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(54) Titre : SYSTEMES ET PROCEDES DE SEPARATION ET D'ISOLEMENT D'EAU ET D'AUTRES CONSTITUANTS SOUHAITES A PARTIR DE SAUMURES PRODUITES DANS DES CHAMPS PETROLIFERES POUR REUTILISATION

(54) Title: SYSTEMS AND METHODS OF SEPARATING AND ISOLATING WATER AND OTHER DESIRED CONSTITUENTS FROM OILFIELD PRODUCED BRINES FOR REUSE

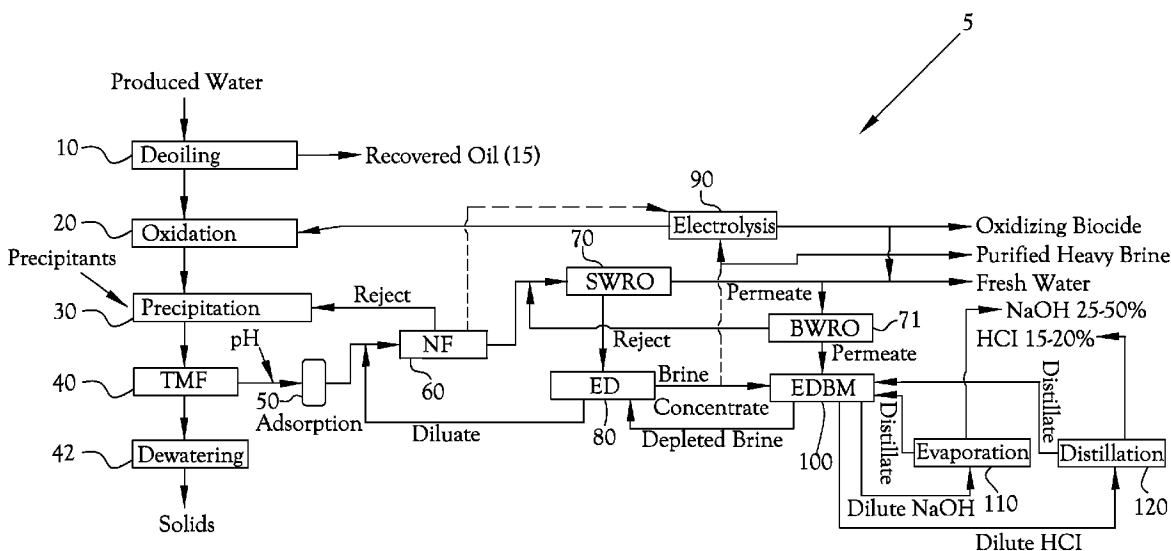


Fig.1

(57) **Abrégé/Abstract:**

An integrated, membrane-based process to produce purified water and conversion of salt to high value chemicals from oil and gas well produced water is described. A liquid stream including water and dissolved salt is flowed through pretreatment units and one or more desalination and concentration units which remove at least a portion of the water to form a brine enriched in dissolved salt. The purified high-density brine may be subjected to electrically- enforced salt dissociation techniques to produce chemicals from oil and gas produced water.

WO 2019/168804 A1

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**Systems and Methods of Separating and Isolating Water and
Other Desired Constituents from Oilfield Produced Brines for Reuse**

REFERENCE TO RELATED APPLICATIONS

5 **[0001]** This application claims the benefit of U.S. Provisional
Application No. 62/636,962 entitled “Systems and Methods Separating and
Isolating Water and Desired Constituents from Oilfield Produced Brines for
Reuse” filed March 1, 2018, which is incorporated by reference in its
entirety.

BACKGROUND

10 **[0002]** Discovery of large reserves of oil and gas in shale formations has
been a major positive development for the energy picture of the U.S.
Hampering the full potential of these valuable resources to be realized are
the complications arising from the water produced along with the recovered
15 oil and gas. The separation of this produced water from the recovered oil
and gas and the subsequent handling, treatment, and safe disposal of the
produced water in combination represent serious challenges facing the oil
and gas production industry.

20 **[0003]** Produced water includes the water trapped in underground
formations that is brought to the surface along with oil or gas, water injected
into the formations, and any chemicals added to the water during drilling,
production, and treatment. Because at least some portion of the produced
water has been in contact with the hydrocarbon-bearing formation for
centuries, the water contains some of the chemical characteristics of the
25 formation and the hydrocarbon itself. Produced water also may be referred
to as “formation water” or “brine”, as the water often has a high salt
content.

