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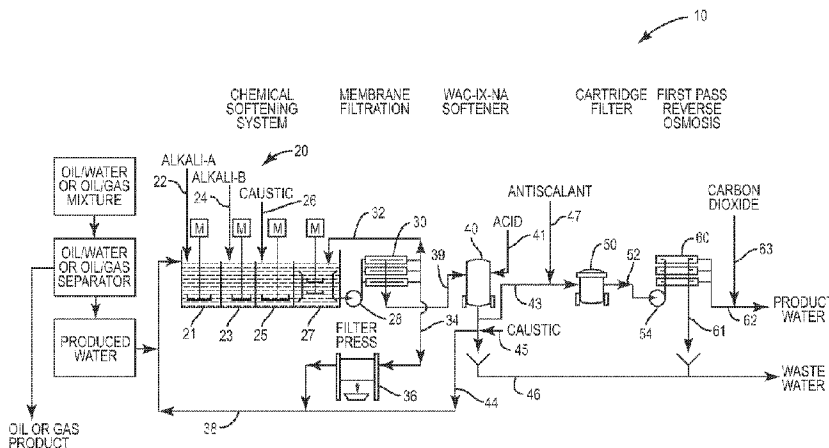
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(57) **Abrégé/Abstract:**

A method or process for treating wastewater containing high organics, silica, boron, hardness, and suspended and dissolved solids. The method includes degasifying the wastewater for the removal of dissolved gases and thereafter chemically softening the wastewater. After the chemical softening step, the wastewater is directed through a media filter or membrane which removes additional solids and precipitants. Thereafter the wastewater is directed through a sodium ion exchange that further softens the wastewater. The effluent from the ion exchange is directed through a cartridge filter and the effluent from the cartridge filter is directed through one or more reverse osmosis units. At a selected phase of the process, prior to the wastewater reaching the reverse osmosis unit or units, the pH of the wastewater is raised and maintained such that the pH of the wastewater reaching a reverse osmosis unit is at a pH greater than 10.5.

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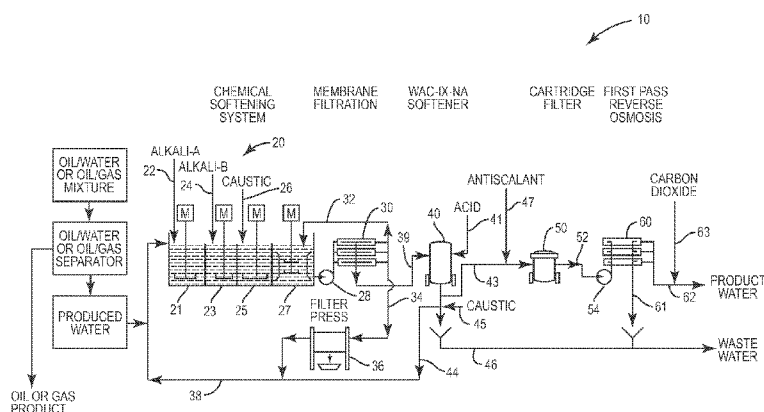


FIG. 1

(57) Abstract: A method or process for treating wastewater containing high organics, silica, boron, hardness, and suspended and dissolved solids. The method includes degasifying the wastewater for the removal of dissolved gases and thereafter chemically softening the wastewater. After the chemical softening step, the wastewater is directed through a media filter or membrane which removes additional solids and precipitants. Thereafter the wastewater is directed through a sodium ion exchange that further softens the wastewater. The effluent from the ion exchange is directed through a cartridge filter and the effluent from the cartridge filter is directed through one or more reverse osmosis units. At a selected phase of the process, prior to the wastewater reaching the reverse osmosis unit or units, the pH of the wastewater is raised and maintained such that the pH of the wastewater reaching a reverse osmosis unit is at a pH greater than 10.5.

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METHOD OF RECOVERING OIL OR GAS AND TREATING THE RESULTING PRODUCED WATER

BACKGROUND OF THE INVENTION

5 Numerous types of wastewater or produced water have relatively high concentrations of organics, silica, boron, hardness, suspended and dissolved solids. For example, oil recovery operations produce water that includes high concentrations of these contaminants. If such wastewater or produced water is to be discharged or used in high purity applications, such as a feed to a boiler or once through a steam generator or process water, then there must be a
10 substantial reduction in silica, total hardness, dissolved solids and organics.

Ion exchange processes and reverse osmosis processes have been used for desalting produced water or wastewater. Some practices involving the operation of reverse osmosis systems usually maintain a neutral pH condition, which is a pH of approximately 6-8. In the case of feed water produced by oil and gas operations, the recovery across reverse osmosis
15 systems is often limited by scaling due to silica or fouling due to organics. That is, high concentrations of silica in the feed water tend to scale the reverse osmosis membranes due to the concentration of silica exceeding solubility limits. Organics that exceed solubility limits also tend to foul the reverse osmosis membranes. Scaling due to silica and fouling due to organics can cause substantial down time of the reverse osmosis unit or units, requiring frequent
20 cleaning, replacement and maintenance. The maintenance is obviously expensive and the down time is costly and inefficient.

In addition, in the case of produced water, for example, processes are designed to remove silica and boron. These contaminants are often present in the form of weakly ionized salts, silicic acid and boric acid, and generally reverse osmosis membranes are not efficient in
25 rejecting such weakly ionized salts.

Therefore, there has been and continues to be a need for an economical process for treating wastewater or produced water that reduces fouling due to organics, reduces scaling due to silica, and which will efficiently reduce the concentrations of silica, organics, dissolved solids and hardness in the wastewater or produced water.
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SUMMARY OF THE INVENTION

The present invention relates to a method for treating a waste stream or produced water derived from an oil or gas recovery operation. Produced water contains organics, silica, hardness, dissolved solids, and suspended solids. Hardness in the produced water is reduced
35 by chemically softening the produced water. During the softening process, the pH of the wastewater is raised to above 10.5. The wastewater is then directed to a mixing tank where it is vigorously mixed to cause the formation of crystals therein. Free oil, emulsified oil in some cases, and the crystals are removed from the wastewater with a filtration membrane. At least a

portion of the reject stream produced by the filtration membrane is recirculated to the mixing tank. The membrane effluent is directed to an ion exchange unit where residual calcium and magnesium hardness is removed therefrom. The effluent from the ion exchange unit is directed to at least one reverse osmosis unit where dissolved solids, organics and boron are removed therefrom.

In accordance with an embodiment of the present invention, there is provided a method of recovering oil or gas from an oil or gas well and treating resulting produced water, comprising: a) recovering an oil/water or gas/water mixture from the oil or gas well; b) separating oil from the oil/water mixture or separating gas from the gas/water mixture to produce an oil or gas product and the produced water, and wherein the produced water includes organics, silica, hardness, dissolved solids and suspended solids; c) reducing hardness in the produced water by chemically softening the produced water which results in the formation of hardness precipitants; d) raising the pH of the produced water to 10.5 and above; e) directing the produced water having said pH of 10.5 and above to a mixing tank and mixing the produced water in said mixing tank and causing crystallization of the precipitants within the produced water; f) after crystallization, removing free oil and crystals from the produced water by directing the produced water through a ceramic membrane and producing a ceramic membrane effluent and a reject stream containing free oil and the crystals; g) recirculating at least a portion of the reject stream to the mixing tank and causing the crystals in the reject stream to grow larger; h) directing the ceramic membrane effluent to an ion exchange unit and further softening the membrane effluent by removing residual calcium and magnesium hardness therefrom and producing an ion exchange effluent and a waste stream; i) after further softening the ceramic membrane effluent, directing the ion exchange effluent to a first reverse osmosis unit and removing dissolved solids from the ion exchange effluent and producing a first permeate stream and a first reject stream; j) directing the first permeate stream through a second reverse

osmosis unit and producing a second permeate stream and a second reject stream; and k) reducing the concentration of ammonium hydroxide contained in the second permeate stream by directing the second permeate stream from the second reverse osmosis unit through a cation exchange resin such that hydrogen
5 ions in the cation exchange resin are exchanged with ammonium ions in the ammonium hydroxide.

In accordance with a further embodiment of the present invention, there is provided a method of recovering oil or gas from an oil or gas well and treating
10 resulting produced water, comprising: a) recovering an oil/water or gas/water mixture from the oil or gas well; b) separating oil from the oil/water mixture or separating gas from the gas/water mixture to produce an oil or gas product and the produced water, and wherein the produced water includes organics, silica, hardness, dissolved solids and suspended solids; c) reducing hardness in the
15 produced water by chemically softening the produced water which results in the formation of hardness precipitants; d) raising the pH of the produced water to 10.5 and above; e) directing the produced water having the pH of 10.5 and above to a mixing tank and mixing the produced water in the mixing tank and causing crystallization of the precipitants within the produced water; f) after crystallization,
20 removing free oil and crystals from the produced water by directing the produced water through a ceramic membrane and producing a ceramic membrane effluent and a reject stream containing free oil and the crystals; g) recirculating at least a portion of the reject stream to the mixing tank and causing the crystals in the reject stream to grow larger; h) directing the ceramic membrane effluent to an ion
25 exchange unit and further softening the membrane effluent by removing residual calcium and magnesium hardness therefrom and producing an ion exchange effluent and a waste stream; i) after further softening the ceramic membrane effluent, directing the ion exchange effluent to at least one reverse osmosis unit and removing dissolved solids from the ion exchange effluent and producing a
30 permeate stream and a reject stream; and j) oxidizing the organic content in the permeate stream by mixing hydrogen peroxide (H_2O_2) with the permeate stream and irradiating the H_2O_2 with ultraviolet radiation to produce hydroxyl radicals ($HO\bullet$) that oxidize the organic content in the permeate stream.

Yet another embodiment of the present invention provides a method of recovering oil or gas from an oil or gas well and treating resulting produced water, comprising: a) recovering an oil/water to gas/water mixture from the oil or gas well; b) separating oil from the oil/water mixture or separating gas from the gas/water mixture to produce an oil or gas product and the produced water, and wherein the produced water includes organics, silica, hardness, dissolved solids and suspended solids; c) reducing hardness in the produced water by chemically softening the produced water which results in the formation of hardness precipitants; d) raising the pH of the produced water to 10.5 and above; e) directing the produced water having the pH of 10.5 and above to a mixing tank and mixing the produced water in the mixing tank and causing crystallization of the precipitants within the produced water; f) after crystallization, removing free oil and crystals from the produced water by directing the produced water through a ceramic membrane and producing a ceramic membrane effluent and a reject stream containing free oil and the crystals; g) recirculating at least a portion of the reject stream to the mixing tank and causing the crystals in the reject stream to grow larger; h) directing the ceramic membrane effluent to an ion exchange unit and further softening the membrane effluent by removing residual calcium and magnesium hardness therefrom and producing an ion exchange effluent and a waste stream; i) after further softening the ceramic membrane effluent, directing the ion exchange effluent to at least one reverse osmosis unit and removing dissolved solids from the ion exchange effluent and producing a first permeate stream and a first reject stream; and j) prior to chemically softening the produced water, directing the produced water to a gas flotation unit and removing total organic carbon from the produced water.

A still further embodiment provides a method of recovering oil or gas from an oil or gas well and treating resulting produced water, comprising: a) recovering an oil/water to gas/water mixture from the oil or gas well; b) separating oil from the oil/water mixture or separating gas from the gas/water mixture to produce an oil or gas product and the produced water, and wherein the produced water includes organics, silica, hardness, dissolved solids and

suspended solids; c) reducing hardness in the produced water by chemically softening the produced water which results in the formation of hardness precipitants; d) raising the pH of the produced water to 10.5 and above; e) directing the produced water having the pH of 10.5 and above to a mixing tank and mixing the produced water in the mixing tank and causing crystallization of the precipitants within the produced water; f) after crystallization, removing free oil and crystals from the produced water by directing the produced water through a ceramic membrane and producing a ceramic membrane effluent and a reject stream containing free oil and the crystals; g) recirculating at least a portion of the reject stream to the mixing tank and causing the crystals in the reject stream to grow larger; h) directing the ceramic membrane effluent to an ion exchange unit and further softening the membrane effluent by removing residual calcium and magnesium hardness therefrom and producing an ion exchange effluent and a waste stream; i) after further softening the ceramic membrane effluent, directing the ion exchange effluent to at least one reverse osmosis unit and removing dissolved solids from the ion exchange effluent and producing a first permeate stream and a first reject stream; and j) prior to chemically softening the produced water, directing the produced water to a gas flotation unit and removing total organic carbon from the produced water by: adding an acid to the produced water such that carbonates and bicarbonates in the produced water are converted into CO₂; adding ferric chloride (FeCl₃) to the produced water to form Fe(OH)₃ such that carbon in the produced water is adsorbed onto the Fe(OH)₃; adding a polymer to the produced water; directing gas upwardly through the produced water such that suspended solids in the produced water move upwardly toward the surface of the produced water; and removing the suspended solids from the produced water.

