsites, regardless of their communication capabilities, that may be treated with mixed disinfectant produced by the systems disclosed herein. Systems disclosed herein may also include hardware and/or software to provide for transmitting and receiving

communications to and from the control system, such as wired or wireless communications from a phone, computer, or satellite, to allow remote monitoring, diagnostics, and/or control of system operations, for example.

[0079] As shown in FIG. 5, the containerized system may include one electrolytic disinfectant producing unit 42. While flow of fracturing or other treatment fluids at the well site may vary or be intermittent, the electrolytic disinfectant producing unit 42 may be continuously when needed. Appropriate sizing of the electrolytic disinfectant producing unit 42 and the buffer tanks 150 is thus important. For example, it may be anticipated that treatment fluid flow rates may vary from 0 barrels per minute to 120 barrels per minute or more during fracturing operations. Depending upon the water quality at the well site, at peak fracturing fluid flow rates, mixed disinfectant solution flow rates may be on the order of 15 to 30 gallons per minute. In such a scenario, a mixed disinfectant producing unit 42 that produces about 20 gallons per minute, and three buffer tanks 150 each holding about 800 gallons could be sufficient to meet the need for disinfecting fluid at the well site throughout the fracturing operation, the buffer tank volume varying due to the intermittent flow of treatment fluid. If desired, however, two or more electrolytic mixed disinfectant producing units 42 of the same or different capacity may be connected in parallel to provide the desired mixed disinfectant supply rate. These units may be housed within a common enclosure 168, or in a separate enclosure 168 located on the same or different modules.

[0080] The mixed disinfectant solutions discussed herein may include hypobromous acid as a disinfectant. In some cases, such as when disinfecting a water source containing ammonia, for example, hypobromous acid may be more effective than other disinfectants, such as hypochlorous acid, possibly due to the stability of the mono halo amines, monochloramine being more stable than monobromamine. For example, fracturing operation operations often used chemicals that generate ammonia as a by-product, such as glutaraldehyde, or contain ammonium salts such as ammonium persulfate, ammonium bisulfite. Hypochlorous acid in the presence of ammonia or ammonium salts may react to form chloramines, which are regarded as a poor disinfectant with less than 5% of the effectiveness of hypochlorous acid. Hypobromous acid in the presence of ammonia reacts to form bromamines, which are

considered to be almost equally effective disinfectant to hypobromous acid, and slightly less effective than hypochlorous acid.

[0081] Methods for disinfecting a treatment fluid according to embodiments disclosed herein may include admixing a mixed disinfectant aqueous solution comprising hypobromous acid generated from a bromide salt solution with a treatment fluid. In one embodiment, the hypobromous acid may be generated by feeding a bromide salt solution to an electrolytic disinfectant producing unit. Optionally, the bromide salt solution may be fed to the electrolytic disinfectant producing unit together with another salt, such as a chloride salt.

[0082] Referring now to FIG. 6, a flow diagram of a process for contacting a mixed disinfectant with a treatment fluid according to embodiments disclosed herein is illustrated, where like numerals represent like parts. In this embodiment, hypobromous acid may be generated by feeding a salt solution 40, such as a chloride salt, to the electrolytic disinfectant producing unit 42. The disinfectant solution produced by the electrolytic disinfectant producing unit 42 may be combined with a bromide salt solution 45 to generate hypobromous acid. For example, hypochlorous acid produced by electrolysis of a chloride salt solution, such as sodium chloride, may be combined with a bromide salt solution, such as sodium bromide or potassium bromide, downstream from the electrolytic cell. The hypochlorous acid disinfectant reacts with free bromide ions in solution formed during dissolution of the bromide salt to produce hypobromous acid and chloride ions. For example, the mixed disinfectant and bromide salt solutions may be combined by mixing of streams 44, 45 at a mixing point 47 or by adding the bromide salt to a reaction vessel, such as storage vessel 46, via line 49. The bromide salt solution may be mixed on-site by admixing the salt and water or transported already pre-mixed. Similar to the formation of a saturated salt solution in tank 34, a bromide salt may be loaded into a tank 54, on site or at a remote site prior to transport to the site, and contacted with water to form a bromide salt solution. Optionally, the premixed bromide salt solution may be further diluted with an aqueous solution before being combined with the disinfectant.

[0083] Mixed disinfectants produced using chlorine salts, as noted above, may contain various chemical species, including hypochlorous acid, hypochlorite, and others. Contact with bromide salts may be at a ratio so as to provide sufficient bromine

content to react with some or all of the hypochlorous acid, the content of which in the mixed disinfectant solution may depend upon numerous factors, including electrolytic cell type and performance, among others. Use of excess bromide salt may be undesirable, as bromide salts are generally more expensive than chlorine salts. In some embodiments, a bromide salt solution and a mixed disinfectant solution formed from a chlorine salt solution may be admixed in respective proportions to provide a bromine to chlorine ratio in the range from about 1:50 to about 1:1; in the range from about 1:20 to about 1:2 in other embodiments; and in the range from about 1:5 to about 1:15, such as about 1:10, in yet other embodiments.

[0084] Referring still to FIG. 6, in other embodiments, quaternary ammonium hypohalite may be generated by feeding a salt solution 40, such as a chloride salt, to the electrolytic disinfectant producing unit 42. The disinfectant solution produced by the electrolytic disinfectant producing unit 42 may be combined with a quaternary ammonium halide salt solution 45 to generate quaternary ammonium hypohalite.

[0085] Referring still to FIG. 6, in other embodiments, a quaternary amine halide salt may be fed to electrolytic disinfectant producing unit 42 to generate, among other disinfectants, quaternary amine hypohalous acid. The disinfectant solution produced by the electrolytic disinfectant producing unit 42 may be combined with an ammonium salt solution 45 to generate haloamines, such as chloramines, in stream 44.

[0086] As the systems disclosed herein may be transportable, the waters to be disinfected that may be encountered between operations may differ in impurities and/or biologicals. As such, it may be desirable to provide additional tanks and feed lines to provide a flexible system having tunable chemistry, so as to meet the different site-to-site disinfecting requirements. For example, as described above, it may be desirable to electrolyze a metal halide salt, a quaternary ammonium salt, or a combination thereof. Also as described above, disinfectants may be generated by first electrolyzing a metal halide salt and then combining the electrolyzed compounds with a quaternary ammonium salt, or similarly, subjecting a quaternary ammonium salt to electrolysis and then combining the resulting solution with ammonium chloride to produce chloramines.

[0087] Referring now to FIG. 7, where like numerals represent like parts, a simplified flow diagram of a system according to embodiments herein is illustrated. In this embodiment, two or more additional feed tanks 54 may be provided to add flexibility to the system both upstream and downstream of electrolysis in unit 42. For example, tank 34 may be used to store metal halide salts and provide metal halide salt solutions to electrolysis and tank 54 may store and provide quaternary ammonium halide salts upstream of electrolysis. Additional feed tanks or flow lines from source feed tanks may also be used to provide the desired flexibility in process operations and disinfectant generation chemistry.

[0088] Also as illustrated in Figure 7, the additional compound added from an additional feed tank (not shown) may be provided to one or more of the storage tanks 46, such as 46B, while the solution from electrolysis may be fed to tank 46A. In this manner, a portion of the solution from electrolysis may be modified, and the resulting disinfectants in tanks 46A and 46B may be different, thus providing flexibility with the disinfectant or disinfectant mixture to be fed via flow line 8 to the water to be treated. Further, while holding tanks 46A and 46B may be used, additional compounds may also be added to the disinfectant solution as it is being fed toward the treatment location, such as immediately upstream or downstream of pumps 154 (FIG. 5). Other flow schemes to provide tunable chemistry may be readily envisioned by the above description, and are also contemplated according to embodiments herein.

[0089] As noted above, the transportable systems disclosed herein may be delivered to wellsites having varying degrees of communication or ability to interface with the control systems used in embodiments herein. As such, the control systems should be flexible to meet the environment encountered at the wellsite. Similarly, transportable systems disclosed herein may encounter wellsites having various types of water, frac water, chemical additives, etc., that may affect the performance of systems disclosed herein. Accordingly, systems as illustrated in FIG. 6, including a bromide salt addition system may provide for flexibility between drill sites and their varying conditions. One wellsite may use bromide salts, possibly due to ammonia, sulfides, oxidizable iron, manganese, or other disinfectant consuming species in the frac water/ treatment fluid, and the next wellsite may not use any bromide salts. Thus, embodiments disclosed herein may include use of analytical or other techniques to

determine if use of bromide salts is necessary (e.g., measuring treatment fluid water quality, communicating with wellsite to determine types of chemicals added, etc.).

[0090] Another embodiment of the method may comprise forming a treatment fluid from an ammonia containing water source by adding hypobromous acid to disinfect the water. As mentioned, other disinfectants, such as hypochlorous acid, may not be as effective as hypobromous acid to disinfect a treatment fluid in the presence of ammonia. Ammonia is often found in flow-back water from fracturing operations. By using hypobromous acid as a disinfectant, fracturing flow-back water may be recycled for re-use during the same or in a subsequent fracturing operation.