[0004] The major constituents of concern in produced water are salt,
oil and grease, inorganic or organic compounds naturally occurring in the

formation, and chemical additives used in the drilling, hydraulic fracturing, and operation of the well. Produced water is by far the largest volume byproduct or waste stream associated with oil and gas exploration and production.

5 **[0005]** The physical and chemical properties of produced water vary considerably depending on the geographic location of the field, the geological host formation, and the type of hydrocarbon product being produced from the well. Produced water properties and volume also vary throughout the production lifetime of a well. High salinity arising from sodium chloride
10 (NaCl) and high hardness levels arising from combinations of magnesium (Mg), calcium (Ca), strontium (Sr), and barium (Ba) are common. Sodium chloride is typically the predominant salt in the produced water.

[0006] The hydraulic fracturing of a well often requires from 2 to 10 million gallons of water. Oxidizing biocides, hydrochloric acid (HCl), and
15 caustic soda (NaOH) are widely used chemicals for oil and gas exploration and hydrocarbon recovery and are thus found in the produced water. Thus, the produced water from a single well can include these chemicals and have a volume in the millions of gallons.

[0007] Despite considerable efforts and investment, presently there are
20 no cost-effective technological solutions available to reduce the huge disposal cost of highly saline produced water from wells. Saltwater desalination technologies can reduce the volume, but do not eliminate the need for disposal of the concentrated brine, which presents significant costs and challenges. Furthermore, conventional ion exchange based water-
25 softening processes are designed for relatively low levels of hardness and not practical for use in softening deep formation produced water with elevated hardness levels and salinities. Furthermore, any presence of iron, manganese, oil, grease, and/or organic matter tends to create serious fouling of conventional ion exchange resins. Ion exchange processes also

require removal of suspended solids to prevent plugging or fouling, another disadvantage in the produced water context.

[0008] Chemical precipitation is a widely used technology for the removal of metals and other inorganics, suspended solids, fats, oils, greases, and some other organic substances from wastewater. The three most common chemical precipitative softening alternatives include lime softening, lime-soda ash softening, and caustic softening. The selection of one of these alternatives is generally based on cost, water quality and owner and operator preferences.

[0009] Water hardness is caused primarily by the dissolution of calcium and magnesium carbonate and bicarbonate compounds in water. Lime (calcium oxide) when added to hard water, reacts to form calcium carbonate, which itself can act as a coagulant, sweeping ions out of solution. Once rendered insoluble, the metal ions will tend to precipitate, thus softening the water. Lime softening facilitates the removal of heavy metals, radioactive elements, and other toxins such as radium 226 & 228, uranium, and arsenic. Lime softening also eliminates iron, manganese, silica and fluoride, as well as certain organic compounds. However, to work effectively precipitation with lime alone requires a great deal of lime.

[0010] Lime softening is typically used for water containing low concentrations of non-carbonate hardness. Lime-soda softening may be required with high concentrations of non-carbonate hardness. Caustic soda softening is typically used when the treated water has inadequate carbonate hardness to react with lime. The treatment process using caustic soda follows the same steps as that of lime-soda ash softening. Compared with lime softening, caustic soda softening has the advantages of stability in storage, lower sludge formation, and easy handling.

[0011] Caustic soda is mainly produced in the chloralkali process by the electrolysis of sodium chloride (NaCl) with concomitant chlorine gas production. Although HCl cannot be directly synthesized in this process

from the concomitant chlorine gas, HCl can be formed by oxidizing the chlorine gas with the hydrogen gas produced at the cathode of the NaCl electrolysis. Thus, NaCl can provide the basis to form both NaOH and HCl.

[0012] However, the transport, storage and handling of concentrated oxidizers, HCl, and NaOH come with serious safety concerns for the industry. Furthermore, in most cases these chemicals are used at relatively low concentrations thus transporting the large amount of water required for low concentration solutions is difficult and costly.

[0013] As can be seen from the above description, there is an ongoing need for simple and efficient systems and methods to separate the water from produced water and to recover the non-water constituents from the produced water for reuse. It also would be advantageous to convert the recovered non-water constituents to chemicals that could be used onsite. The systems and methods of the present invention overcome at least one of the disadvantages associated with conventional produced water treatment.