Other embodiments of the invention include treating the reverse osmosis membrane effluent in an ammonia polisher and/or an oxidation system.

5 Additional embodiments of the invention include pretreating the produced water in a degasification system or a gas flotation system.

Other objects and advantages of the present invention will become apparent and obvious from a study of the following description and the accompanying drawings which are merely illustrative of such invention.

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BRIEF DESCRIPTION OF DRAWINGS

Figure 1 is a schematic illustration of the process of the present invention.

Figure 2 is a schematic illustration of the process of the present invention including a double pass reverse osmosis system.

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Figure 3 is a schematic illustration of the process of the present invention including an ammonia polisher.

Figures 4A-4B are schematic illustrations of the process of the present invention including an oxidation system.

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Figures 5A-5B are schematic illustrations of the process of the present invention including a heat exchanger and a cooling tower.

Figures 6A-6B are schematic illustrations of the process of the present invention including a pretreatment degasification system.

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Figures 7A-7B are schematic illustrations of the process of the present invention including a pretreatment gas flotation system.

DESCRIPTION OF THE INVENTION

The present invention relates to a wastewater treatment process for treating wastewater or produced water that typically contains organics, silica, boron, dissolved solids and suspended solids. Various types wastewater may contain these contaminants. For example, in the petroleum industry, produced water typically includes these contaminants. As used herein, the term "produced water" means water that is produced along with oil or gas in an oil or gas recovery process. Typically, the oil or gas is separated from the water and the separated water is referred to as produced water which is one type of wastewater. The present invention

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presents a process that can be utilized to treat various types and forms of wastewaters including, but not limited to, produced water and cooling tower blowdown.

As described subsequently herein, the process of the present invention entails chemically softening the wastewater in a process that removes hardness. Thereafter the wastewater is subjected to membrane filtration and ion exchange softening. The wastewater is then directed through one or more reverse osmosis units. To prevent scaling and fouling of the membranes in the reverse osmosis units, an antiscalant is mixed with the wastewater upstream from the reverse osmosis units and the pH of the wastewater is preferably maintained above 10.5. The wastewater can be further treated in an ammonia polisher and an oxidation system. Further, the wastewater can be directed through a heat exchanger so that the temperature of the wastewater is cooled prior to treatment in the reverse osmosis unit(s). Depending on the quality of the wastewater prior to chemical softening, the wastewater may be pretreated in a degasification system or a gas flotation system.

In Figure 1, the wastewater treatment system of the present invention is indicated generally by the numeral 10. The system includes a chemical softening unit 20, a membrane filter 30, an ion exchange filtration unit 40, a cartridge filter 50, and at least one reverse osmosis unit 60.

Chemical softening unit 20 includes a series of reactors 21, 23, 25 disposed sequentially in relation to one another. Each of the reactors 21, 23, and 25 includes a mixer and inlets 22, 24, and 26 respectively. As discussed in more detail herein, Inlets 22, 24, and 26 are used to inject chemicals such as softening reagents into the water held in reactors 21, 23, and 25. Downstream from the reactors 21, 23, 25 is disposed reactor 27 which includes a vertical tube mixer or crystallization tank. A pump 28 is operative to pump wastewater from reactor 27 to the downstream membrane filter 30.

In one embodiment the membrane filter 30 is a ceramic ultrafiltration membrane and is used to remove suspended solids and precipitants in the water passing through the membrane. Typically, ceramic membranes reject particles having a size of 0.2 μm or larger. However, ceramic membranes can be designed such that they reject particle sizes as low as 0.03 μm . Subsequently, herein is a general discussion on ceramic membranes and their applicability to treating feed water streams having one or more of the contaminants discussed here. In another embodiment, the membrane filter 30 is a polymeric membrane. Ceramic membranes are desirable when dealing with water having a very high temperature. For example, ceramic membranes are desirable when the water passing therethrough has a temperature approaching 300°F.

As will be appreciated from subsequent portions of this disclosure, a reject recycle line 32 that extends from the membrane filter 30 to the reactor 27. In addition, there is provided a reject waste line 34 that extends from the membrane filter 30 to a filter press 36. Wastewater produced by the filter press 36 is directed through line 38 back to the chemical softening system

20. Membrane filter 30 produces a permeate or effluent that is directed from the membrane filter 30 via line 39 which extends to an ion exchange unit 40. Further, the membrane filter produces a reject stream, a portion of which is recycled via line 32 back to the mixing reactor 27.

5 Ion exchange unit 40 includes a chemical inlet 41 for regeneration of the ion exchange resin upon exhaustion. A recycle line 44 is operatively connected between the ion exchange unit 40 and the chemical softening unit 20. Ion exchange unit 40 is also operatively connected to a waste line 46 that directs waste produced in the ion exchange unit 40 to disposal. A caustic inlet 45 is disposed downstream from the ion exchange unit 40 and is used to inject a caustic
10 solution into the waste stream produced by the ion exchange unit 40. Ion exchange unit 40 also includes a treated effluent line 43 that extends from the ion exchange unit 40 to a cartridge filter 50. As will be discussed subsequently, the ion exchange unit 40 is utilized to remove residual hardness from the wastewater and, in the case of the embodiment disclosed herein, the ion exchange unit 40 is operated in the sodium mode.

15 Cartridge filter 50 further filters the water which exits the cartridge filter 50 through filtered water line 52. An antiscalant inlet 47 is disposed upstream of the cartridge filter 50, as shown in Fig. 1, which injects an antiscalant reagent into the water in line 43. Addition of the antiscalant reagent provides a soluble chemical equilibrium for scale forming compounds across the downstream reverse osmosis unit 60. In another embodiment however, the antiscalant inlet
20 can be disposed downstream of the cartridge filter 50 and upstream from the reverse osmosis unit 60. A pump 54 is operatively interconnected between cartridge filter 50 and reverse osmosis unit 60. A line 52 directs the effluent from the cartridge filter 50 to the inlet of the reverse osmosis unit 60.

A reject line 61 extends from the reverse osmosis unit 60 and is operatively connected to
25 the waste line 46 which directs waste produced in the reverse osmosis unit 60 to disposal. Treated effluent line 62 extends from the reverse osmosis unit 60 to a discharge area or to a point where the treated water is subjected to additional treatment. A carbon dioxide inlet 63 is disposed downstream from the reverse osmosis unit 60 and is used to inject carbon dioxide into the treated effluent. It is appreciated that the reverse osmosis unit 60 produces a reject stream
30 that is directed into line 61 and a permeate stream that is directed into line 62. In this embodiment and in all subsequent embodiments, the treated effluent can be utilized as a water source for a steam generation device such as a boiler or a once through steam generator. In one example, the treated effluent is used to generate steam which is injected into an oil and/or gas bearing formation in order to extract oil and/or gas therefrom.

35 As stated above, the wastewater treatment system 10 of the present invention can be used to treat various types and forms of influent wastewater streams such as a produced water stream or a cooling tower blowdown stream. Fig. 1A illustrates the present invention being utilized to treat a produced water stream. In this case, an oil/water mixture or a gas/water

mixture is pumped up through an oil or gas-gathering well and the mixture is sent to a separator which, in the case of an oil/water mixture, separates the oil from the water to yield an oil product and separated water which is termed produced water. The produced water becomes the feed stream that is directed into the wastewater treatment system 10. In the case of a gas/water mixture, the separator separates the gas from the water to form a gas product and produced water. The produced water becomes the feed stream to the wastewater treatment system 10.

While Fig. 1A discloses one basic embodiment of the wastewater treatment system, it should be appreciated that any of the embodiments for the wastewater treatment system 10 shown in Figs. 1-7 could be utilized for treating produced water, cooling tower blowdown, or other waste streams.

With reference to Figure 2, the wastewater treatment system 10 can further include a second reverse osmosis unit 70. This embodiment is generally referred to as a double pass reverse osmosis system because the filtered water from the cartridge filter 50 is treated in two sequential reverse osmosis units 60, 70. A caustic inlet 64 is disposed downstream from the first reverse osmosis unit 60 and upstream from the second reverse osmosis unit. Caustic inlet 64 is used to inject a caustic solution into the treated effluent in line 62. A pump 65 is operatively connected between the first reverse osmosis unit 60 and the second reverse osmosis unit 70. Permeate produced by the first reverse osmosis unit 60 is pumped from the first reverse osmosis unit 60 to the second reverse osmosis unit 70 by pump 65.

Second reverse osmosis unit 70 produces a permeate stream and a reject stream. The reject stream is directed into line 72 and recycled to a point upstream of the first reverse osmosis unit 60. The permeate produced by the second reverse osmosis unit 70 is directed into line 74. In this embodiment, a carbon dioxide inlet 63 is disposed downstream of the reverse osmosis unit 70 and is used to inject carbon dioxide into the permeate passing through line 74.

Figure 3 illustrates an embodiment of the wastewater treatment system 10 having the chemical softening unit 20, membrane filter 30, ion exchange unit 40, first and second reverse osmosis units 60, 70 and an ammonia polisher 80. In this embodiment, the treated effluent line 74 extends from the second reverse osmosis unit 70 to the ammonia polisher 80. Ammonia polisher 80 includes a chemical inlet line 82 for regeneration of the ion exchange resin upon exhaustion and a recycle line 88 that is operative to recycle waste from the ammonia polisher 80 to the chemical softening unit 20. Ammonia polisher 80 is also operatively connected to the waste line 46 that directs waste produced in the ammonia polisher 80 to disposal. Ammonia polisher 80 further includes a treated effluent line 84 that extends from the ammonia polisher 80 to a discharge area or to a point where the treated water is subjected to additional treatment. A caustic inlet 89 is disposed downstream from the ammonia polisher 80 and injects a caustic solution into the treated effluent in line 84.

Figures 4A-4B illustrate an embodiment of the wastewater treatment system 10 having the chemical softening unit 20, membrane filter 30, ion exchange unit 40, first and second

reverse osmosis units 60, 70, ammonia polisher 80, and an oxidation system 90. Fig. 4A illustrates the chemical softening unit 20, membrane filter 30, and ion exchange unit 40, as described above in Fig. 1. Fig. 4B illustrates the cartridge filter 50, first and second reverse osmosis units 60, 70, and the ammonia polisher 80 as described above in Figs. 2 and 3B. Fig. 4B also includes the oxidation system 90. In this embodiment, the treated effluent line 84 extends from the ammonia polisher 80 to an ultraviolet light unit 92 in the oxidation system 90. Oxidation system 90 includes a hydrogen peroxide (H_2O_2) inlet 91 that injects a H_2O_2 solution into the treated effluent in line 84 upstream from the ultraviolet light unit 92. Oxidation system 90 further includes an irradiated treated effluent line 93 that extends from the ultraviolet light unit 92 to a discharge-area or to a point where the treated water is subjected to additional treatment. A sodium bisulfite inlet 94 and a caustic inlet 95 are disposed downstream from the ultraviolet light unit 92 and inject sodium bisulfite and a caustic solution, respectively, into the irradiated treated effluent in line 93.

Figures 5A-5B illustrate an embodiment of the wastewater treatment system 10 having the chemical softening unit 20, membrane filter 30, ion exchange unit 40, first and second reverse osmosis units 60, 70, ammonia polisher 80, oxidation system 90, and heat exchanger 100. Fig. 5A illustrates the chemical softening unit 20, membrane filter 30, and ion exchange unit 40, as described above in Fig. 1. Fig. 5B illustrates the cartridge filter 50, first and second reverse osmosis units 60, 70, ammonia polisher 80, and oxidation system 90, as shown above in Figs. 2, 3B, and 4B.

In the process depicted in Figs. 5A-5B, there is provided a heat exchanger 100 that is disposed generally between the ion exchange unit 40 and the cartridge filter 50. The heat exchanger cools the effluent produced by the ion exchange unit 40 prior to the effluent reaching the one or more reverse osmosis units. As seen in Fig. 5B, the cooling medium or water utilized by the heat exchanger 100 is directed from the heat exchanger 100 through line 104 to a cooling tower 102. There the cooling medium or water is cooled and recirculated back to the heat exchanger 100 via return line 103. From time to time, it may be necessary to provide make-up water for use by the heat exchanger 100. Thus, make-up water is taken from the permeate of the reverse osmosis unit 70, in the Fig. 5B example, and directed through line 108 to the cooling tower 102. Further, from time to time, some of the water is removed from the cooling tower 102 and directed into the waste line 46.