[0091] Some formations or water sources already contain bromide salts that may be used to generate the hypobromous acid. For example, flow-back waters from fracturing operation in some locations in the U.S. state of Arkansas contain bromide salts. Thus, in some embodiments, the treatment fluid may be disinfected by admixing a disinfectant, like hypochlorous acid generated by electrolysis as disclosed herein, with the bromide salt-containing water to produce the hypobromous acid with the already existing bromide salt. Thereby, the need to transport bromide salt to the site of disinfection operation may be reduced or eliminated.

[0092] As described above, a system for generating a mixed disinfectant useful for disinfecting a treatment fluid is provided. The system may provide for virtually chemical-free sterilization, using a mixed disinfectant that has low or no toxicity, a short half life, and which degrades rapidly to naturally occurring chemicals following use or contact with the downhole formation. Thus, the disinfecting process provided by systems disclosed herein may have no or minimal environmental impact. The system is robust, may tolerate the harsh conditions of a well site, including dusting and other environmental conditions, and may use available surface water, thus minimizing the impact on the potable water supply at the well site.

[0093] In some embodiments, the system for generating a mixed disinfectant may be contained and transportable. The system herein may have a small footprint, may be transported to the well site when needed, and may be set up and removed from a drill site rapidly. Further, pre-loading of chemicals in storage tanks before transport of the

system to a well site may minimize or eliminate the need for chemical delivery and handling at the well site.

[0094] Embodiments disclosed herein relate to disinfecting wellbore treatment fluids to reduce biological contamination of the fluid prior to placement of the treatment fluid into the wellbore and use of the treatment fluid downhole. More specifically, embodiments disclosed herein relate to disinfecting treatment fluids using a mixed disinfectant generated at a well site. Embodiments disclosed herein also relate to disinfecting wellbore treatment fluids to reduce biological contamination of the wellbore and rock formations in contact with the treatment fluid, and the flow back water recovered from the wellbore.

[0095] Overall, embodiments of the processes and systems disclosed herein may have one or more of the following properties:

- The treatment may be used for all fresh or recycled water (flow back, produced, water from drilling fluids, in frac tanks, water produced during air drilling, stagnant ponds, etc.), water and steam injection (enhanced recovery), packer fluids, oilfield pipelines, disposal wells, workovers, production (replace biocides, remove slime), and other applications in the downstream areas.
- The treatment is non-damaging to frac fluids.
- The treatment is non-damaging to the wellbore, pumps, pipelines, etc.
- The treatment is effective under all foreseeable conditions; pH, temperature, pressure, etc.
- The treatment will oxidize and reduce other harmful components in the fluid, such as, but not limited to, organics forming food for bacteria and help prevent re-growth, and H2S, iron and possibly some other inorganics.
- The treatment can remove slime.
- The residual may be sufficient to prevent re-growth in the wellbore and effectively reduce the bacteria in the flow-back fluid.
- The equipment is responsive to changing water properties.
- The equipment may have single well autonomy, able to treat a frac without re-supply (except for diesel fuel).
- The equipment may be mobile – able to go to any frac site or other application.

- The process may have complete redundancy – back-up power supply, control system and pumps, back-up disinfectant, etc.
- The process may reduce the carbon footprint and improve HSE over existing processes.

[0096] As described above, systems and processes disclosed herein may provide for one or more of the following embodiments, among others.

[0097] In one aspect, a process for disinfecting a treatment fluid may include admixing an aqueous solution comprising a mixed disinfectant generated via electrolysis of a quaternary ammonium halide salt solution with a treatment fluid. In embodiments, the process may comprise admixing one or more quaternary ammonium halide salts and water to form the salt solution. In other embodiments of the process, the salt solution may comprise one or more salts comprising at least one of an alkali metal halide, an alkaline earth metal halide, and a transition metal halide. In other embodiments, the process may further comprise converting the salt solution to an aqueous solution comprising the mixed disinfectant via electrolysis. In other embodiments of the process, the mixed disinfectant may comprise two or more of quaternary ammonium hypohalite, quaternary ammonium hypohalous acid, ozone, hydrogen peroxide, hypochlorite, hypochlorous acid, chlorine dioxide, hypobromous acid, bromine, and chlorine. In other embodiments, the process may comprise contacting the treatment fluid with the mixed disinfectant for a time in the range from 1 second to 2 hours. In other embodiments, the process may comprise measuring at least one of a residual disinfectant content, a pH, a free available halogen content, and an oxidation reduction potential. In other embodiments, the process may comprise adjusting at least one of a volumetric ratio of the aqueous solution to the treatment fluid and a contact time based upon the measured at least one of a residual disinfectant content, a pH, a free available halogen content, and an oxidation reduction potential. In other embodiments, the process may comprise treating the water prior to the admixing the water with the one or more salts. In yet other embodiments, the treating may comprise at least one of filtering, softening, heating, and cooling. In yet other embodiments, the process may comprise admixing an ammonium salt with the aqueous solution after electrolysis and prior to contact with the treatment fluid. In yet other embodiments, the ammonium salt may comprise at

least one of ammonium chloride, ammonium sulfate, ammonium bromide, ammonium iodide.

[0098] In another aspect of the present disclosure, a method of servicing a wellbore may comprise transporting a portable tank containing a quantity of one or more quaternary ammonium halide salts or a quantity of a quaternary ammonium halide salt solution comprising one or more quaternary ammonium halide salts to a well site to be serviced, generating a salt solution by passing water through the portable tank to dissolve a portion of the salt or admixing water with the quaternary ammonium halide salt solution, converting the salt solution to an aqueous solution comprising a mixed disinfectant via electrolysis, contacting the aqueous solution with a treatment fluid to form a treated treatment fluid, and placing the treated treatment fluid into the wellbore. In embodiments of the method, the quaternary ammonium halide salt may comprise at least one of benzalkonium chloride, didecyldimethylammonium chloride, cetyltrimethylammonium chloride, octyltrimethylammonium chloride, tetramethylammonium chloride, tetraethylammonium chloride, tetrapropylammonium chloride, tetrabutylammonium chloride, cetylpyridinium chloride, benzalkonium bromide, didecyldimethylammonium bromide, cetyltrimethylammonium bromide, octyltrimethylammonium bromide, tetramethylammonium bromide, tetraethylammonium bromide, tetrapropylammonium bromide, tetrabutylammonium bromide, cetylpyridinium bromide, benzalkonium iodide, didecyldimethylammonium iodide, cetyltrimethylammonium iodide, octyltrimethylammonium iodide, tetramethylammonium iodide, tetraethylammonium iodide, tetrapropylammonium iodide, tetrabutylammonium iodide, cetylpyridinium iodide and polymeric quaternary ammonium compounds. In other embodiments of the method, the salt solution may comprise one or more salts comprising at least one of an alkali metal halide, an alkaline earth metal halide, and a transition metal halide. In other embodiments of the method, the mixed disinfectant may comprise one or more of quaternary ammonium hypohalite, quaternary ammonium hypohalous acid, ozone, hydrogen peroxide, hypochlorite, hypochlorous acid, chlorine dioxide, hypobromous acid, bromine, and chlorine. In other embodiments of the method, the converting may comprise admixing the generated salt solution with additional water to produce a diluted salt solution, and electrolyzing the diluted salt solution to form the aqueous solution. In

other embodiments of the method, the diluted salt solution may contain from 0.01% to 5% by weight dissolved quaternary ammonium halide salts. In other embodiments of the method, contacting may comprise contacting the treatment fluid with the mixed disinfectants for a time in the range from 1 second to 2 hours before placing the treated treatment fluid into the wellbore. In other embodiments, the method may comprise measuring at least one of a residual disinfectant content, a pH, a free available halogen content, and an oxidation reduction potential of the treated treatment fluid. In other embodiments, the method may comprise treating the water prior to the use of the water in at least one of the generating and the converting. In yet other embodiments of the method, treating may comprise at least one of filtering, softening, heating, and cooling.