SUMMARY

[0014] In one aspect, the invention provides a method of processing hydrocarbon produced water, where the method includes deoiling the hydrocarbon produced water to provide a deoiled feed stream; introducing an oxidant to the deoiled feed stream to provide an oxidized feed stream; precipitating the oxidized feed stream to provide a precipitated slurry; passing the precipitated slurry through a tubular membrane filter unit to produce a permeate ; reducing the pH of the permeate to provide a reduced pH permeate ; passing the reduced pH permeate through a nanofiltration membrane unit to produce a NF permeate and a NF reject; passing the NF permeate to one of an electrolysis cell, a seawater reverse osmosis membrane, and both the electrolysis cell and the seawater reverse osmosis membrane, where the electrolysis cell provides the oxidant, and where the seawater reverse osmosis membrane provides freshwater and a concentrated sodium chloride retentate; passing the concentrated sodium chloride

retentate to an electrodialysis device including univalent anion and univalent cation membranes and electrodes to produce a diluate depleted in sodium chloride and a sodium chloride concentrate; passing the diluate to the nanofiltration membrane unit; passing at least a portion of the sodium chloride concentrate to one of a bipolar membrane electrodialysis unit, the electrolysis cell, and both the bipolar membrane electrodialysis unit and the electrolysis cell; and generating a hydrochloric acid stream and a sodium hydroxide stream from the bipolar membrane electrodialysis unit.

[0015] In another aspect of the invention, there is a method of processing hydrocarbon produced water, where the method includes deoiling the hydrocarbon produced water to provide a deoiled feed stream; introducing an oxidant to the deoiled feed stream to provide an oxidized feed stream; transferring the oxidized feed stream to a partially complete precipitation and to a substantially complete precipitation; where the substantially complete precipitation precipitates the oxidized feed stream to provide a precipitated slurry, and the partially complete precipitation precipitates the oxidized feed stream to remove from 10% to 95% by weight of total hardness in the oxidized feed stream to provide a less-concentrated precipitated slurry; passing the precipitated slurry from the complete precipitation through a first tubular membrane filter unit to produce a permeate ; passing the less-concentrated precipitated slurry from the partially completed precipitation through a second tubular membrane filter unit to produce a hydraulic fracturing brine; reducing the pH of the permeate to provide a reduced pH permeate ; passing the reduced pH permeate through a first nanofiltration membrane unit to produce a NF permeate and a NF reject; passing the NF permeate to an electrolysis cell, where the electrolysis cell provides the oxidant.

[0016] Other systems, methods, features and advantages of the invention will be, or will become, apparent to one with skill in the art upon examination of the following figures and detailed description. It is intended that all such additional systems, methods, features, and advantages be

included within this description, be within the scope of the invention, and be protected by the claims that follow. The scope of the present invention is defined solely by the appended claims and is not affected by the statements within this summary.

5 **BRIEF DESCRIPTION OF THE FIGURES**

[0017] The invention can be better understood with reference to the following drawings and description. The components in the figures are not necessarily to scale, emphasis instead being placed upon illustrating the principles of the invention.

10 **[0018]** FIG. 1 represents a system for treating produced water having a low (<40 g/L) concentration of total dissolved solids (TDS).

[0019] FIG. 2 represents a system for treating produced water having a high (≥ 40 g/L) concentration of total dissolved solids (TDS).

15 **[0020]** FIG. 3 provides the initial TDS and contaminant content, intermediate treatment content, and percent TDS removal from produced water obtained during production at the DJ Basin.

20 **[0021]** FIG. 4 provides the initial TDS and contaminant content, intermediate treatment content, and percent TDS removal from produced water obtained during flowback (60-90 days after hydraulic fracturing) at the DJ Basin.

[0022] FIG. 5 provides the initial TDS and contaminant content, intermediate treatment content, and percent TDS removal from produced water obtained during production at the DJ Basin.

25 **[0023]** FIG. 6 provides the initial TDS and contaminant content, intermediate treatment content, and percent TDS removal from produced water obtained during production at the Permian Basin.

[0024] FIG. 7 provides the initial TDS and contaminant content, intermediate treatment content, and percent TDS removal from produced water obtained during production at the Ardmore Basin.