Figures 6A-6B illustrate an embodiment of the wastewater treatment system 10 having the chemical softening unit 20, membrane filter 30, ion exchange unit 40, first and second reverse osmosis units 60, 70, ammonia polisher 80, oxidation system 90, heat exchanger 100, and a pretreatment degasification system 110. Fig. 6A illustrates the pretreatment degasification system 110. In this embodiment, pretreatment degasification system 110 is disposed upstream from the chemical softening unit 20 and includes an acid inlet 112 and a water outlet 114. Acid inlet 112 is disposed upstream from a degasification chamber 113 and

injects an acidic solution into the feed water prior to water entering the degasification chamber 113. In one embodiment the degasification chamber 113 is a forced draft degasifier chamber. The degasification system 110 further includes a water outlet 114 operatively connected to the degasification chamber 113 and to the first reactor 21 of the chemical softening unit 20.

5 Figures 7A-7B illustrate an embodiment of the wastewater treatment system 10 having the chemical softening unit 20, membrane filter 30, ion exchange unit 40, first and second reverse osmosis units 60, 70, ammonia polisher 80, oxidation system 90, heat exchanger 100, and a pretreatment gas flotation system 120. Fig. 7A illustrates the pretreatment gas flotation system 120. In this embodiment, the pretreatment gas flotation system 120 is disposed
10 upstream from the chemical softening unit 20 and includes an acid inlet 121 and a ferric chloride (FeCl_3) (for example) inlet 122. Acid inlet 121 and the FeCl_3 inlet 122 inject an acidic solution and FeCl_3 into the feed water or wastewater respectively prior to the water entering a gas flotation chamber 124. Gas flotation chamber 124 includes a mixer, a polymer inlet 123, and a gas inlet 125. Gas flotation system 120 further includes a water outlet 126 operatively
15 connected to the gas flotation chamber 124 and to the first reactor 21 of the chemical softening unit 20. A recycle line 127 extends from the water outlet 126 to the gas flotation chamber 124. A pump 128 is disposed along the recycle line 127 and functions to pump water through the recycle line 127 and into the gas flotation chamber 124.

 With reference to the specific processes illustrated in the figures, feed water or
20 wastewater influent is directed to the chemical softening unit 20. The purpose of the chemical softening process is to reduce total hardness in the feed water to solubility limits, typically less than approximately 55 mg/l as CaCO_3 . Further, the softening process carried out in the chemical softening unit 20 removes at least a portion of the silica from the feed water.

 As shown in the figures, a first alkali based reactant is added to the wastewater in
25 reactor 21 through inlet 22. In one embodiment the first alkali based reactant is calcium hydroxide ($\text{Ca}(\text{OH})_2$). As $\text{Ca}(\text{OH})_2$ is mixed with the wastewater, carbon dioxide (CO_2), calcium bicarbonate ($\text{Ca}(\text{HCO}_3)_2$, and magnesium bicarbonate ($\text{Mg}(\text{HCO}_3)_2$) dispersed throughout the wastewater react with the $\text{Ca}(\text{OH})_2$ to precipitate some calcium carbonate (CaCO_3) and some magnesium hydroxide ($\text{Mg}(\text{OH})_2$). $\text{Ca}(\text{OH})_2$ also reacts with magnesium sulfate (MgSO_4) and
30 magnesium chloride (MgCl_2) in the wastewater to precipitate magnesium hydroxide ($\text{Mg}(\text{OH})_2$).

 In one embodiment, magnesium oxide (MgO) is also added to the wastewater. MgO can be added to the water prior to the water entering reactor 21 or MgO can be added to the water while in reactor 21. As MgO is mixed with the water, it is converted into magnesium hydroxide ($\text{Mg}(\text{OH})_2$) which acts as an adsorbent. $\text{Mg}(\text{OH})_2$ in the water, created through the addition of
35 $\text{Ca}(\text{OH})_2$ and/or MgO , adsorbs silica dispersed throughout the water.

 Wastewater is transferred from reactor 21 to reactor 23 where a second alkali based reactant is added to the water through inlet 24. In one embodiment, the second alkali based

reactant is sodium carbonate (Na_2CO_3). As Na_2CO_3 is mixed with the water, the Na_2CO_3 reacts with calcium sulfate (CaSO_4) and calcium chloride (CaCl_2) in the water to precipitate CaCO_3 .

The addition of these reagents, for example $\text{Ca}(\text{OH})_2$, MgO , and Na_2CO_3 , causes hardness compounds to precipitate from the wastewater stream being treated. After precipitation, these precipitants can be removed by filtration such as with the filtration membrane and cartridge filter.

After the wastewater is treated in the reactor 23, the wastewater is directed to reactor 25 where a third alkali based reactant can be added to the water through inlet 26. In one embodiment, the third alkali based reactant is a caustic solution, such as sodium hydroxide (NaOH). The third alkali based reactant raises the pH of the water to above 10.5. As discussed in more detail below, it is often preferable to maintain the pH of the water in the range of 10.5 to 11.5.

The above description includes the addition of several alkaline reagents and a caustic reagent. However, it is noted that the addition of each of the above reagents is merely an exemplary embodiment of the present invention. Further, the present invention encompasses embodiments in which only one or two alkaline reagents and a caustic reagent are added to the water. For example, it may be effective to add only one alkaline reagent and one caustic reagent to the water to remove hardness from the water and effectively increase the pH of the water.

After the water has been treated in reactor 23, the water is directed to the mixing reactor 27 where the wastewater is vigorously mixed in the vertical mixer. Mixing in the mixing reactor 27 causes precipitants to grow larger which makes it easier for the downstream membrane filter 30 to reject the precipitants. As discussed below, the reject stream of the membrane filter 30 is recycled via line 32 to the mixing reactor 27. The mixing action of the vertical tube mixer in reactor 27, coupled with the recycle of solids or precipitants from the membrane filter 30, gives rise to a crystallization process where the solids form crystals and the mixing action realized in the reactor 27 causes the crystals to grow larger. Note, that in mixing reactor 27, the vertical tube mixer includes a tube-like structure disposed in the reactor and one or more mixers disposed within the two structures. In mixing the various reagents and precipitants, wastewater in reactor 27 is induced into the top of the tube and caused to move downwardly through the tube and out the bottom of the tube. This continuous mixing action causes the wastewater, along with the precipitants or crystals to move back up toward the top of the reactor outside of the tube. Thereafter the wastewater re-enters the top of the tube. Thus, this continuous mixing action causes the wastewater to be drawn down through the tube, out of the tube, and up the sides of the reactor and back down through the tube. This type of mixing action promotes an efficient crystallization process where the precipitants tend to grow larger. After the crystals or precipitants have increased in size, the effluent from the mixing reactor 27 is directed to membrane filter 30 via the pump 28. Typically, the effluent from the mixing reactor 27 is

directed through the membrane filter 30 at a pressure of approximately 30 psi to approximately 60 psl.

Membrane filter 30 removes suspended solids and particulates. The present wastewater treatment system and process is effective in treating produced water which typically includes free oil and even emulsified oil. The membrane filter 30 is effective to remove both free oil and emulsified oil. Removing free oil and emulsified oil with the membrane filter 30 increases the life of the downstream reverse osmosis unit(s) 60, 70. Generally, manufacturers of reverse osmosis units suggest that the reject stream of a reverse osmosis unit should have no more than 1 ppm of free oil therein. Thus, it is preferred to remove as much free oil and emulsified oil from the wastewater or produced water prior to being treated in a reverse osmosis unit. Thus, in one embodiment it is desirable for the filtrate produced by the membrane filter 30 to have a total hardness of less than 50 mg/l CaCO_3 , a free oil concentration of less than 0.50 mg/l and a turbidity of less than 0.5. As noted above, membrane filter 30 produces a reject stream in which at least a portion thereof is directed through recycle line 32 to the mixing reactor 27 where it mixed with the wastewater in the mixing reactor 27. Another portion of the reject stream is directed to waste line 34 that directs the reject stream from the membrane filter 30 to a filter press 36. Filter press 36 removes excess water from the reject stream which is directed to recycle line 38 and directed to the chemical softening unit 20. The remaining solids recovered from the filter press 36 are directed to disposal.

Membrane filter 30 also produces a filtrate which is directed to the ion exchange unit 40 through filtrate line 39. As the filtrate passes through the ion exchange unit 40, Ca^{2+} and Mg^{2+} in the filtrate are removed through a cation exchange process. For example, in one embodiment, the ion exchange unit 40 includes a Na^+ based cation resin. The Ca^{2+} and Mg^{2+} in the filtrate are exchanged with the Na^+ in the resin. Moreover, other metal cations present in the filtrate are exchanged with the Na^+ in the resin. Thus, the ion exchange unit 40 further reduces the total hardness of the wastewater and reduces the concentration of other soluble metals in the water.

As the resin in the ion exchange unit 40 becomes saturated with Ca^{2+} and Mg^{2+} , and other metal ions, the resin needs to be regenerated to maintain its effectiveness. To regenerate the resin, an acid solution added to the ion exchange unit 40 through inlet 41 is directed through the resin. A portion of the waste produced through the resin regeneration is recycled to the chemical softening unit 20 through recycle waste line 44. A caustic solution is added to the waste stream in the waste line 44 through inlet 45. This addition reduces the pH of the acidic waste stream. Another portion of the waste stream produced through resin regeneration is directed to the waste line 46 and sent for disposal.

The softened effluent from the ion exchange unit 40 is directed from the ion exchange unit 40 through line 43 to the cartridge filter 50 which removes fine particulates present in the effluent. An antiscalant is added to the effluent through inlet 47 upstream of the cartridge filter

50 to maintain a soluble chemical equilibrium for the scale forming compounds across the downstream reverse osmosis unit(s) 60, 70. In processes such as described herein, it is difficult to eliminate scaling or fouling of the membranes associated with the reverse osmosis unit(s) by chemical softening and softening in the ion exchange unit 40. For that reason, the antiscalant is added to the feed water or wastewater stream ahead of a first reverse osmosis unit 60. In another embodiment, the antiscalant inlet 47 can also be disposed downstream from the cartridge filter 50 and upstream from the reverse osmosis unit 60. The filtered water exits the cartridge filter 50 through filtered water line 52 and is directed to a first reverse osmosis unit 60 via a pump 54. To ensure that the downstream reverse osmosis units do not experience extensive fouling or scaling, in one embodiment it is desirable that the filtered water from the cartridge filter 50 have a total hardness of less than 0.20 mg/l CaCO_3 , a free oil concentration of less than 0.50 mg/l, and a silt density index of less than 4.0.

The first reverse osmosis unit 60 reduces organics, silica, boron, and total dissolved solids present in the water. Accordingly, the first reverse osmosis unit 60 produces a reject stream having a relatively high concentration of contaminants and a treated effluent stream having a relatively low concentration of contaminants. The reject stream is directed through reject line 61 to waste line 46 for disposal. The treated effluent or permeate is directed through the treated effluent line 62 to a discharge area or to a point where the treated effluent is subjected to additional treatment. In one embodiment, it is desirable for the treated effluent or permeate for the first reverse osmosis unit 60 to have less than 1,000 $\mu\text{S}/\text{cm}$ conductivity. Carbon dioxide (CO_2) is injected into the treated effluent in the treated effluent line 62 through inlet 63. The addition of CO_2 decreases the pH of the wastewater. As discussed above, the treated effluent from the reverse osmosis unit 60 has a generally high pH. When CO_2 is added to the water it dissolves and forms a carbonic acid, H_2CO_3 , a generally weak acid. Thus, the addition of CO_2 is beneficial when the treated effluent is discharged or subjected to downstream treatment and requires a downward adjustment in pH.

Appearing below under Table 1 is a summary of exemplary data for a cooling tower blowdown feed water treated in the process described above. Note that calcium hardness is reduced in the chemical softening unit 20 from 500 ppm to 8 ppm. In addition, magnesium hardness is reduced in the chemical softening unit from 100 ppm to 2 ppm. Further, silica is reduced in the chemical softening unit from 150 ppm to 80 ppm. Again, the pH in the chemical softening process is raised to 10.7. The table below refers to free oil, emulsified oil, and soluble oil. As used herein, if an oil particle is 30 μm or greater, it is referred to as free oil. If the oil particle is between 1 and 30 μm , it is referred to as emulsified oil. If the oil particle is less than 1 μm , it is referred to as soluble oil.

It is noted that the chemical softening unit 20 does not decrease the total alkalinity in the feed water. Rather, the chemical softening unit actually increases the alkalinity in the feed water. For example, in preliminary tests and as described below, the feed water had a total

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alkalinity of 150 ppm as CaCO_3 . After treatment in the chemical softening unit, the effluent had a total alkalinity of 400 ppm as CaCO_3 . A decrease in total alkalinity only occurs after treatment in the RO system. Maintaining a high alkalinity in the water increases the rejection rate of organics in the water passing through the RO system.