In another aspect of the present disclosure, a portable system for disinfecting water may comprise a fluid connection for connecting to a water supply, a treatment system for conditioning the water supplied, a quaternary ammonium halide salt or quaternary ammonium halide salt solution storage tank, a mixing device for admixing at least a portion of the conditioned water with one or more quaternary ammonium halide salts to form a salt solution, at least one electrolytic disinfectant producing unit for converting at least a portion of the salt solution to an aqueous solution comprising mixed disinfectants, and a fluid connection for transporting the aqueous solution from the one or more tanks for storing a fluid to be disinfected. In embodiments, the portable system may further comprise at least one of: one or more tanks for storing the aqueous solution; an acid supply tank for supplying acid to periodically clean the at least one electrolytic disinfectant producing unit; a sampling system for sampling the fluid following contact with the aqueous solution; a process returns tank for accumulating materials from one or more of the treatment system, the tank for admixing, the electrolytic disinfectant producing unit(s), the one or more tanks for storing, the acid supply tank, the sampling system; and piping, pumps, and equipment associated therewith; a fluid connection for transporting accumulated materials from the process returns tank; one or more fluid conduits for transporting treated fluid to the sampling system; and a control system for controlling a feed rate of the aqueous solution. In other embodiments, the portable system may comprise at least one of: a tank for admixing at least a portion of the conditioned water with at least one of an

alkali metal halide, an alkaline earth metal halide, and a transition metal halide to form a second salt solution; at least one electrolytic disinfectant producing unit for converting at least a portion of the second salt solution to a second aqueous solution comprising mixed disinfectants; a mixing device for admixing the second salt solution and the salt solution; and a mixing device for admixing the aqueous solution and the second aqueous solution. In other embodiments of the portable system, the treatment system may comprise at least one of: a filter for reducing a solids content of the water, a water softening system for reducing a metals content of the water, and a heat exchanger for adjusting a temperature of the water. In other embodiments of the portable system, the at least one electrolytic disinfectant producing unit may be an enclosure having a filtered air cooling system. In other embodiments, the portable system may comprise a first module no greater in size than one twenty-foot equivalent unit (TEU) (container 20 feet long by 8 feet wide by 9.5 feet tall) (6.1 m x 2.4 m x 2.9 m) (1520 cu ft or 43 m^3). In other embodiments, the portable system may comprise a second module no greater in size than one forty-foot equivalent unit (FEU) (container 40 feet long by 8 feet wide by 9.5 feet tall) (12.2 m x 2.4 m x 2.9 m) (3040 cu ft or 87 m^3). In other embodiments of the portable system, the one or more tanks for storing the aqueous solution may comprise at least two tanks each having a volume of at least 500 gallons. In other embodiments, the portable system may comprise one or more communication conduits for sending or receiving a signal with the control system from a local or remote source, where the signal may be used to monitor or control the system and/or may provide an indication of at least one of: an indication of when to start or stop feeding the aqueous solution, such as to avoid mixing of the aqueous solution during an acid spear, commonly used at the beginning of a fracturing operation; at least one of a residual disinfectant content, a pH, a free available halogen content, and an oxidation reduction potential of the treated fluid; a flow rate of at least one of the fluid to be disinfected, a treatment fluid precursor, and the treated fluid; and a property of at least one of the fluid to be disinfected, a treatment fluid precursor, and the treated fluid after contact of the aqueous solution with the fluid to be disinfected, for example, a composition of the treatment fluid, such as a treatment fluid additive amount or type. In yet other embodiments of the portable system, the

control system may control the feed rate of the aqueous solution both in the presence of and absence of receiving the signal with the control system from the remote source.

[0099] In yet another aspect of the present disclosure, a method of disinfecting a fluid may comprise disposing a quantity of one or more quaternary ammonium halide salts in a tank, receiving water from a water supply, treating the water received in a water treatment system to form a conditioned water stream, generating a salt solution by admixing a first portion of the conditioned water with a portion of the one or more quaternary ammonium halide salts, combining the salt solution with a second portion of the conditioned water to form a diluted salt solution, feeding the diluted salt solution to one or more electrolytic disinfectant producing units to convert the salt solution to an aqueous solution comprising one or more disinfectants via electrolysis, and contacting the aqueous solution with a fluid to form a treated fluid. In embodiments, the method may further comprise sampling the treated fluid using a sampling system and measuring at least one of a residual disinfectant content, a pH, a free available halogen content, and an oxidation reduction potential of the treated fluid. In other embodiments of the method, the treating may comprise at least one of filtering, softening, heating, and cooling. In other embodiments, the method may comprise cleaning or purging at least one of the tank, the electrolytic disinfectant producing unit(s), the sampling system, and the water treatment system using at least one of the water received, a third portion of the conditioned water, the salt solution, and an acid. In other embodiments, the method may comprise accumulating a process returns stream from the cleaning or purging. In other embodiments of the method, the fluid is a treatment fluid, the process may further comprise using at least a portion of the process returns stream to form at least a portion of the treatment fluid. In other embodiments, the method may comprise placing the treated treatment fluid into a wellbore. In yet other embodiments, the method may comprise transporting the tank containing the disposed quantity of one or more quaternary ammonium halide salts to a well site to be serviced.

[00100] In yet other aspects of the present disclosure, a method of fracturing a subterranean formation may comprise disposing a quantity of one or more quaternary ammonium halide salts in a tank, receiving water from a water supply, treating the water received in a water treatment system to form a conditioned water stream,

generating a salt solution by admixing a first portion of the conditioned water with a portion of the one or more quaternary ammonium halide salts, optionally combining the salt solution with a second portion of the conditioned water to form a diluted salt solution, feeding the diluted salt solution to one or more electrolytic disinfectant producing units to convert the salt solution to an aqueous solution comprising a mixed disinfectant via electrolysis, contacting the aqueous solution with a fluid to form a treated fluid, and using at least a portion of the treated fluid in a fracturing operation. In embodiments, the method may comprise transporting the tank containing the disposed quantity of one or more salts to a well site to be serviced.

[00101] In yet another aspect of the present disclosure, a method of servicing a wellbore may comprise contacting a treatment fluid or treatment fluid precursor with an aqueous solution comprising a mixed disinfectant produced via electrolysis of a quaternary ammonium halide salt solution to form a treated fluid, and placing the treated fluid in the wellbore. In embodiments of the method, the treatment fluid may comprise a fracturing fluid used in a fracturing operation. In other embodiments, the method may comprise measuring at least one of a residual disinfectant content, a pH, a free available halogen content, and an oxidation reduction potential of the treated fluid. In other embodiments, the method may comprise adjusting a rate of the aqueous solution provided for the contacting based upon at least one of: the measured at least one of a residual disinfectant content, a pH, a free available halogen content, and an oxidation reduction potential of the treated fluid; flow rate of at least one of the treatment fluid, the treatment fluid precursor, and the treated fluid; and measured property of the treatment fluid or treatment fluid precursor fed to the contacting. In other embodiments, the method may comprise forming a salt solution comprising water and one or more quaternary ammonium halide salts and forming a second salt solution comprising one or more salts comprising at least one of an alkali metal halide, an alkaline earth metal halide, and a transition metal halide and at least one of: converting the salt solution via electrolysis to form the aqueous solution; converting the second salt solution via electrolysis to form a second aqueous solution; admixing the second salt solution with the salt solution and converting the resulting admixed salt solution via electrolysis to form the aqueous solution; and admixing the second aqueous solution with the aqueous solution. In other embodiments, the method may

comprise storing a quantity of one or more of the salt solution, the second salt solution, the admixed salt solution, the aqueous solution, and the second aqueous solution in a storage vessel. In other embodiments, the method may comprise controlling one or more of the electrolysis, the forming a salt solution, the forming a second salt solution, the converting the salt solution, the storing, the adjusting, and the measuring using a control system. In other embodiments, the method may comprise receiving a signal with the control system from a local or remote source, where the signal provides an indication of at least one of: the measured at least one of a residual disinfectant content, a pH, a free available halogen content, and an oxidation reduction potential of the treated fluid; a flow rate of at least one of the treatment fluid, the treatment fluid precursor, and the treated fluid; and a measured property of the treatment fluid or treatment fluid precursor fed to the contacting. In yet other embodiments of the method, the control system may control the one or more of the electrolysis, the forming a salt solution, the converting the salt solution, the storing, the adjusting, and the measuring both in the presence of and absence of receiving the signal with the control system from the remote source.

[00102] In yet another aspect of the disclosure, a method for disinfecting a treatment fluid may comprise admixing an aqueous solution comprising at least one of quaternary ammonium hypohalous acid and quaternary ammonium hypohalite generated from a quaternary ammonium halide salt solution with a treatment fluid. In embodiments of the method, the aqueous solution may be generated by a method comprising feeding the quaternary ammonium halide salt solution to an electrolytic cell. In other embodiments of the method, the aqueous solution is generated by a method comprising: feeding a chloride salt solution to an electrolytic cell to form a disinfectant solution comprising hypochlorous acid, and admixing the disinfectant solution to the quaternary ammonium halide salt solution. In other embodiments of the method, the aqueous solution may be generated by a method comprising feeding a quaternary ammonium halide salt solution to an electrolytic cell to form a disinfectant solution comprising hypochlorous acid and admixing the disinfectant solution to an ammonium salt solution. In other embodiments of the method, the aqueous solution may be generated by a method comprising feeding the quaternary ammonium halide salt solution and a chloride salt solution to an electrolytic cell. In

yet other embodiments, the method may comprise admixing at least one quaternary ammonium halide salt and water to form the quaternary ammonium halide salt solution.