[0025] FIG. 8 provides the initial TDS and contaminant content,
5 intermediate treatment content, and percent TDS removal from produced water obtained during production at the Williston Basin.

DETAILED DESCRIPTION

[0026] Systems and methods are described that remove at least a
10 portion of contaminants such as oil, suspended solids, scale-forming ions, and volatile organic material from produced water to provide a partially treated brine stream for reuse in oil and/or gas extraction processes. A portion of the partially treated brine stream may undergo desalination to produce fresh water and concentrated brine. The systems and methods may
15 be configured to produce a sterile, substantially particle free brine; a concentrated heavy brine; in some embodiments an ultra-high purity brine; an oxidizing biocide; HCl; NaOH; and fresh water. The chemicals produced may be used in hydraulic fracturing, stimulation in oil and gas extraction, or other industrial applications. When desalination is used, the fresh water
20 produced may be used for irrigation, industrial use, and/or other applications.

[0027] FIG. 1 represents a system **5** for treating produced water having a low (<40 g/L) concentration of total dissolved solids (TDS). The produced water from the well enters deoiling **10** to produce recovered oil **15** and a
25 deoiled feed stream. The deoiling function is provided by gravity separation methods as known in oil and gas industry, or through other methods known in the art. Produced water may enter the deoiling **10** from a two or three phase separator, a free water knockout, a gun barrel, a heater treater,

hydro-cyclone, or other primary separation unit process for hydrocarbon removal.

[0028] The deoiled feed stream is then passed to oxidation **20** where an oxidant is introduced to the deoiled feed stream. The oxidant is in the form of a mixed oxidant generated from undivided or divided electrolysis cell **90**. Undivided electrolysis cells produce an oxidant strength of 0.01-0.25 % as Cl_2 by weight, while membrane divided electrolysis cells produce Cl_2 at 5-12% by weight concentration – thus at least three orders of magnitude higher. Undivided electrolysis cells are generally fed seawater strength brine while membrane divided cells are generally fed a near saturation strength brine.

[0029] Purified, halogen-containing brine generated by the system **5** is fed to the electrolysis cell **90** for enhanced oxidation or reduction. In the event of an undivided electrolysis cell **90**, the seawater strength brine is obtained from the NF **60**, as discussed further below. In the event of a divided electrolysis cell **90**, the near saturation brine is obtained from the ED **80**, as discussed further below.

[0030] The enhanced oxidation or reduction provided by the electrolysis cell **90** destructs contaminants in either brine and generates a liquid with a significantly enhanced oxidation potential. The enhanced oxidation potential liquid serves as an oxidant in the oxidation **20** and as an oxidizing biocide. In addition to producing sodium hypochlorite for direct use as an oxidizing biocide, the produced sodium hypochlorite may be combined with the produced HCl to generate a first reaction product and then introducing sodium chlorite from an outside source to form a product stream comprising chlorine dioxide (ClO_2) and free available chlorine.

[0031] There are two basic types of electrolysis (electrolytic) cells, namely divided cells and undivided cells. In both cell types, certain ions may travel between the electrodes. In a divided cell, the cathode and anode sides of the cell are separated (divided) in some manner such that most or

all of the reactants and products on each side of the cell are kept separate. In the undivided cells, the cathode and anode sides of the cell are not separated (undivided) and the reactants and products on each side of the cell can mix. Suitable electrolysis cells are sold, for example, by De Nora,
5 Japan, as electrochlorination systems.

[0032] After the oxidation **20**, the resulting oxidized feed stream is introduced to precipitation **30** to soften the oxidized feed stream. A modified lime-soda precipitation may be used to soften the oxidized feed stream. The modified lime-soda precipitation process may be preferred as conventional
10 lime methods often require large amounts of lime and conventional caustic soda softening cannot remove as many contaminants as lime. Thus, the modified process includes lime, but also introduces caustic (NaOH) from the EDBM unit **100**. Depending on the produced water, conventional softening agents including lime-softening, lime-soda ash softening, and caustic
15 softening may be used. The precipitation **30** preferably includes the use of mechanical agitators to disperse the reagents more effectively into the oxidized feed stream and to maintain precipitated solids in suspension to enhance agglomeration of small precipitates into larger precipitates.