5

Table 1

	Cooling Tower Blowdown Feed Water	Chemical Softening Effluent	Ceramic Membrane Filtrate	Ion Exchange Effluent	RO System Permeate	Treated Effluent
pH (S.U.)	6.5-8.5	10.7	10.7	10.7	10.2	7.5
Total Alkalinity (ppm as CaCO_3)	150	400	400	400	<75	<75
Ca- Hardness (ppm as CaCO_3)	500	8.0	8.0	0.08	Non- detect	Non- detect
Mg- Hardness (ppm as CaCO_3)	100	2.0	2.0	0.02	Non- detect	Non- detect
Dissolved Silica (ppm)	150	80	80	80	<0.5	<0.5
Free Oil (ppm)	10.0	10.0	<0.2	<0.2	Non- detect	Non- detect
Emulsified Oil (ppm)	5.0	5.0	<0.2	<0.2	Non- detect	Non- detect
Soluble Oil (ppm)	10.0	10.0	10.0	10.0	<0.5	<0.5
TSS (ppm)	30	1,000	<0.2	<0.2	Non- detect	Non- detect
TDS (ppm)	4,000	4,500	4,500	4,500	150	150

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Boron (ppm)	5.0	5.0	5.0	5.0	<0.5	<0.5
Total Organic Carbon (ppm)	30	30	30	30	<0.5	<0.5

In another embodiment, shown in Figure 2, a double pass reverse osmosis system is employed. In this embodiment, the treated effluent is directed to a second reverse osmosis unit 70 that further reduces organics, silica, boron, and total dissolved solids present in the water.

5 When using a double pass reverse osmosis system, a pH adjustment of the treated effluent may be required between the two reverse osmosis units in order to facilitate increased rejection of the boron remaining in the water. Accordingly, a caustic solution can be injected into the treated effluent through inlet 64 which is disposed downstream from the first reverse osmosis unit 60 and upstream from the second reverse osmosis unit 70. The amount of caustic injected is
10 calculated so as to maintain the pH greater than 10.5 and preferably to a pH of 11.

Second reverse osmosis unit 70 also produces a reject stream having a relatively high concentration of contaminants and a permeate or treated effluent stream having a relatively low concentration of contaminants. The reject stream is directed through recyclable waste line 72 to the first reverse osmosis unit 60. CO₂ is injected into the treated effluent through inlet 76
15 disposed downstream from the second reverse osmosis unit 70. As mentioned above, the addition of CO₂ decreases the pH of the water and thus is beneficial if the treated effluent is being discharged or subjected to downstream treatment which requires a downward adjustment in pH. Figure 2 shows that the treated effluent is directed through the treated effluent line 74 to a discharge area or to a point where the treated effluent is subjected to additional treatment. In
20 one embodiment, it is desirable for the treated effluent or permeate from the second reverse osmosis unit 70 to have less than 75 μ S/cm conductivity and a boron concentration of less than 0.83 mg/l.

The present process aims to control the pH of the wastewater passing through the one or more reverse osmosis units 60, 70 above 10.5. Maintaining a high pH of the water
25 substantially reduces organic fouling and silica scaling of the membranes in the reverse osmosis units. Further, the solubility of organics generally increases with pH. For example, at a pH over 10 the solubility of organics is approximately 350 mg/l. However, at a pH of 6 the solubility of organics is just above 50 mg/l. The same relationship holds true for the solubility of silica. For example, the solubility of silica at a pH of about 10.5 is almost 900 mg/l. However, at
30 a pH of 8 the solubility of silica is about 100 mg/l. By maintaining the pH of the feed water above 10.5, these particular scaling and fouling contaminants are maintained in solution and can be rejected by the one or more reverse osmosis units 60 or 70 without scaling or fouling.

The process described above can also be modified to include other processes. For example, as shown in Figure 3, the treated effluent from the double pass reverse osmosis system is directed to the ammonia polisher 80 via treated effluent line 74. Ammonia polisher 80 includes a cation exchange resin. As the treated effluent passes through the cation exchange resin, the H^+ in the cation exchange resin are exchanged with NH_4^+ in the treated effluent. The treated effluent exiting the reverse osmosis unit 70 may, in some cases, have an ammonium hydroxide (NH_4OH) concentration that can be toxic to the environment if discharged. However, after NH_4^+ are exchanged for H^+ in the ammonia polisher 80, the treated water exiting the ammonia polisher 80 has a significantly smaller concentration in NH_4OH . In one embodiment, it is desirable for the ammonia polisher 80 to reduce the ammonia in the water to less than 0.3 mg/l as N.

As the resin in the ammonia polisher 80 becomes saturated with NH_4^+ , the resin needs to be regenerated to maintain its effectiveness. To regenerate the resin, an acid solution is added to the ion exchange unit 40 through inlet 82. A portion waste produced through resin regeneration is recycled to the chemical softening unit 20 through recyclable waste line 88. Another portion of the waste stream produced through the resin regeneration is directed to the waste line 46 and sent for disposal. After the water is treated in the ammonia polisher 80, a caustic solution is added to the treated water in the treated water line 84 through inlet 89 disposed downstream from the ammonia polisher 80. The addition of the caustic solution is preferred if the treated water exiting the ammonia polisher 80 has a generally low pH. Typically, caustic solution is added to the treated water to increase the pH of the treated water to between approximately 6.5 and approximately 9 in order to meet environmental regulations. Then, the treated water in treated water line 84 is directed toward a discharge area or to a point where the treated water is subjected to additional treatment.

In the embodiment shown in Figures 4A-4B, the treated water is directed to an oxidation system 90 through the treated water line 84. A hydrogen peroxide solution is injected into the treated water through inlet 91. Treated water and the hydrogen peroxide (H_2O_2) solution is then directed to the ultraviolet light unit 95 where it is irradiated with ultraviolet light. Irradiation by ultraviolet light converts the H_2O_2 in the water into hydroxyl radicals ($HO\cdot$). These radicals oxidize the organic content in the water. In one embodiment it is desirable for the oxidation system 90 to remove the carbon biological oxygen demand (CBOD) in the water to a concentration of less than 25 mg/l.

The irradiated water exits the ultraviolet light unit 92 through line 93 and is then injected with a sodium bisulfite solution through inlet 94. The sodium bisulfite solution removes residual H_2O_2 from the water. The irradiated water can also be injected with a caustic solution through inlet 95. The addition of a caustic solution is preferred if the irradiated water has a generally low pH. As described above, the caustic solution is added to the water to increase the pH of the water to between approximately 6.5 and approximately 9 in order to meet environmental regulations.

Then, the irradiated water in line 93 is either directed toward a discharge area or to a point where the treated water is subjected to additional treatment.

In another embodiment, shown in Figures 5A-5B, the temperature of the treated effluent exiting the ion exchange unit 40 is cooled through the use of a heat exchanger 100 and a cooling tower 102. In typical produced water applications, the produced water influent has a temperature of approximately 160°F to approximately 200°F. It is beneficial to cool the water prior to treatment in the reverse osmosis unit(s). Accordingly, treated effluent in line 43 is directed to the heat exchanger 100 where it is cooled to a temperature of approximately 95°F. Cooling water is directed from the cooling tower 102 to the heat exchanger 100 through line 103. Cooling water from the heat exchanger 100 is then directed back to the cooling tower 102 via line 104. A portion of the cooling water can also be directed from cooling tower 102 to the waste line 46 and sent for disposal.

Further, after the treated effluent is treated in the first and second reverse osmosis units 60, 70, a portion of the treated water from the second reverse osmosis unit 70 is directed to the cooling tower 102 through line 108. This water is used as make-up cooling water for use in the heat exchanger 100.

Appearing below under Tables 2 and 3 is a summary of exemplary data for oil field produced water treated in the process described above. Note that calcium hardness (expressed as CaCO_3) was reduced in the chemical softening unit 20 from 400 ppm to 8 ppm. In addition, magnesium hardness (expressed as CaCO_3) was reduced in the chemical softening unit from 100 ppm to 2 ppm. Further, silica was reduced in the chemical softening unit from 300 ppm to 80 ppm. The pH in the chemical softening process was raised to 10.7. Again, it is noted that the chemical softening unit does not decrease the total alkalinity in the feed water. Rather, the chemical softening unit actually increases the alkalinity in the feed water. For example, in the preliminary test described below, the feed water had a total alkalinity of 300 ppm as CaCO_3 . After treatment in the chemical softening unit, the effluent had a total alkalinity of 400 ppm as CaCO_3 . A decrease in total alkalinity only occurs after treatment in the RO system. Maintaining a high alkalinity in the water increases the rejection rate of organics in the water passing through the RO system.

Table 2

	Oil Field Produced Water	Chemical Softening Effluent	Ceramic Membrane Filtrate	Ion Exchange Effluent
pH (S.U.)	6.5-8.5	10.7	10.7	10.7
Total Alkalinity (ppm as CaCO_3)	300	400	400	400
Ca-Hardness (ppm as CaCO_3)	400	8.0	8.0	0.08

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Mg-Hardness (ppm as CaCO ₃)	100	2.0	2.0	0.02
Dissolved Silica (ppm)	300	80	80	80
Free Oil (ppm)	100.0	100.0	<0.2	<0.2
Emulsified Oil (ppm)	10.0	10.0	<0.2	<0.2
Soluble Oil (ppm)	100.0	100.0	100.0	100.0
TSS (ppm)	50	1,000	<0.2	<0.2
TDS (ppm)	7,000	7,500	7,500	7,500
Boron (ppm)	26.0	26.0	26.0	26.0
Total Organic Carbon (ppm)	100	100	100	100
Total Ammonia (ppm)	20.0	20.0	20.0	20.0

Table 3

	RO System Permeate	Ammonia Polisher Effluent	Advanced Oxidation Effluent	Treated Effluent
pH (S.U.)	10.2	4.5	6.5	7.5
Total Alkalinity (ppm as CaCO ₃)	<75	Non-detect	20	20
Ca-Hardness (ppm as CaCO ₃)	Non-detect	Non-detect	Non-detect	Non-detect
Mg-Hardness (ppm as CaCO ₃)	Non-detect	Non-detect	Non-detect	Non-detect
Dissolved Silica (ppm)	<0.5	<0.5	<0.5	< 0.5
Free Oil (ppm)	Non-detect	Non-detect	Non-detect	Non-detect
Emulsified Oil (ppm)	Non-detect	Non-detect	Non-detect	Non-detect
Soluble Oil (ppm)	<0.5	<0.5	<0.5	< 0.5
TSS (ppm)	Non-detect	Non-detect	Non-detect	Non-detect
TDS (ppm)	150	<10	<20	<20
Boron (ppm)	<0.5	<0.5	<0.5	< 0.5
Total Organic Carbon (ppm)	<0.5	<0.5	Non-detect	Non-detect
Total Ammonia (ppm)	20.0	<0.1	<0.1	<0.1

Other embodiments of the present invention include pretreatments of the feed water prior to treatment in the chemical softening unit 20. For example, in Figure 6A, the feed water is subjected to a degassing process in a degasification system 110 prior to treatment in the chemical softening unit 20. The degasification process is particularly useful for feed waters containing volatile organic carbons and dissolved gases. In such cases, an acid is injected through inlet 112 and mixed with the feed water to partially convert the bicarbonates present in the feed water to CO₂ and to maintain hydrogen sulfide or other dissolved gases in a gaseous state. Gases present in the water are pulled from the system through the degasifier and

scrubbed using activated carbon canisters. In one embodiment, the degasification process utilizes a force draft degasifier or DO_x stripper to reduce the CO_2 and the hydrogen sulfide present in the feed water. Other types of degasifiers such as vacuum, membrane or depurator type degasifiers can also be used for this application. Typically, the pH is lowered to a range of 4.5 to 6.5 ahead of the degasifier and the effluent from the degasifier is typically in the pH range of 5.0 - 7.0. Degassed water exits the degasification system 110 through outlet 114 and is then directed to the chemical softening unit 20, where it undergoes treatment described above.

The present invention may also include a pretreatment gas flotation system 120. For example, in Figure 7, the feed water is subjected to gas flotation prior to treatment in the chemical softening unit 20. Typically gas flotation systems are useful for removing free oil from the feed water and reducing turbidity and the organic concentration in the feed water. In one embodiment, the water is dosed with an acidic solution through acid inlet 121 and FeCl_3 , for example, through inlet 122. Typically, the FeCl_3 dosage for COD removal is between 100 - 200 mg/l. After the feed water has been injected with an acidic solution and FeCl_3 , the feed water is directed into gas flotation chamber 124. A polymer is then added to and mixed with the water in gas flotation chamber 124 through inlet 123. A gas, such as nitrogen (N_2) or methane (CH_4), is directed through the water in the gas flotation chamber 124 through inlet 125. The gas bubbles facilitate the removal of free oil and insoluble organic particulates, which rise to the top of the water where they are skimmed off as waste. The treated water exits the gas flotation system 120 through outlet 126. A portion of the treated water is directed to the chemical softening unit 20, where it undergoes treatment as described above. The remainder of the water exiting the gas flotation system 120 is directed through recycle line 127 back to the gas flotation chamber 124 via pump 128.