[00103] For the sake of brevity, certain ranges are explicitly disclosed herein. However, ranges from any lower limit may be combined with any upper limit to recite a range not explicitly recited, as well as, ranges from any lower limit may be combined with any other lower limit to recite a range not explicitly recited, in the same way, ranges from any upper limit may be combined with any other upper limit to recite a range not explicitly recited. Additionally, within a range may include every point or individual value between its end points even though not explicitly recited. Thus, every point or individual value may serve as its own lower or upper limit combined with any other point or individual value or any other lower or upper limit, to recite a range not explicitly recited.

[00104] All priority documents are herein fully incorporated by reference for all jurisdictions in which such incorporation is permitted and to the extent such disclosure is consistent with the description of the present disclosure. Further, all documents and references cited herein, including testing procedures, publications, patents, journal articles, etc. are herein fully incorporated by reference for all jurisdictions in which such incorporation is permitted and to the extent such disclosure is consistent with the description of the present disclosure.

[00105] Although a few example embodiments have been described in detail above, those skilled in the art will readily appreciate that many modifications are possible in the example embodiments without materially departing from this disclosure. Accordingly, all such modifications are intended to be included within the scope of this disclosure as defined in the following claims. In the claims, means-plus-function clauses are intended to cover the structures described herein as performing the recited function and not only structural equivalents, but also equivalent structures. Thus, although a nail and a screw may not be structural equivalents in that a nail employs a cylindrical surface to secure wooden parts together, whereas a screw employs a helical surface, in the environment of fastening wooden parts, a nail and a screw may be equivalent structures. It is the express intention of the applicant not to invoke 35

U.S.C. § 112, paragraph 6 for any limitations of any of the claims herein, except for those in which the claim expressly uses the words 'means for' together with an associated function.

CLAIMS

What is claimed:

1. A method of disinfecting a treatment fluid, comprising:
   admixing an aqueous solution comprising a mixed disinfectant generated via electrolysis of a salt solution comprising a quaternary ammonium halide salt with a treatment fluid or treatment fluid precursor.
2. The method of claim 1, further comprising at least one of:
   disposing a quantity of one or more quaternary ammonium halide salts in a tank;
   transporting the tank containing the disposed quantity of one or more quaternary ammonium halide salts to a well site to be serviced;
   receiving water from a water supply;
   treating the water received in a water treatment system to form a conditioned water stream, wherein the treating comprises at least one of filtering, softening, heating, and cooling;
   admixing the one or more quaternary ammonium halide salts and the water to form the salt solution, wherein the water may be a first portion of the conditioned water stream;
   combining the salt solution with additional water to form a diluted salt solution, wherein the additional water may be a second portion of the conditioned water stream; and
   converting the salt solution to an aqueous solution comprising the mixed disinfectant via electrolysis in one or more electrolytic disinfectant producing units.
3. The method of claim 1 or claim 2, wherein the quaternary ammonium halide salt comprises at least one of benzalkonium chloride, didecyldimethylammonium chloride, cetyltrimethylammonium chloride, octyltrimethylammonium chloride, tetramethylammonium chloride, tetraethylammonium chloride, tetrapropylammonium chloride, tetrabutylammonium chloride, cetylpyridinium chloride, benzalkonium bromide, didecyldimethylammonium bromide, cetyltrimethylammonium bromide, octyltrimethylammonium bromide, tetramethylammonium bromide, tetraethylammonium bromide, tetrapropylammonium bromide, tetrabutylammonium bromide, cetylpyridinium bromide, benzalkonium iodide, didecyldimethylammonium

iodide, cetyltrimethylammonium iodide, octyltrimethylammonium iodide, tetramethylammonium iodide, tetraethylammonium iodide, tetrapropylammonium iodide, tetrabutylammonium iodide, cetylpyridinium iodide and polymeric quaternary ammonium compounds.

4. The method of any one of claims 1-3, wherein the salt solution further comprises one or more salts comprising at least one of an alkali metal halide, an alkaline earth metal halide, and a transition metal halide, and wherein the mixed disinfectant comprises two or more of ozone, hydrogen peroxide, hypochlorite, hypochlorous acid, chlorine dioxide, hypobromous acid, bromine, and chlorine.
5. The method of any one of claims 1-4, wherein the salt solution further comprises at least one of ammonia, an ammonia salt, and dissolved oxygen.
6. The method of any one of claims 1-5, wherein the aqueous solution comprising the mixed disinfectant is formed by at least one of:

   electrolysis of a salt solution comprising a quaternary ammonium halide salt;

   electrolysis of a salt solution comprising a chloride salt and a quaternary ammonium halide salt;

   admixing an aqueous solution comprising hypochlorous acid, formed by electrolysis of a salt solution comprising a chloride salt, with a salt solution comprising a quaternary ammonium halide salt; and

   admixing an ammonium salt with a stream formed by electrolysis of a salt solution comprising a quaternary ammonium halide salt.
7. A method of servicing a wellbore, the method comprising:

   transporting a portable tank containing a quantity of one or more quaternary ammonium halide salts to a well site to be serviced;

   generating a salt solution by admixing water with the quaternary ammonium halide salt;

   converting the salt solution to an aqueous solution comprising a mixed disinfectant via electrolysis;

   contacting the aqueous solution with a treatment fluid to form a treated treatment fluid; and

   providing the treated treatment fluid for placement into the wellbore.

8. The method of claim 7, wherein the salt solution further comprises at least one of an alkali metal halide, an alkaline earth metal halide, and a transition metal halide, and wherein the mixed disinfectant comprises one or more of quaternary ammonium hypohalite, ozone, hydrogen peroxide, hypochlorite, hypochlorous acid, chlorine dioxide, hypobromous acid, bromine, and chlorine.
9. The method of any one of claims 7-8, wherein the generating a salt solution comprises at least one of:

admixing a quaternary ammonium halide salt with water;

diluting a quaternary ammonium halide salt solution; and

admixing a quaternary ammonium halide salt solution with a second salt solution comprising at least one of an alkali metal halide, an alkaline earth metal halide, and a transition metal halide.

10. The method of any one of claims 7-9, wherein the converting comprises:

admixing the generated salt solution with additional water to produce a diluted salt solution;

electrolyzing the diluted salt solution to form the aqueous solution.

11. A portable system for disinfecting water, the system comprising:

(a) a fluid connection for connecting to a water supply;

(b) a treatment system for conditioning the water supplied;

(c) a quaternary ammonium halide salt or quaternary ammonium halide salt solution storage tank;

(d) a mixing device for admixing at least a portion of the conditioned water with one or more quaternary ammonium halide salts to form a salt solution;

(e) at least one electrolytic disinfectant producing unit for converting at least a portion of the salt solution to an aqueous solution comprising a mixed disinfectant;

(f) a fluid connection for transporting the aqueous solution for contact with a fluid to be disinfected.

12. The system of claim 11, further comprising at least one of:

(g) one or more tanks for storing the aqueous solution;

(h) an acid supply tank for supplying acid to periodically clean the at least one electrolytic disinfectant producing unit;

(i) a sampling system for sampling the fluid following contact with the aqueous solution;

(j) a process returns tank for accumulating materials fed from one or more of the treatment system, the tank for admixing the at least one electrolytic disinfectant producing unit, the one or more tanks for storing, the acid supply tank, the sampling system; and piping, pumps, and equipment associated therewith;

(k) a fluid connection for transporting accumulated materials from the process returns tank;

(l) one or more fluid conduits for transporting treated fluid to the sampling system; and

(m) a control system for controlling a feed rate of the aqueous solution.

13. The system of any one of claims 11-12, further comprising at least one of:

a tank for admixing at least a portion of the conditioned water with at least one of an alkali metal halide, an alkaline earth metal halide, and a transition metal halide to form a second salt solution;

at least one electrolytic disinfectant producing unit for converting at least a portion of the second salt solution to a second aqueous solution comprising mixed disinfectants;

a mixing device for admixing the second salt solution and the salt solution; and

a mixing device for admixing the aqueous solution and the second aqueous solution.