[0033] After the precipitation **30**, the resulting concentrated sodium
20 chloride containing ultra-high purity brine slurry is introduced to tubular membrane filter unit (TMF) **40**, where the concentrated slurry is preferably overdosed from a stoichiometric perspective with additional precipitating agent, such as lime, soda ash, and/or caustic soda (NaOH), to enhance precipitation. Stoichiometric overdosing is preferred because chemical
25 equilibriums require more than the stoichiometric quantity of the reagents to drive the precipitation reaction near completion. Barium removal by sulfate precipitation also may be performed in precipitation **30** and/or TMF **40**.

[0034] The TMF **40** uses a semipermeable tubular membrane including
30 sub-micron filtration media – thus a filtration membrane having a pore size

of less than 1 micron. The permeate from the concentrated slurry of the precipitation **30** is received into the tubes of the tubular membrane from the outside of the tubular membrane and includes less dissolved solids than would be predicted by the solubility limits of the dissolved solids.

5 **[0035]** The semipermeable tubular membrane of the TMF **40** is preferably a polymeric polyvinylidene fluoride (PVDF) or polyethylene (PE) membrane having an absolute pore size of 0.05 to 0.1 microns. Such tubular PVDF membranes are available from Porex Filtration, Fairburn, GA, for example. While less preferred, a ceramic membrane of similar pore size
10 range may be used in the TMF **40**.

[0036] The semipermeable tubular membrane may be cleaned of surface precipitates with the dilute HCl solution produced by EDBM **100**. The dilute HCl solution may be circulated through the TMF **40** membrane until the precipitate is dissolved to an acceptable level. In the event the TMF
15 **40** membrane fouls with organic compounds, the membrane may be cleaned by circulating the sodium hypochlorite solution generated in the electrolysis cell **90** through the membrane until acceptable flow through the membrane is restored.

[0037] When the TMF **40** has concentrated the solids to an acceptable
20 level from the concentrated slurry, the solids are transferred to dewatering **42**. The solids include residue created from the precipitation **30** and may be very high in calcium carbonate or a mixture of calcium carbonate and magnesium hydroxide. The dewatering **42** is preferably performed with a filter press. However, lagooning, vacuum filtration, or centrifugation also
25 may be used.

[0038] The permeate from the TMF **40** is sterile and substantially particle free and will generally have a pH greater than 10, which needs to be reduced. Preferably, the HCl generated from EDBM **100** may be used to reduce the pH of the permeate. Less preferably, carbon dioxide or a mineral
30 acid may be used.

[0039] In combination the precipitation **30** and the TMF **40** can remove a broad range of dissolved contaminants to acceptable levels. The removed contaminants include Ca, Mg, Ba, Sr, Fe, Mn, Cu, Zn, Al, Si, total organic carbon (TOC), oil, grease, and suspended solids.

5 [0040] Once the pH of the TMF **40** permeate is reduced, the reduced pH permeate is transferred to adsorption **50**. The adsorption **50** dechlorinates the permeate to prevent oxidation of the later NF **60** and SWRO **70** membranes. The adsorption **50** preferably includes granular carbon to dechlorinate the permeate. Alternatively, powdered activated
10 carbon may be added to the concentrated lime slurry before transferring to the TMF **40**. Alternatives to the granular carbon include chemical reducing agents, such as sodium metabisulfite and ascorbic acid. More preferably, a combination of granular carbon and a chemical reducing agent is used in the adsorption **50**.

15 [0041] The dechlorinated permeate from **50** is then transferred to a nanofiltration membrane unit (NF) **60**. The NF **60** is used under pressure to selectively change the concentration of one solute, such as sodium chloride having monovalent ions, from another solute, such as sodium sulfate having multivalent ions. The NF **60** allows for the substantial removal of sulfate,
20 phosphate, calcium, magnesium, aluminum, and silica monovalent and divalent ions from the dechlorinated permeate.

[0042] The NF **60** membrane is structurally similar to a reverse osmosis (RO) membrane, however, unlike RO membranes, the NF **60** membrane is characterized by a larger pore size in the "skin layer" and a net
25 negative electrical charge inside the individual pores of the NF membrane. This negative charge is responsible for rejection of anionic species, according to the anion surface charge density. Accordingly, divalent anions, such as sulfate (SO₄), are more strongly rejected than monovalent anions, such as Cl⁻. NF membranes are available from Dow as part of the FILMTEC™ NF90
30 and NF270 series, for example.