It is further noted that the present invention is not limited to the specific combination of elements described above or shown in the drawings. Rather, the present invention encompasses embodiments that do not include all of the above elements. For example, the embodiments shown in Figs. 6 and 7 do not necessarily require the use of an ammonia polisher, an oxidation system, and/or a heat exchanger. Likewise, the embodiment shown in Fig. 5 does not necessarily require the use of an ammonia polisher and/or an oxidation system.

However, each of the embodiments in the present invention includes a membrane filtration unit. As described above, the membrane filtration unit can comprise a ceramic membrane. Specific details of ceramic membranes are not dealt with herein because the details of such membranes not per se material to the present invention, and further, ceramic membranes are known in the art. For a review of general ceramic membrane technology, one is referred to the disclosures found in U.S. Patent Nos. 6,165,553 and 5,611,931.

These ceramic membranes, useful in the processes disclosed herein, can be of various types. In some cases the ceramic membrane may be of the type that produces both a permeate stream and a reject stream. On the other

hand, the ceramic membranes may be of the dead end type, which only produces a permeate stream and from time-to-time the retentate is backflushed or otherwise removed from the membrane. For example, when treating produced water, the ceramic membrane may require cleaning by back pulsing the permeate through the membrane. However, when the
5 transmembrane pressure across the ceramic membrane reaches a substantially high pressure, such as between approximately 40 psi and 45 psi, it may be desirable to perform a "clean-in-place" of the ceramic membrane.

The structure and materials of the ceramic membranes as well as the flow characteristics of ceramic membranes varies. When ceramic membranes are used to purify
10 produced water, the ceramic membranes are designed to withstand relatively high temperatures as it is not uncommon for the produced water being filtered by the ceramic membranes to have a temperature of approximately 90°C or higher.

Ceramic membranes normally have an asymmetrical structure composed of at least two, mostly three, different porosity levels. Indeed, before applying the active, microporous top layer,
15 an intermediate layer with a pore size between that of the support, and a microfiltration separation layer. The macroporous support ensures the mechanical resistance of the filter.

Ceramic membranes are often formed into an asymmetric, multi-channel element. These elements are grouped together in housings, either a single element in a housing or multiple elements in a housing, and these membrane modules can withstand high
20 temperatures, extreme acidity or alkalinity and high operating pressures, making them suitable for many applications where polymeric cannot be used. Several membrane pore sizes are available to suit specific filtration needs covering the microfiltration, the ultrafiltration, and nanofiltration ranges from 1 micron down to 250 Dalton MWCO).

Ceramic membranes today run the gamut of materials (from alpha alumina to silicon
25 carbide). The most common membranes are made of Al, Si, Ti or Zr oxides, with Ti and Zr oxides being more stable than Al or Si oxides. In some less frequent cases, Sn or Hf are used as base elements. Each oxide has a different surface charge in solution. Other membranes can be composed of mixed oxides of two of the previous elements, or are established by some additional compounds present in minor concentration. Non-oxide membranes are also available
30 such as silicon nitride or silicon carbide with silicon carbide membranes being most prevalent. Low fouling polymeric coatings for ceramic membranes are also available.

Ceramic membranes are typically operated in the cross flow filtration mode. This mode has the benefit of maintaining a high filtration rate for membrane filters compared with the direct flow filtration mode of conventional filters. Cross flow filtration is a continuous process in which
35 the feed stream flows parallel (tangential) to the membrane filtration surface and generates two outgoing streams.

A small fraction of feed called permeate or filtrate, separates out as purified liquid passing through the membrane. The remaining fraction of feed, called retentate or concentrate contains materials rejected by the membrane.

5 The separation is driven by the pressure difference across the membrane, or the trans-membrane pressure. The parallel flow of the feed stream, combined with the boundary layer turbulence created by the cross flow velocity, continually sweeps away particles and other material that would otherwise build up on the membrane surface.

10 The process of the present invention has many applications. The process can be used in oil field produced water treatment for surface discharge or for use in steam generating devices to generate steam for use in oil recovery. Likewise, the process can be used in gas field produced water treatment for surface discharge. In addition, the process of the present invention can be used to treat refinery wastewater for reuse with zero liquid discharge. Moreover, the process of the present invention has applications for treating cooling tower blowdown as well as FGD scrubber blowdown. Still further, the process of the present invention
15 has applications in treating industrial wastewater, such as automotive wastewater.

The embodiments of the present invention for which an exclusive property or privilege is claimed are defined as follows:

1. A method of recovering oil or gas from an oil or gas well and treating resulting produced water, comprising:

- a. recovering an oil/water or gas/water mixture from the oil or gas well;
- b. separating oil from the oil/water mixture or separating gas from the gas/water mixture to produce an oil or gas product and the produced water, and wherein the produced water includes organics, silica, hardness, dissolved solids and suspended solids;
- c. reducing hardness in the produced water by chemically softening the produced water which results in the formation of hardness precipitants;
- d. raising the pH of the produced water to 10.5 and above;
- e. directing the produced water having said pH of 10.5 and above to a mixing tank and mixing the produced water in said mixing tank and causing crystallization of the precipitants within the produced water;
- f. after crystallization, removing free oil and crystals from the produced water by directing the produced water through a ceramic membrane and producing a ceramic membrane effluent and a reject stream containing free oil and the crystals;
- g. recirculating at least a portion of the reject stream to the mixing tank and causing the crystals in the reject stream to grow larger;
- h. directing the ceramic membrane effluent to an ion exchange unit and further softening the membrane effluent by removing residual calcium and magnesium hardness therefrom and producing an ion exchange effluent and a waste stream;
- i. after further softening the ceramic membrane effluent, directing the ion exchange effluent to a first reverse osmosis unit and removing dissolved solids from the ion exchange effluent and producing a first permeate stream and a first reject stream;
- j. directing the first permeate stream through a second reverse osmosis unit and producing a second permeate stream containing ammonium hydroxide and a second reject stream;
- k. reducing the concentration of ammonium hydroxide contained in the second permeate stream by directing the second permeate stream from the second reverse osmosis unit through a cation exchange resin such that hydrogen ions in the cation exchange resin are exchanged with ammonium ions in the ammonium hydroxide;

- l. after reducing the concentration of the ammonium hydroxide contained in the second permeate stream, adding a caustic to the second permeate stream and raising the pH of the second permeate stream to between about 6.5 to about 9;
 - m. after reducing the concentration of ammonium hydroxide, oxidizing the organic content in the second permeate stream;
 - n. wherein oxidizing the organic content comprises mixing hydrogen peroxide (H_2O_2) with the second permeate stream and irradiating the H_2O_2 with ultraviolet radiation to produce hydroxyl radicals ($\text{HO}\cdot$) that oxidize the organic content in the second permeate stream; and
 - o. after oxidizing the organic content in the second permeate stream, adding a sodium bisulfite solution to the second permeate stream to remove residual H_2O_2 from the second permeate stream.
2. The method of claim 1 wherein chemically softening the produced water comprises mixing magnesium oxide (MgO) with the produced water to form magnesium hydroxide ($\text{Mg}(\text{OH})_2$) such that silica in the produced water is adsorbed onto the $\text{Mg}(\text{OH})_2$.
 3. The method of claim 1 wherein chemically softening the produced water comprises reducing hardness from the produced water by mixing calcium hydroxide ($\text{Ca}(\text{OH})_2$) with the produced water such that carbon dioxide (CO_2), calcium bicarbonate ($\text{Ca}(\text{HCO}_3)_2$), and magnesium bicarbonate ($\text{Mg}(\text{HCO}_3)_2$) in the produced water react with the $\text{Ca}(\text{OH})_2$ to precipitate calcium carbonate (CaCO_3) and magnesium hydroxide ($\text{Mg}(\text{OH})_2$).
 4. The method of claim 1 wherein chemically softening the produced water comprises reducing hardness in the produced water by:
 - a. mixing $\text{Ca}(\text{OH})_2$ with the produced water such that magnesium sulfate (MgSO_4) and magnesium chloride (MgCl_2) in the produced water react with the $\text{Ca}(\text{OH})_2$ to precipitate magnesium hydroxide ($\text{Mg}(\text{OH})_2$); and
 - b. mixing Na_2CO_3 with the produced water such that calcium sulfate (CaSO_4) and calcium chloride (CaCl_2) in the produced water react with the Na_2CO_3 to precipitate CaCO_3 .
 5. The method of claim 1 wherein chemically softening the produced water comprises adding a caustic to the produced water.

6. The method of claim 5 wherein adding the caustic to the produced water comprises adding sodium hydroxide (NaOH) to the produced water.
7. The method of claim 1 further comprising cooling the produced water by directing the produced water through a heat exchanger disposed downstream from the filtration membrane and upstream from the reverse osmosis unit.
8. The method of claim 7 wherein cooling the produced water further comprises reducing the temperature of the treated water stream to 95°F or lower.
9. The method of claim 1 further comprising directing the produced water to a degasification unit and removing dissolved gases in the produced water prior to chemically softening the produced water.
10. The method of claim 1 further comprising directing the produced water to a gas flotation unit and removing total organic carbon in the produced water prior to chemically softening the produced water.
11. The method of claim 10 further comprising prior to chemically softening the produced water:
 - a. adding an acid to the produced water such that carbonates and bicarbonates in the produced water are converted into CO₂;
 - b. adding ferric chloride (FeCl₃) to the produced water to form Fe(OH)₃ such that carbon in the produced water is adsorbed onto the Fe(OH)₃;
 - c. adding a polymer to the produced water;
 - d. directing gas upwardly through the produced water such that suspended solids in the produced water move upwardly toward the surface of the produced water; and
 - e. removing the suspended solids from the produced water.
12. The method of claim 1 further comprising adsorbing free oil onto the crystals in the mixing tank.

13. The method of claim 11 further comprising cooling the produced water by directing the produced water through a heat exchanger disposed downstream from the filtration membrane and upstream from the reverse osmosis unit.
14. The method of claim 13 wherein cooling the produced water further comprises reducing the temperature of the treated water stream to 95°F or lower.
15. The method of claim 13 further comprising directing the produced water to a gas flotation unit and removing total organic carbon in the produced water prior to chemically softening the produced water.
16. The method of claim 13 further comprising directing the produced water to a degasification unit and removing dissolved gases in the produced water prior to chemically softening the produced water.
17. The method of claim 1 including raising the pH of the produced water to a range of 10.5 to 11.5.
18. A method of recovering oil or gas from an oil or gas well and treating resulting produced water, comprising:
 - a. recovering an oil/water or gas/water mixture from the oil or gas well;
 - b. separating oil from the oil/water mixture or separating gas from the gas/water mixture to produce an oil or gas product and the produced water, and wherein the produced water includes organics, silica, hardness, dissolved solids and suspended solids;
 - c. reducing hardness in the produced water by chemically softening the produced water which results in the formation of hardness precipitants;
 - d. raising the pH of the produced water to 10.5 and above;
 - e. directing the produced water having said pH of 10.5 and above to a mixing tank and mixing the produced water in said mixing tank and causing crystallization of the precipitants within the produced water;
 - f. after crystallization, removing free oil and crystals from the produced water by directing the produced water through a ceramic membrane and producing a ceramic membrane effluent and a reject stream containing free oil and the crystals;

- g. recirculating at least a portion of the reject stream to the mixing tank and causing the crystals in the reject stream to grow larger;
- h. directing the ceramic membrane effluent to an ion exchange unit and further softening the membrane effluent by removing residual calcium and magnesium hardness therefrom and producing an ion exchange effluent and a waste stream;
- i. after further softening the ceramic membrane effluent, directing the ion exchange effluent to a reverse osmosis unit and removing dissolved solids from the ion exchange effluent and producing a permeate stream containing ammonium hydroxide and a reject stream;
- j. reducing the concentration of ammonium hydroxide contained in the permeate stream by directing the permeate stream from the reverse osmosis unit through a cation exchange resin such that hydrogen ions in the cation exchange resin are exchanged with ammonium ions in the ammonium hydroxide;
- k. after reducing the concentration of the ammonium hydroxide contained in the permeate stream, adding a caustic to the permeate stream and raising the pH of the permeate stream to between about 6.5 to about 9;
- l. after reducing the concentration of ammonium hydroxide, oxidizing the organic content in the permeate stream;
- m. wherein oxidizing the organic content comprises mixing hydrogen peroxide (H_2O_2) with the permeate stream and irradiating the H_2O_2 with ultraviolet radiation to produce hydroxyl radicals ($HO\cdot$) that oxidize the organic content in the permeate stream; and
- n. after oxidizing the organic content in the permeate stream, adding a sodium bisulfite solution to the permeate stream to remove residual H_2O_2 from the permeate stream.