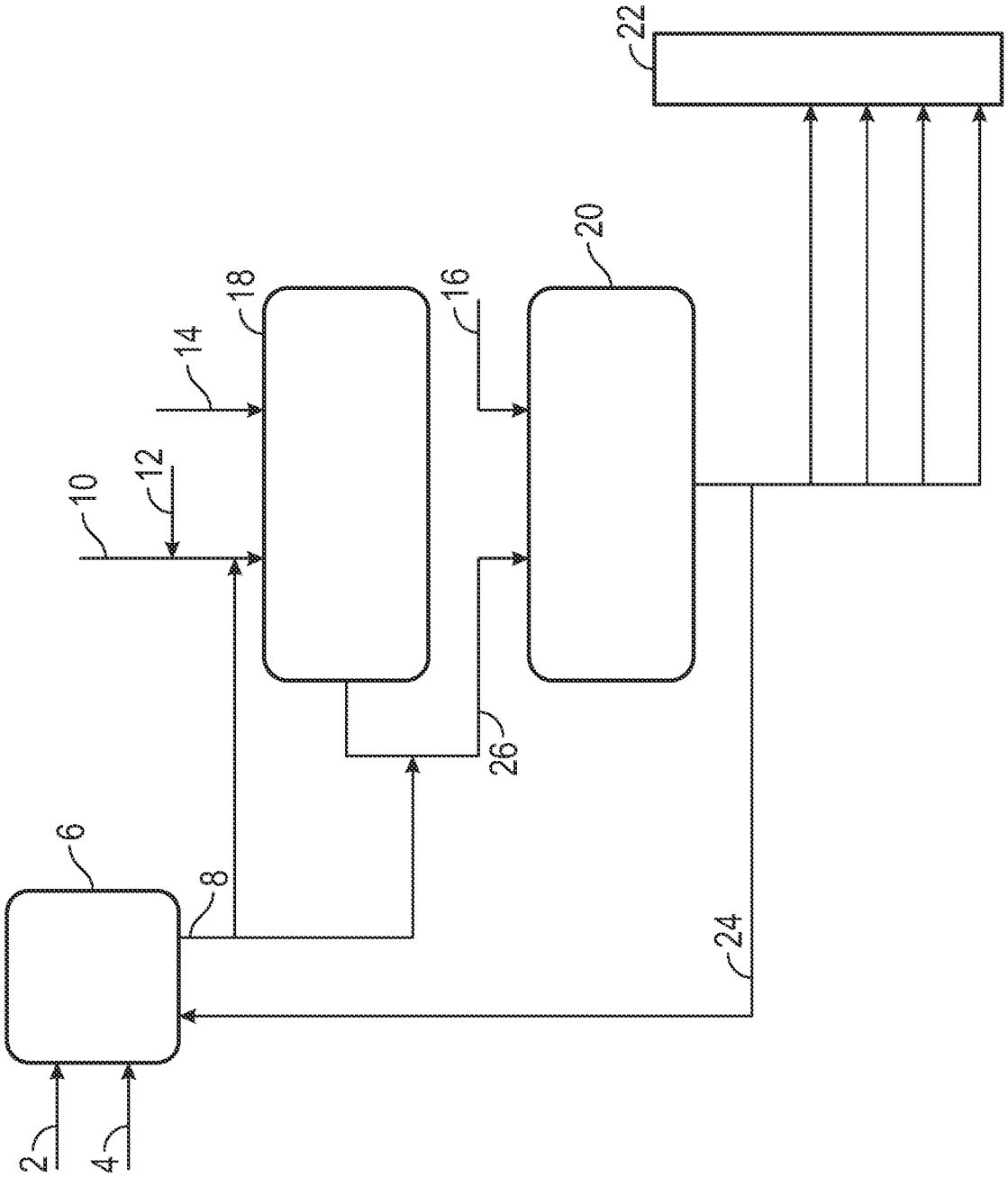


FIG. 1

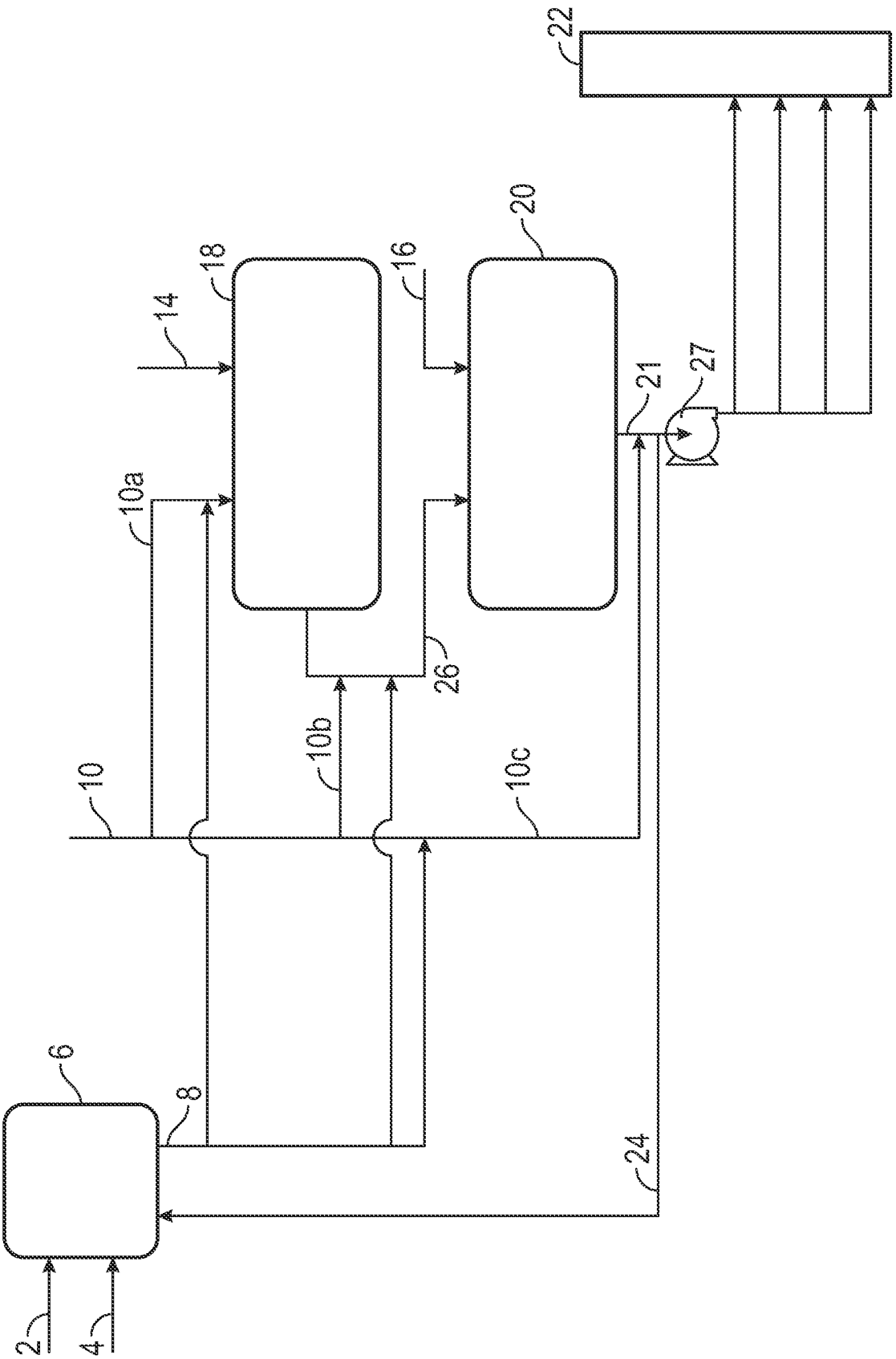


FIG. 2

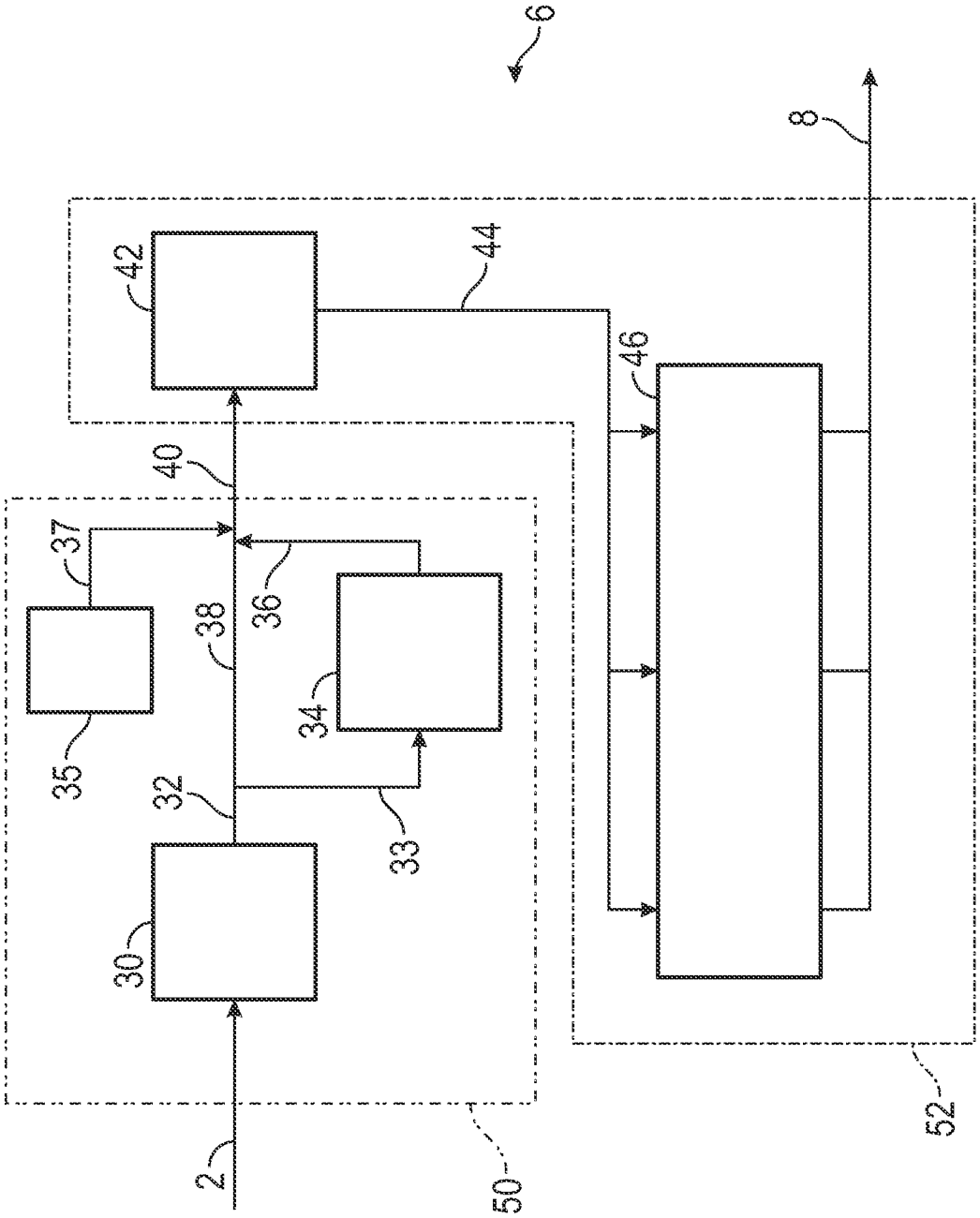


FIG. 3

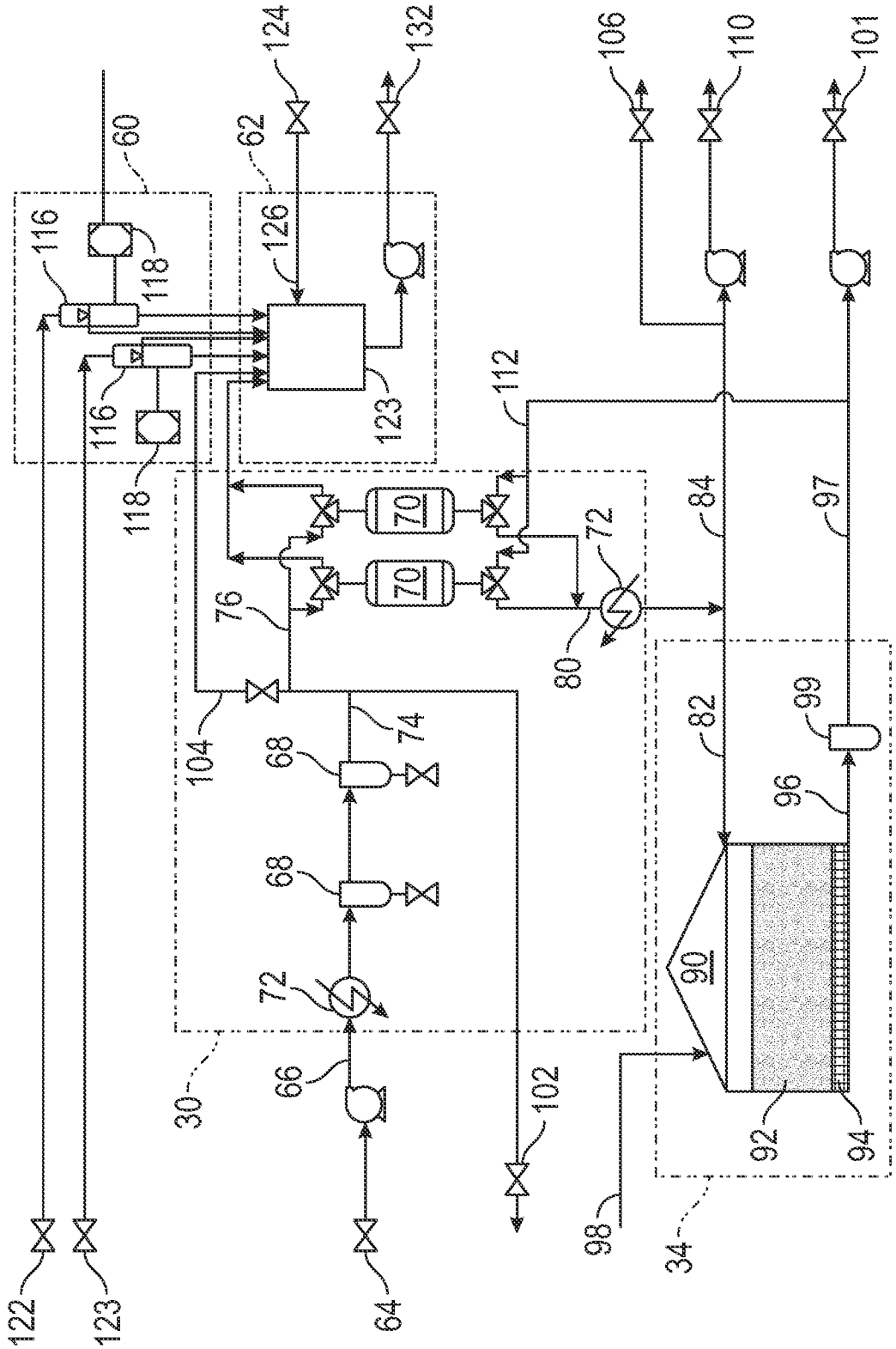