[0043] The nanofiltration performed by the NF **60** membrane is characterized by a fractionation capacity for organic solutes with a molecular "cut-off" range of about 300 g/mol; and a fractionation capacity for multivalent vs. monovalent ions, which is especially pronounced for anions. The sulfate containing concentrate (reject or retentate from the NF **60**) is returned to the precipitation **30** to enrich/enhance (calcium and barium sulfate) precipitant growth.

[0044] The permeate from the NF **60** is then transferred to the electrolysis cell **90** if an undivided cell, or to SWRO **70** where sodium chloride and purified water are recovered. The SWRO **70** is a conventional seawater reverse osmosis (RO) membrane. Such SWRO membranes are available from DOW as part of the FILMTEC™ SW30 series, for example.

[0045] SWRO is generally accepted as the most economical and energy-efficient method for desalination of highly saline water. Modern SWRO membranes have high salt rejection and are capable of producing potable water, <500 ppm salinity, from seawater (nominally 35 g/L) in a single pass through the membrane. Modern SWRO systems are capable of achieving up to 50% recovery of fresh water from seawater. With 50% recovery, the salinity of the concentrated brine (reject/retentate) increases to about 70 g/L.

[0046] A first portion of the permeate lacking concentrated sodium chloride from the SWRO **70** is passed to brackish water RO membrane (BWRO) **71**. The BWRO further reduces salinity for use in EDBM **100** or for cooling water makeup. Such BWRO membranes are available from DOW as part of the FILMTEC™ LE and BW30 series, for example. A second portion of the permeate lacking concentrated sodium chloride from the SWRO **70** is considered fresh water.

[0047] The reject/retentate including concentrated sodium chloride from the SWRO **70** is passed to an electrodialysis device (ED) **80** that includes univalent anion and univalent cation selective membranes. The ED

80 includes a pair of electrodes (anode and cathode) and has a plurality of membranes, with at least one electrodialysis membrane being a univalent anion-selective membrane and another electrodialysis membrane being a univalent cation-selective membrane. The plurality of alternating anion-permeable and cation-permeable membranes are disposed between the anode and the cathode to form a series of alternating dilute and concentrate channels between the alternating membranes. The anion-permeable membranes allow the passage of anions through the membrane, while the cation-permeable membranes allow the passage of cations through the membrane. In combination, these membranes separate the reject/retentate into a diluate that is depleted in sodium chloride and a concentrate that is concentrated in sodium chloride. The concentrate may be considered a “heavy brine” having a from 1.1 to 1.2 kg/L salt concentration. Suitable ED’s sold under the Acilyzer ED name may be obtained from Astom, Japan, for example.

[0048] The diluate from the ED **80** is recycled to the NF **60** and at least a first portion of the ED concentrate is transferred to the electrolysis cell **90** in the event the electrolysis cell **90** is divided, while a second portion of the ED concentrate is transferred to the EDBM **100**. The bipolar membrane electrodialysis unit (EDBM) **100** converts the sodium chloride into a dilute sodium hydroxide (NaOH) solution and a dilute hydrochloric acid (HCl) solution. Preferably, the second portion of the ED concentrate transferred to the EDBM **100** has a sodium chloride concentration in excess of 17% by weight.

[0049] The EDBM **100** produces an acidic HCl stream and a basic NaOH stream. In the EDBM **100**, the salt, acid, and base streams are distributed between membranes that are stacked up in repeating sequences called repeat units. Anions are transported across the anion permeable membrane; cations are transported across the cation permeable membrane; and the production of protons and hydroxide ions occurs in the bipolar membrane. The produced hydroxide ions and protons move towards the

(positive) anode and the (negative) cathode, respectively, by means of migration in an electrical field. Ideally, they are trapped in the compartments adjacent to the two sides of the bipolar membrane in the respective base and acid compartment which results in the concentration of the base and acid in the respective base and acid compartments. The concentrated acid, the concentrated base, and the resulting reduced salt solution are collected and leave the EDBM **100**. Suitable EDBM's sold under the Acilyzer BPED name may be obtained from Astom, Japan, for example.

[0050] The pre-concentration of the salt by the ED **80** and the SWRO **70**/BWRO **71** allow the EDBM **100** to operate at sufficiently high current density to convert a significant portion of the salt to acid and base and efficiently use the electricity consumed. The return of the depleted brine from the EDBM **100** to the ED **80** for concentration is also of benefit in this regard as the depleted brine is not "waste", but can be re-concentrated to the elevated salt level required for higher current density in further EDBM **100** processing.