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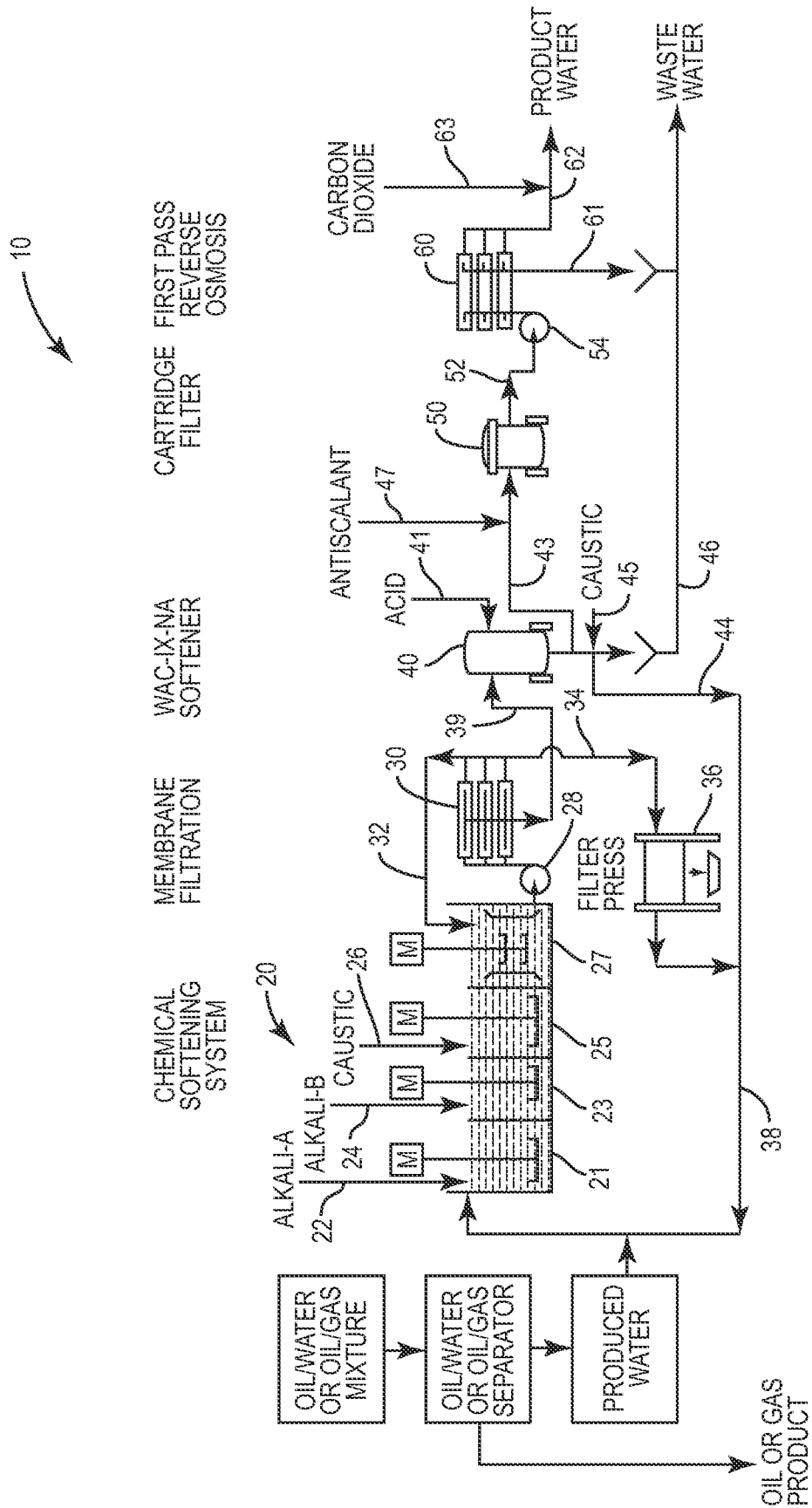


FIG. 1

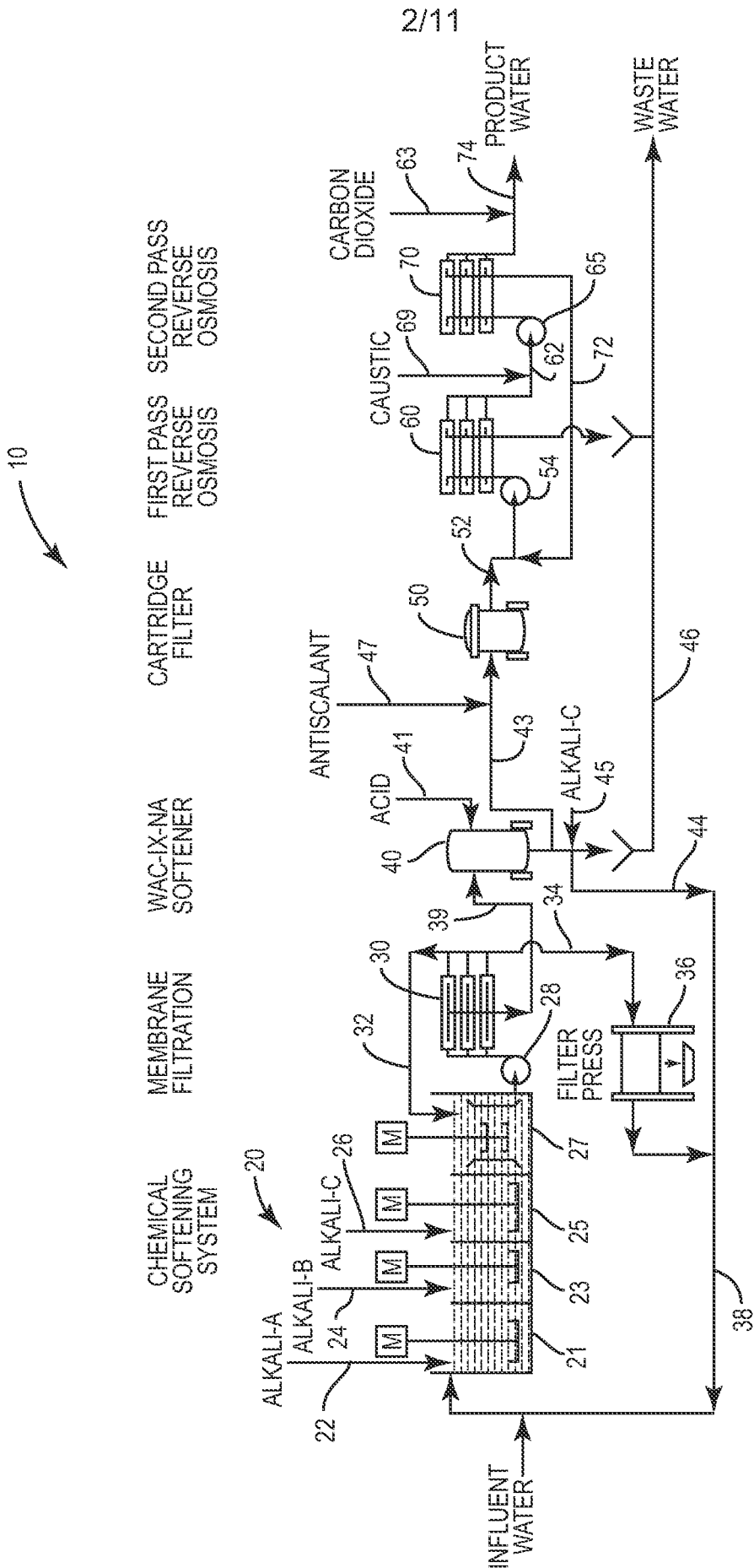


FIG. 2

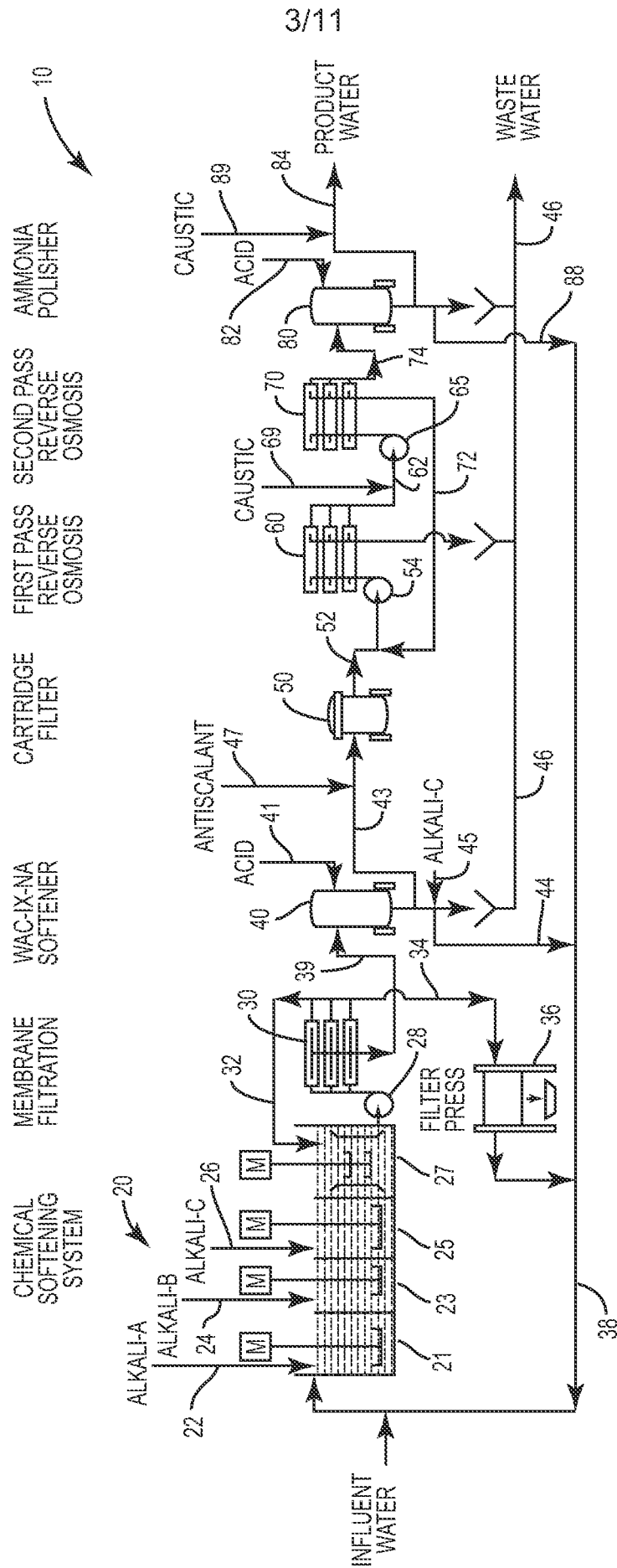


FIG. 3

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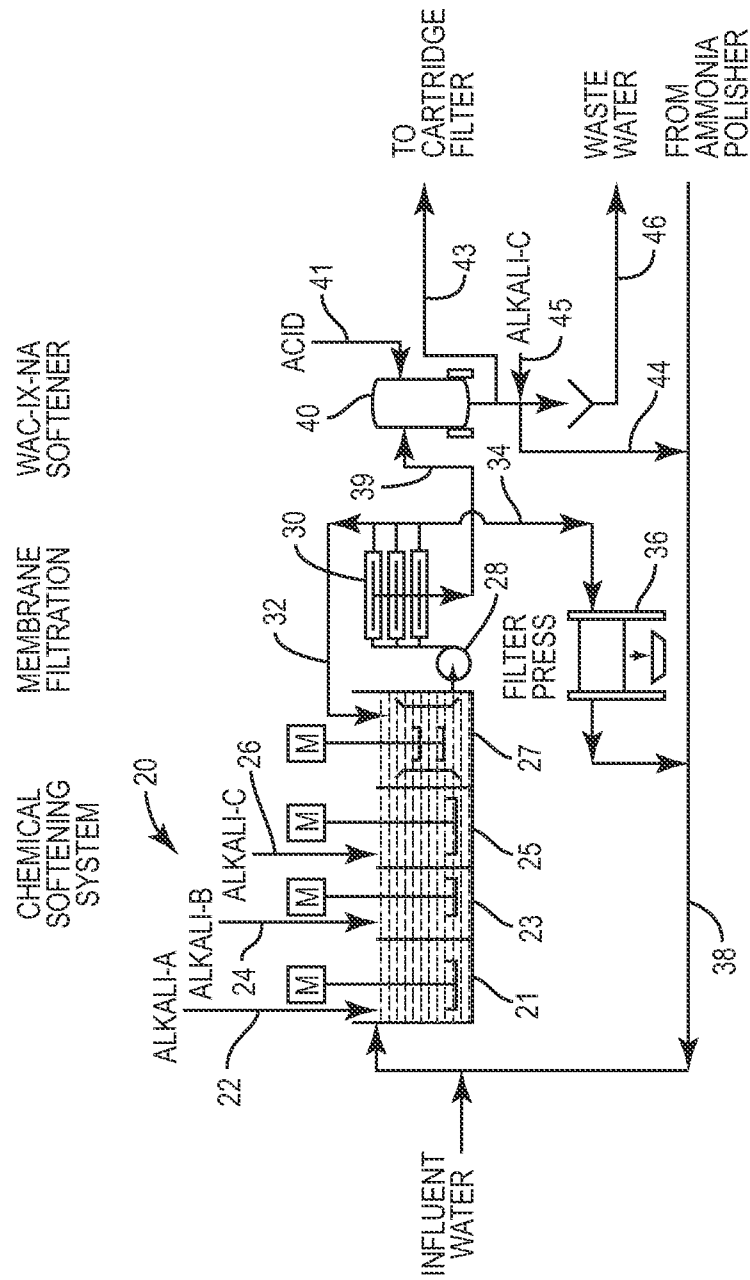