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FIG. 4A

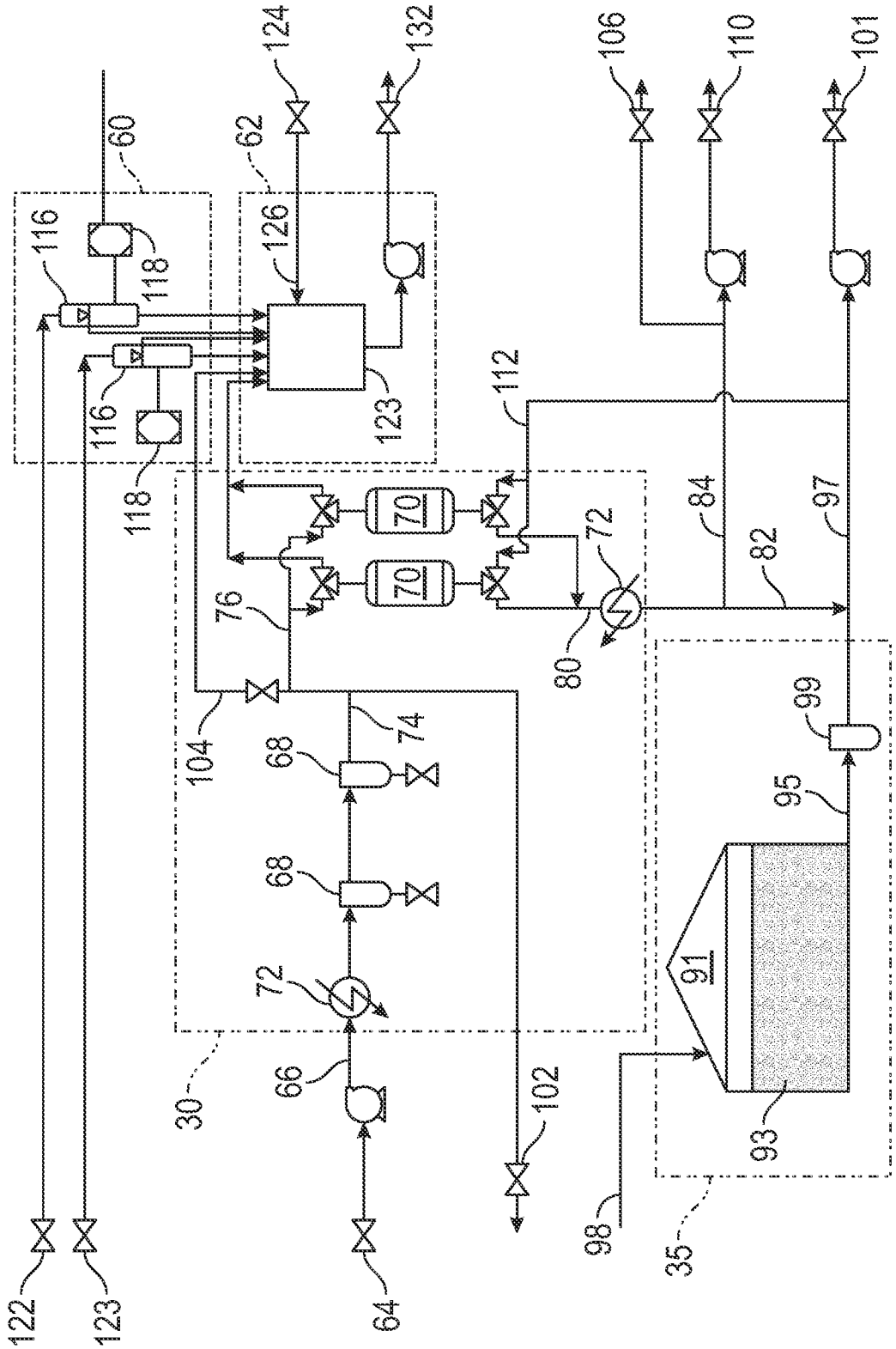

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93
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122
123