[0051] Unlike membranes used for separation purposes, such as the previously described ED **80**, species should not be transported from one side to the other of the EDBM **100** membranes. The desired function of the EDBM **100** membranes is a reaction in the bipolar junction of the membrane where the anion and the cation permeable layers are in direct contact. A disproportionation reaction splits water into hydroxide ions and protons. The produced hydroxide ions and protons are separated by migration in the respective membrane layer out of the membrane. Unlike water splitting at electrodes during electrolysis, no gases are formed as a side product of the disproportionation reaction, nor are gases consumed.

[0052] The NaOH base stream leaving the EDBM **100** may undergo evaporation **110** to increase the NaOH concentration and provide a dilute NaOH/water solution back to the base loop of the EDBM **100** and a finished

caustic product. Preferably the evaporation **110** increases the 3% to 4% by weight NaOH base stream leaving the EDBM **100** to from 25% to 50% by weight to form the finished caustic product.

[0053] Similarly, the HCl acid stream leaving the EDBM **100** may undergo distillation **120** to increase the HCl concentration and provide a dilute HCl/water solution back to the acid loop of the EDBM **100** and a finished acid product. Preferably the distillation **120** increases the 4% to 8% by weight HCl acid stream leaving the EDBM **100** to from 15% to 20% by weight to form the finished acid product.

[0054] The system **5** of FIG. 1 may be used to treat the produced water represented in FIG. 3, FIG. 4, and FIG. 5 as the system **5** is optimized to operate up to 40,000 TDS (40 g/L).

[0055] FIG. 2 represents a system for treating produced water having a high (≥ 50 g/L) concentration to total dissolved solids (TDS). To process the much higher TDS concentration in relation to system **5** of FIG. 1, the system represented in FIG. 2 adds additional precipitation, TMF, NF, and ED units. Thus, the initial processing system **6** may include an optional fresh water production system **7**, and/or an optional chemical production system **8**.

[0056] For the initial processing system **6**, the produced water enters the deoiling **10** and is then transferred to the oxidation **20** as previously described in the context of FIG. 1. However, unlike the single precipitation **30** of FIG. 1, the precipitation function is performed in parallel by the precipitation **30**, where substantially complete precipitation is still performed as previously described in the context of FIG. 1, and by the addition of partially complete precipitation **31**.

[0057] The substantially complete precipitation **30** of FIG. 2 functions as with the prior precipitation **30** and removes substantially all hardness from the water. Thus, the substantially complete precipitation **30** provides the concentrated sodium chloride containing ultra-high purity brine slurry

suitable for the electrolysis cell **90**, as previously discussed in the context of FIG. 1. In contrast, the partially complete precipitation **31** is operated to remove from 10% to 95% of the total hardness by weight in the water so the output is a less-concentrated sodium chloride containing brine slurry
5 suitable for additional processing and reuse in hydraulic fracturing, or may be further desalinized in the water production system **7**. In relation to the substantially complete precipitation **30**, the partially complete precipitation **31** uses less softening agent to target the 10% to 95% hardness removal as opposed to the 100% target removal used for the substantially complete
10 precipitation **30**. Thus, in the partially complete precipitation **31**, stoichiometric overdosing with the softening agent is not used as less than a 100% precipitation target is desired.

[0058] The initial processing system **6**, adds a second TMF **41** to process the less-concentrated precipitated slurry operating in combination
15 with the TMF **40** as previously described in the context of FIG. 1. The second TMF **41** produces a permeate which is suitable for reuse as a hydraulic fracturing brine and solids that may be transferred for the dewatering **42** as previously described in the context of FIG. 1. Carbon dioxide may be added from an external source to the hydraulic fracturing
20 brine produced by the second TMF **41**. The parallel precipitations **30/31** allow for the two TMF **40/41**, and thus a near doubling in capacity in relation to the system **5** of FIG. 1.

[0059] Unlike with the system **5** of FIG. 1, the higher TDS produced water does not allow direct connection of a NF unit to a SWRO unit as was
25 possible for the system **5**. Instead, regarding FIG. 2, the first NF **60** and a second NF **61** transfer to first ED **80** and second ED **81**, respectively. This is done because ED units can make a brine of considerably higher concentration (200 g/L or greater) than can be recovered from SWRO.