FIG. 4A

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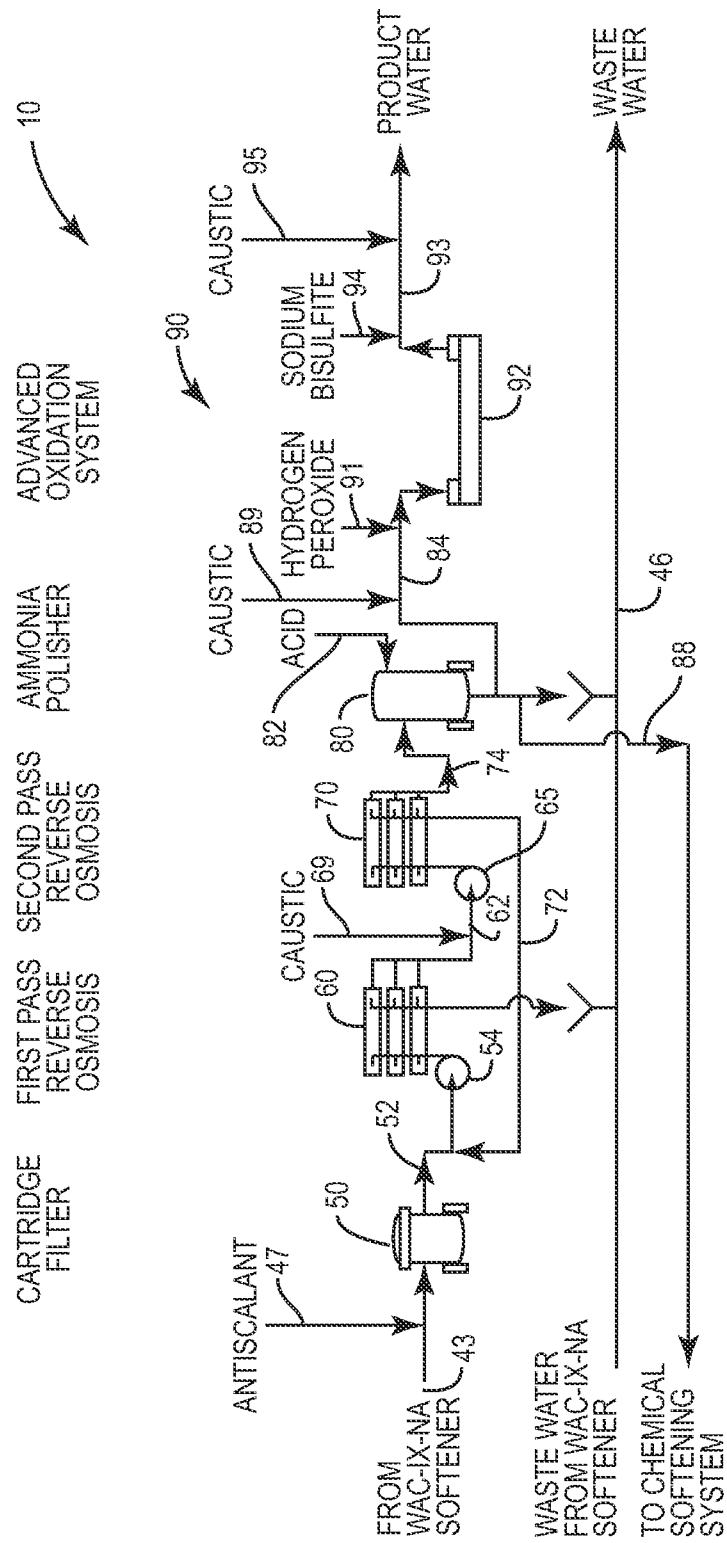


FIG. 4B

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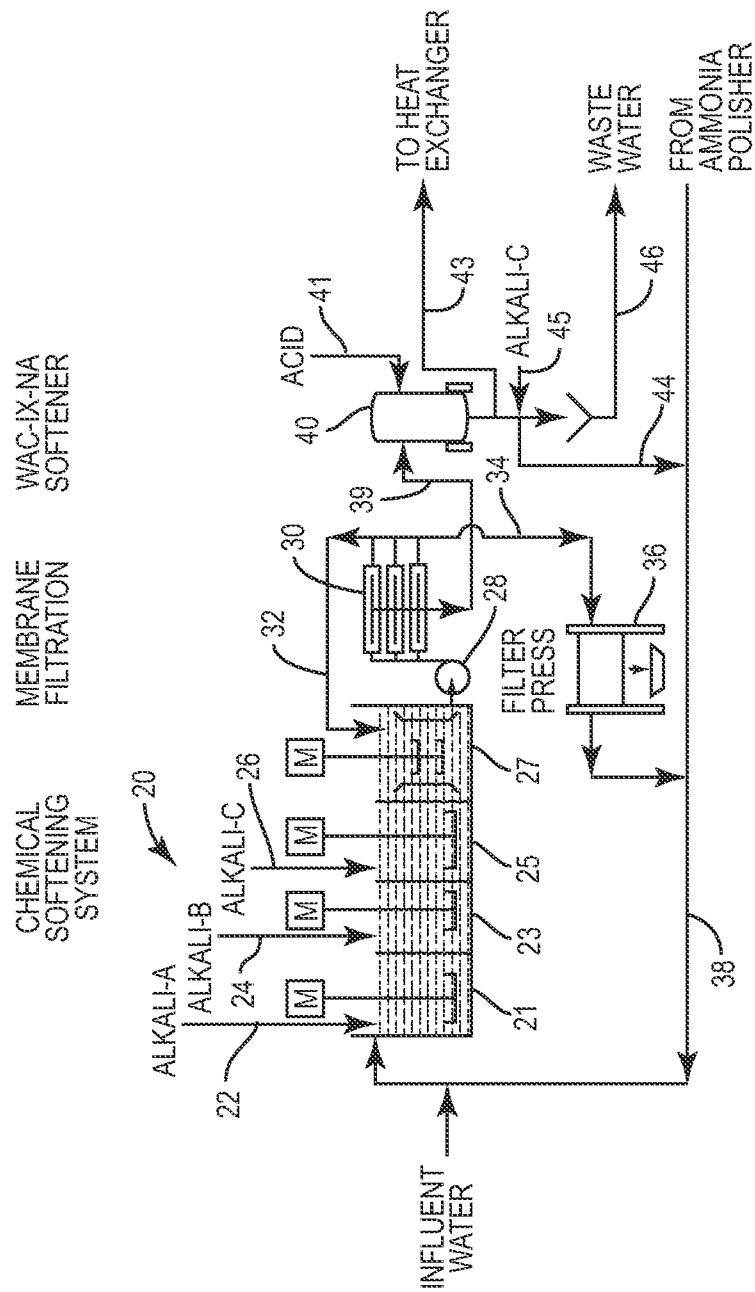


FIG. 5A

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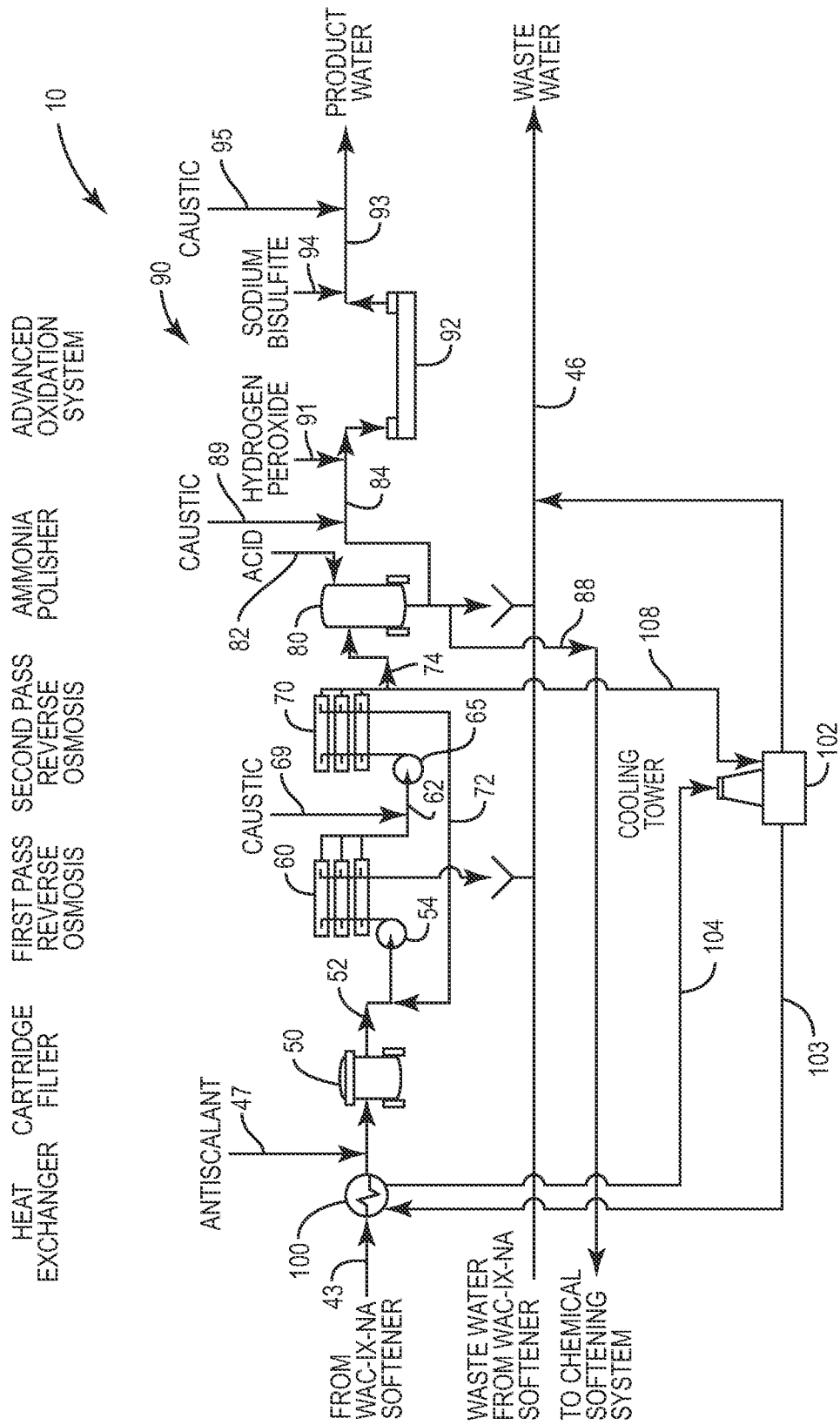