FIG. 4B

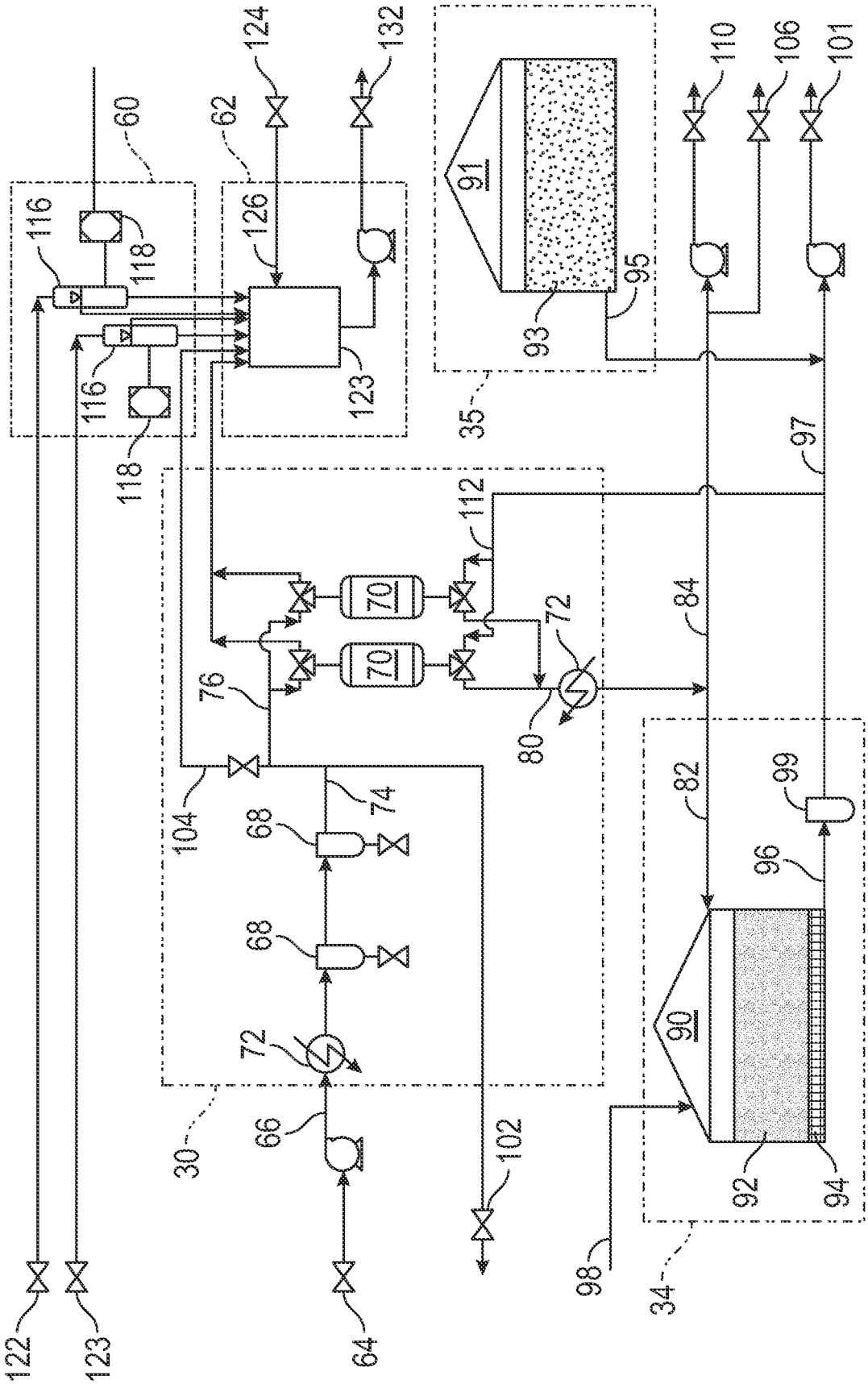

60
62
124
132
126
116
118
123
91
93
95
35
110
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72
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122
123

FIG. 4C

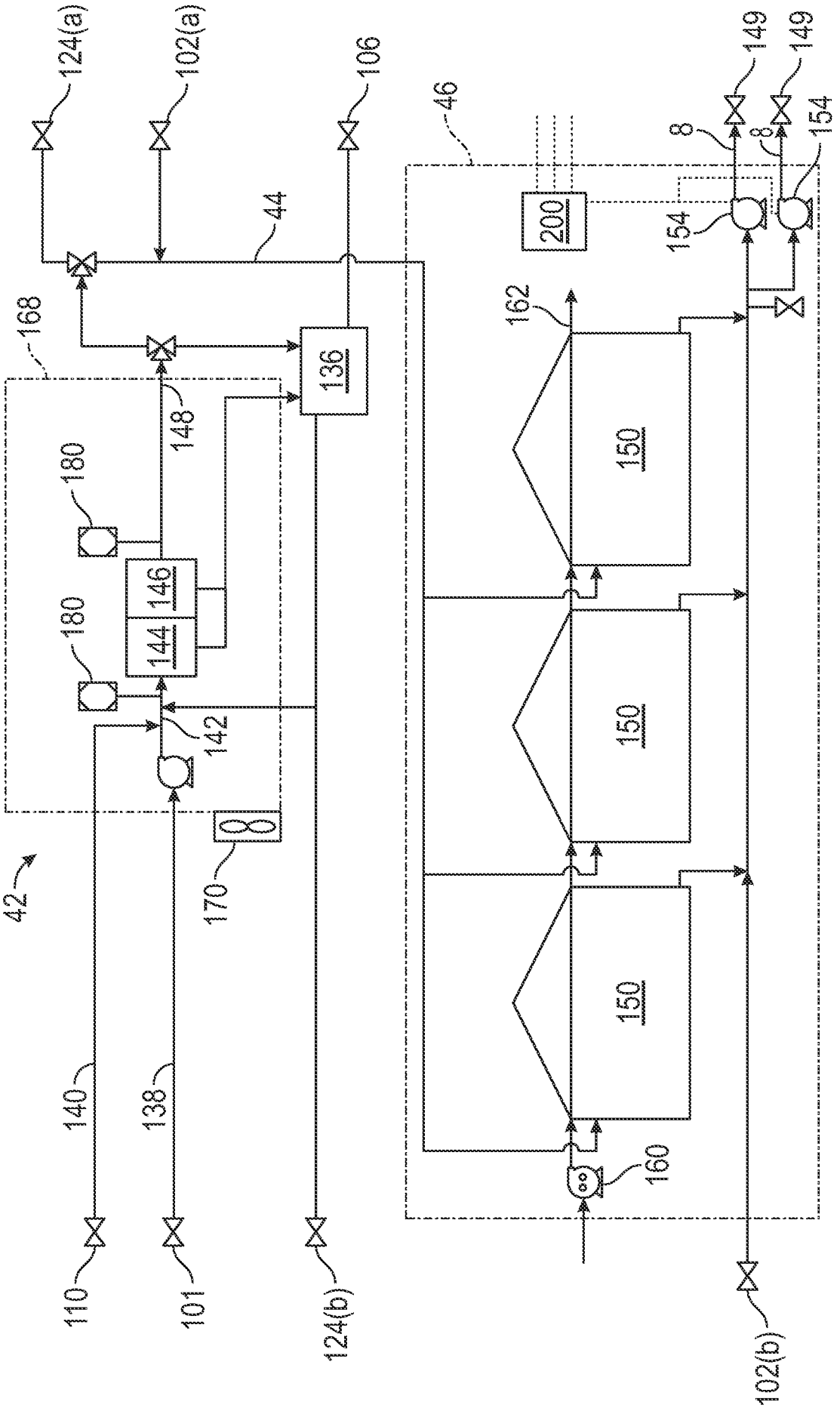

124(a)
102(a)
106
46
149
149
44
8
8
154
154
200
168
136
162
148
150
180
146
144
180
150
142
150
42
170
160
140
138
110
101
124(b)
102(b)