FIG. 5B

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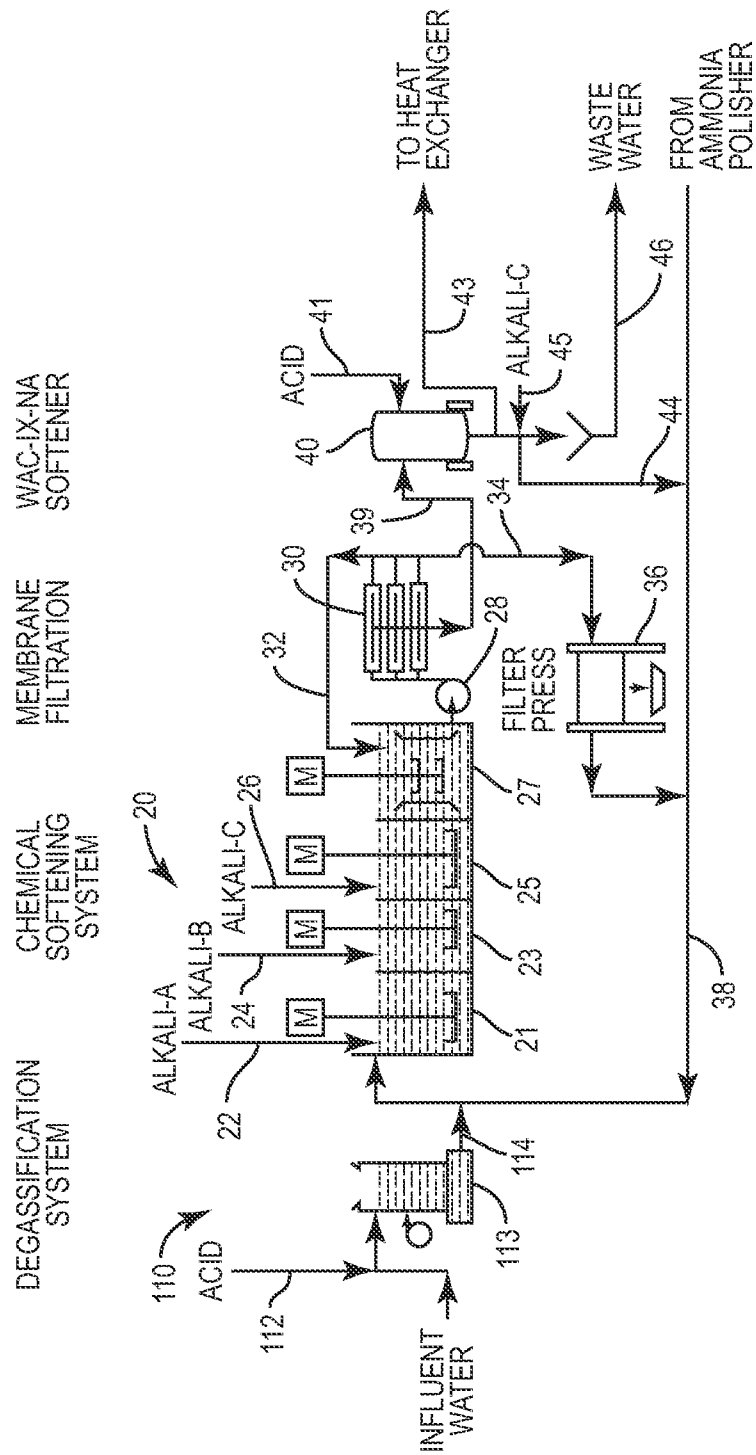


FIG. 6A

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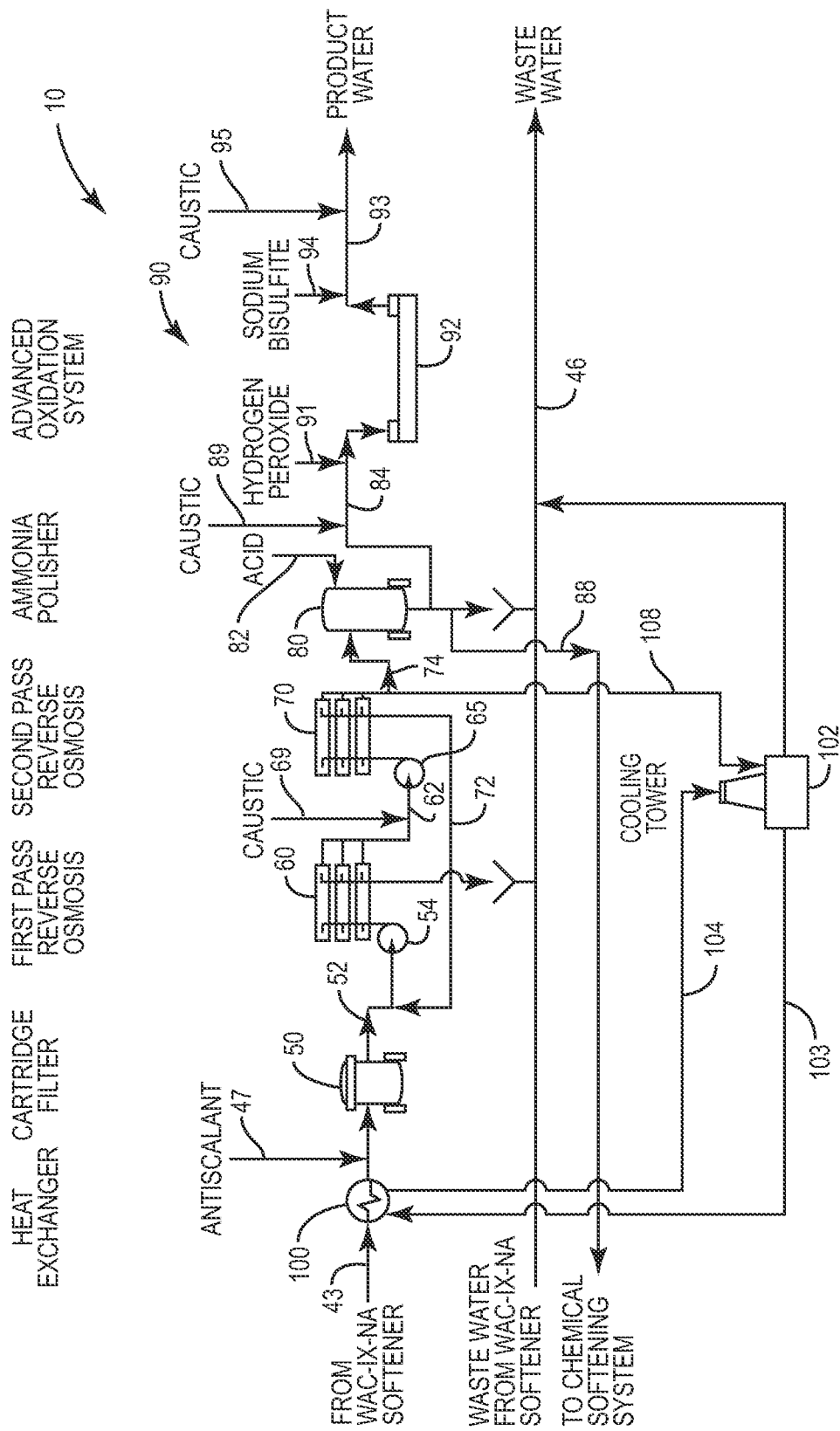


FIG. 6B

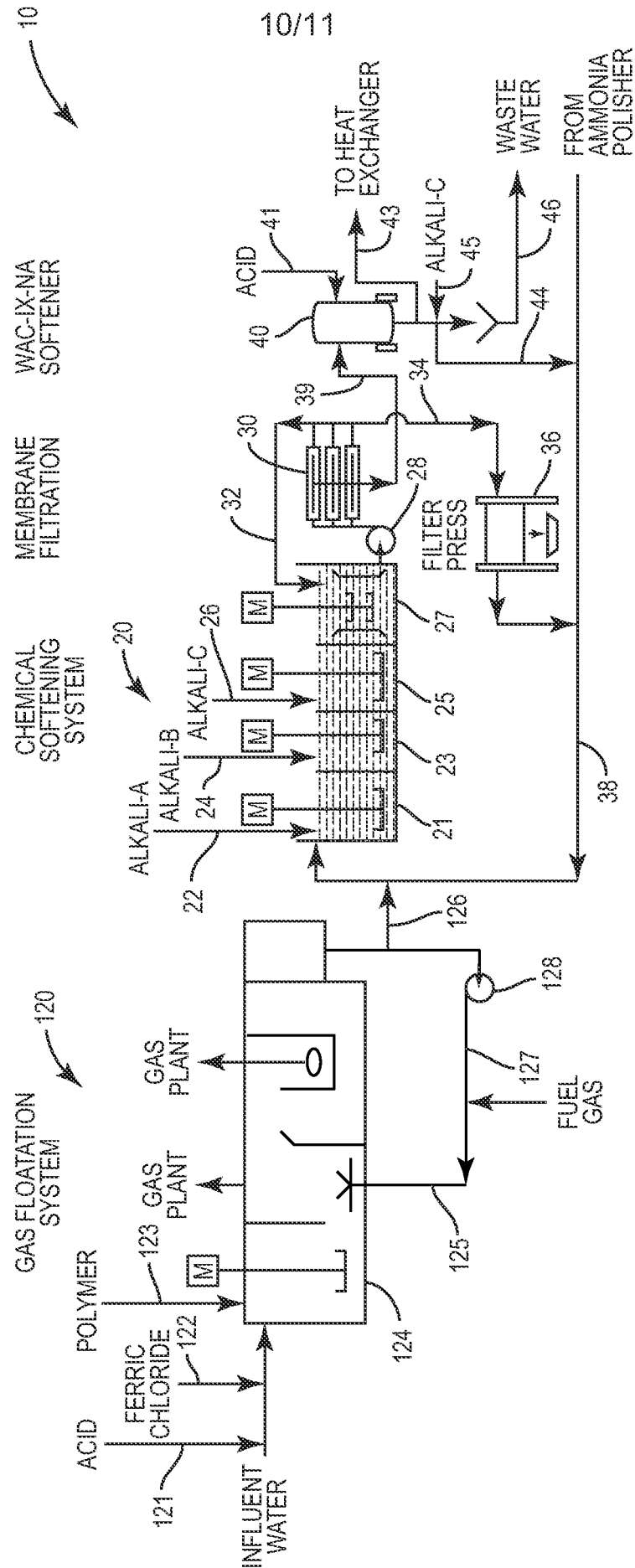


FIG. 7A

11/11

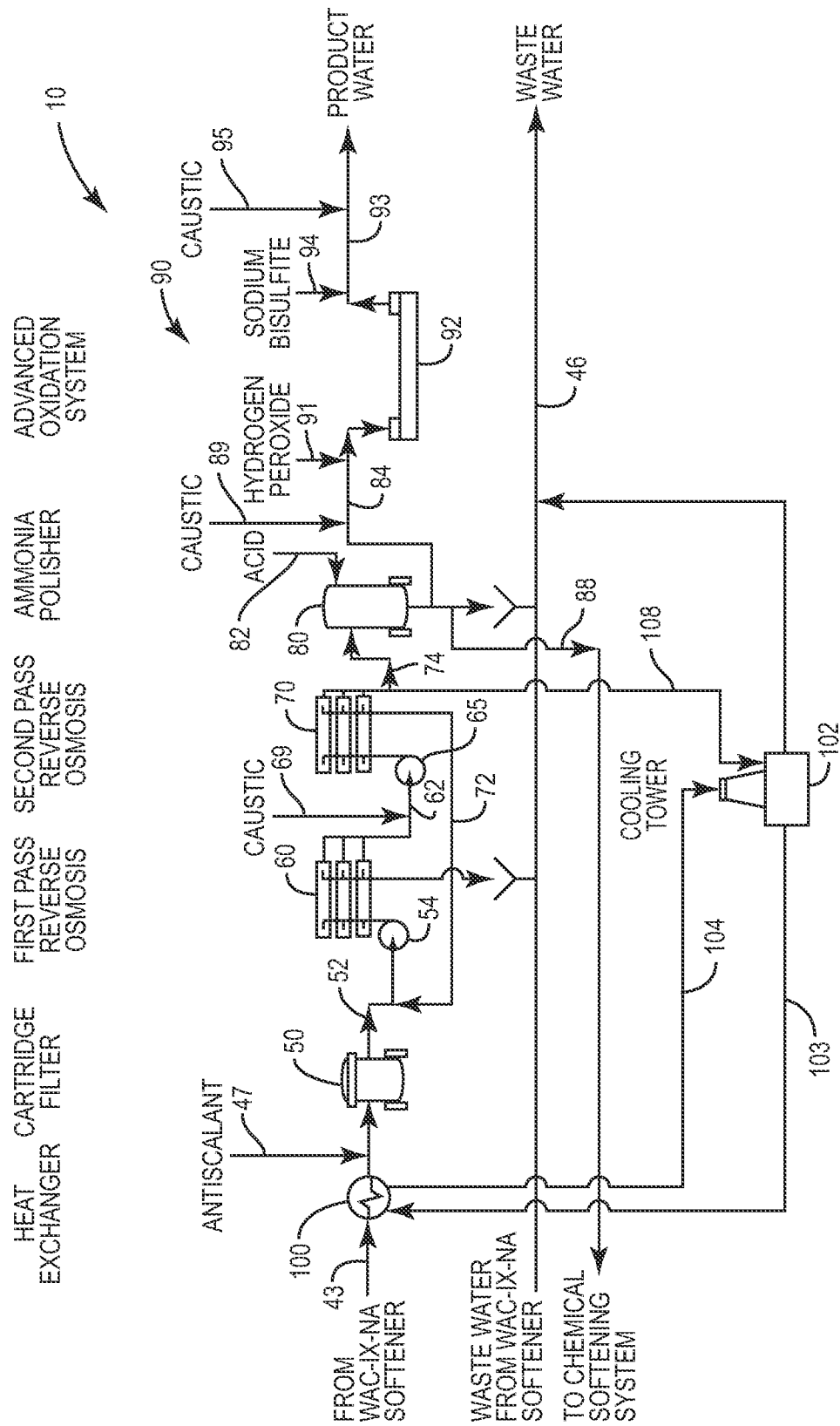


FIG. 7B

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CHEMICAL
SOFTENING
SYSTEM

MEMBRANE
FILTRATION

WAC-IX-NA
SOFTENER

CARTRIDGE
FILTER

FIRST PASS
REVERSE
OSMOSIS