FIG. 5

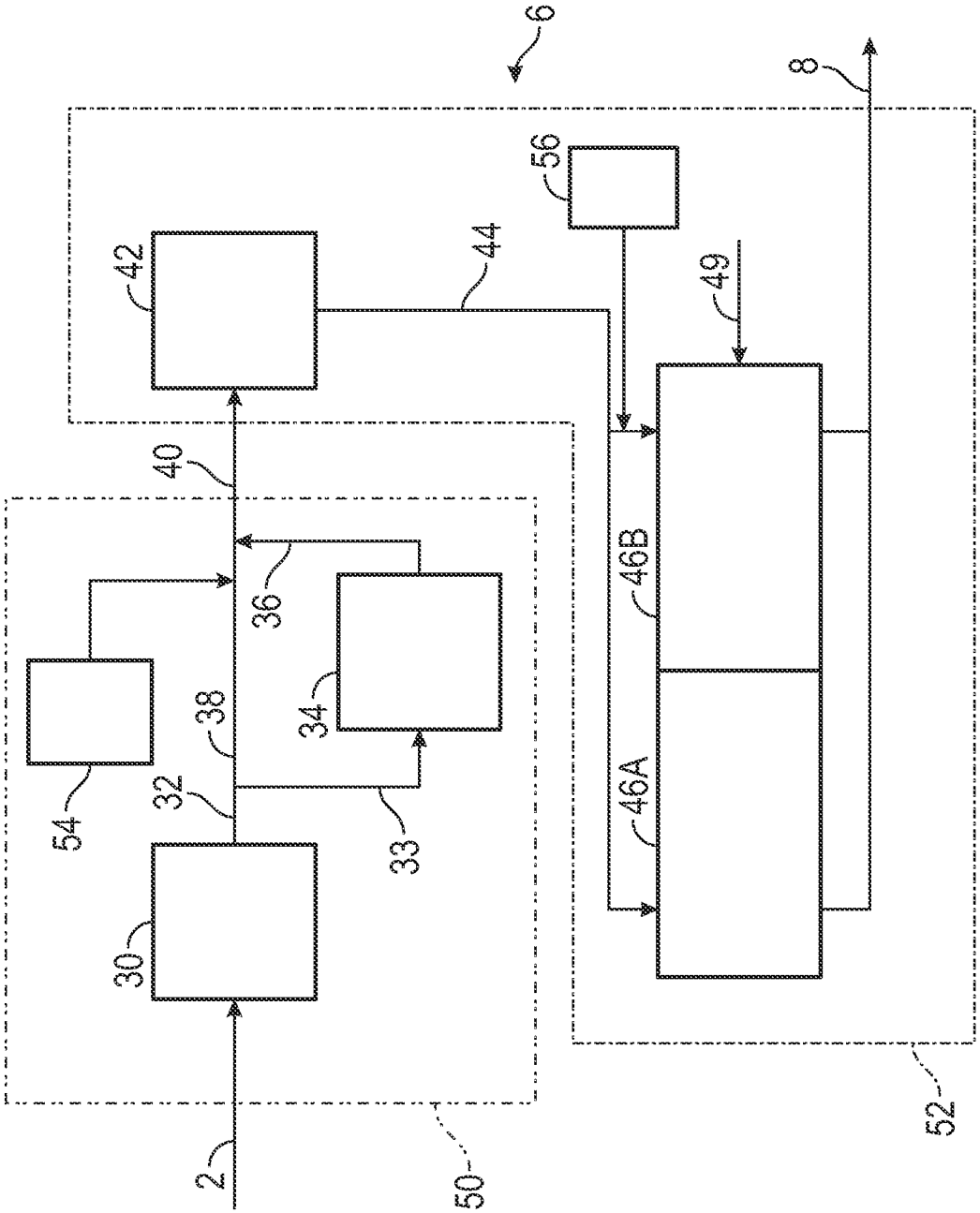


FIG. 6

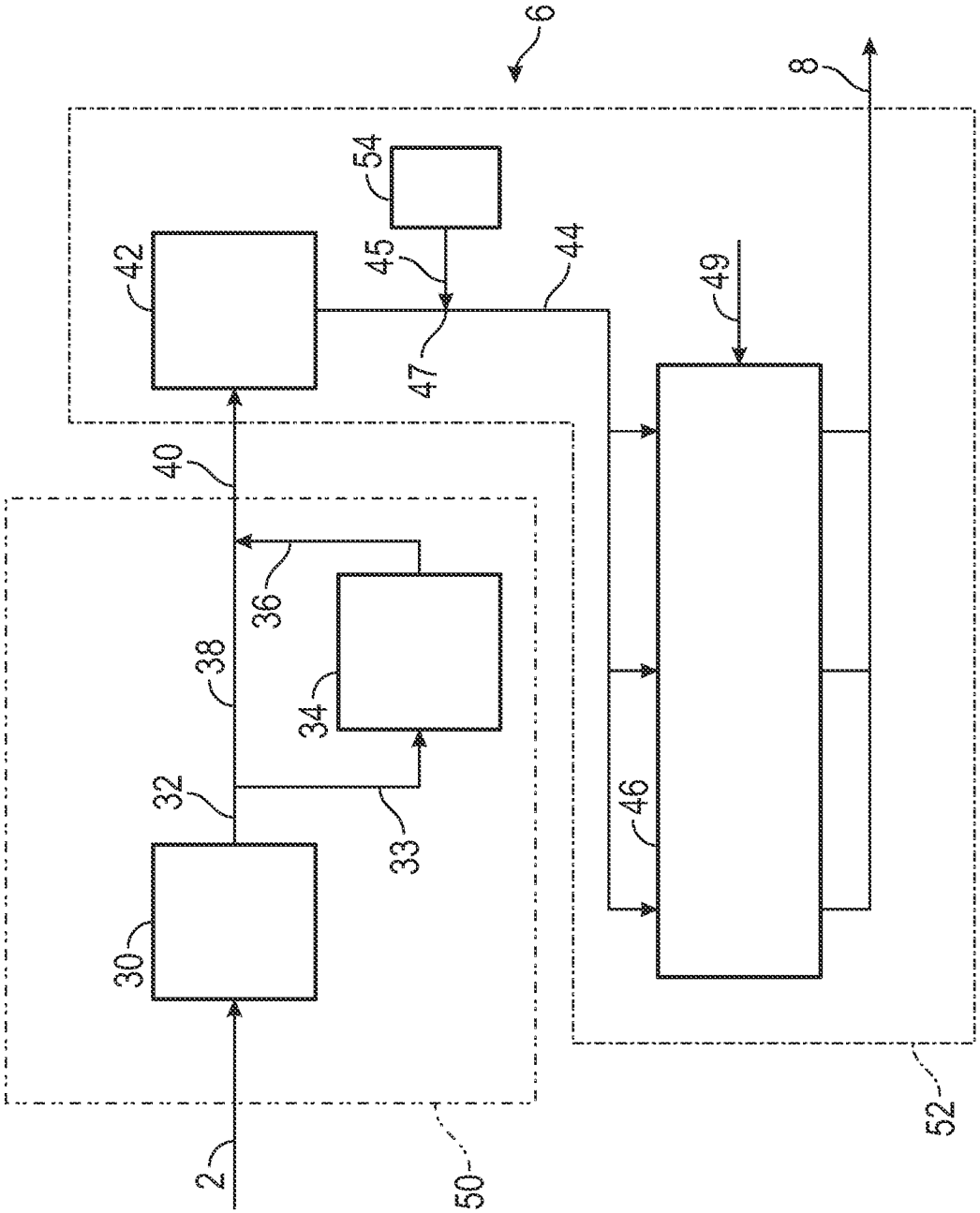


FIG. 7

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2013/065037

A. CLASSIFICATION OF SUBJECT MATTER

C02F 1/50(2006.01)i, C02F 1/467(2006.01)i

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)
C02F 1/50; C25B 11/02; C11D 1/62; C02F 1/46; C02F 1/461; C25B 1/24; C11D 1/75; C02F 1/68; C02F 1/467

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean utility models and applications for utility models
Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKOMPASS(KIPO internal) & keywords: disinfecting, electrolysis, quaternary ammonium halide salt

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2012-0228149 A1 (BOAL, ANDREW K. et al.) 13 September 2012 See abstract, [0032]-[0035], [0039], claim 1 and figure 3.	1-3,7-9,11-13
A	US 2005-0016932 A1 (ARBA, JOHN W. et al.) 27 January 2005 See abstract, claim 1 and figure 1.	1-3,7-9,11-13
A	US 2004-0035803 A1 (CRONAN, JOHN M. JR. et al.) 26 February 2004 See abstract and claims 1-8.	1-3,7-9,11-13
A	US 6315886 B1 (ZAPPI, GUILLERMO DANIEL et al.) 13 November 2001 See abstract, claim 1 and figure 1.	1-3,7-9,11-13
A	US 6255270 B1 (BARGER, BRUCE et al.) 3 July 2001 See abstract and claims 1, 5.	1-3,7-9,11-13

☐ 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
"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
26 December 2013 (26.12.2013)	**27 December 2013 (27.12.2013)**

Name and mailing address of the ISA/KR
Korean Intellectual Property Office
189 Cheongsa-ro, Seo-gu, Daejeon Metropolitan City, 302-701, Republic of Korea
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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2013/065037

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.: 4-6, 10
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:

1. ☐ As all required addtional 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 an additional fees, this Authority did not invite payment of any 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.:

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.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/US2013/065037

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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US 2005-0016932 A1	27/01/2005	AU 2001-94726 A1	08/04/2002
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/US2013/065037

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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