[0060] The first ED **80** produces a first diluate depleted in sodium
30 chloride and a first sodium chloride concentrate. The first diluate is

returned to the electrolysis cell **90**. The first sodium chloride concentrate may be passed to the electrolysis cell **90** or to the EDBM **100** as previously described in the context of FIG. 1. The EDBM **100** can form acid and base streams which may be used in the system **6** as previously described or
5 converted to finished acid and base products.

[0061] The second ED **81** produces a second diluate depleted in sodium chloride and a second sodium chloride concentrate. The second diluate is a partially desalted brine that may be directly used or passed to the SWRO **70** as previously described in the context of FIG. 1 to produce
10 fresh water. The reject from the SWRO **70** may be returned to the ED **81** for continued concentrations.

[0062] The system **6** of FIG. 2 may be used to treat the produced water represented in FIG. 6, FIG. 7, and FIG. 8 as the system **6** is optimized to operate at and above 40,000 TDS (40 g/L).

15 **[0063]** Unless the context clearly dictates otherwise, where a range of values is provided, each intervening value to the tenth of the unit of the lower limit between the lower limit and the upper limit of the range is included in the range of values.

20 **[0064]** While various aspects of the invention are described, it will be apparent to those of ordinary skill in the art that other embodiments and implementations are possible within the scope of the invention. Accordingly, the invention is not to be restricted except in light of the attached claims and their equivalents.

CLAIMS

1. A method of processing hydrocarbon produced water, the method comprising:

deoiling the hydrocarbon produced water to provide a deoiled feed
5 stream;

introducing an oxidant to the deoiled feed stream to provide an
oxidized feed stream;

precipitating the oxidized feed stream to provide a precipitated slurry;

passing the precipitated slurry through a tubular membrane filter unit
10 to produce a permeate;

reducing the pH of the permeate to provide a reduced pH permeate;

passing the reduced pH permeate through a nanofiltration membrane
unit to produce a NF permeate and a NF reject;

passing the NF permeate to one of an electrolysis cell, a seawater
15 reverse osmosis membrane, and both the electrolysis cell and the seawater
reverse osmosis membrane,

where the electrolysis cell provides the oxidant, and

where the seawater reverse osmosis membrane provides
freshwater and a concentrated sodium chloride retentate;

20 passing the concentrated sodium chloride retentate to an
electrodialysis device including univalent anion and univalent cation
membranes and electrodes to produce a diluate depleted in sodium chloride
and a sodium chloride concentrate;

passing the diluate to the nanofiltration membrane unit;

25 passing at least a portion of the sodium chloride concentrate to one of
a bipolar membrane electrodialysis unit, the electrolysis cell, and both the
bipolar membrane electrodialysis unit and the electrolysis cell; and

generating a hydrochloric acid stream and a sodium hydroxide stream from the bipolar membrane electrodialysis unit.

2. The method of claim 1, where the deoiling includes recovering a hydrocarbon fraction from the produced water.

5 3. The method of claim 1, where the electrolysis cell is undivided or divided.

4. The method of claim 1, where the precipitating includes adding lime and sodium hydroxide to the oxidized feed stream.

5. The method of claim 4, where the sodium hydroxide includes the
10 sodium hydroxide stream from the bipolar membrane electrodialysis unit.

6. The method of claim 1, further comprising stoichiometrically overdosing the precipitated slurry with a precipitation agent selected from lime, soda ash, caustic soda, and combinations thereof.

7. The method of claim 1, where the tubular membrane filter unit
15 comprises a semipermeable tubular membrane having a pore size of less than 1 micron.

8. The method of claim 7, further comprising cleaning the semipermeable tubular membrane with a cleaning solution selected from hydrochloric acid, sodium hypochlorite, and combinations thereof.

20 9. The method of claim 8, where

the hydrochloric acid includes the hydrochloric acid stream from the bipolar membrane electrodialysis unit, and

the sodium hypochlorite includes the oxidant from the electrolysis cell.

10. The method of claim 1, further comprising removing and dewatering solids from the tubular membrane filter unit.

11. The method of claim 1, where the reducing the pH of the permeate includes contacting the permeate with hydrochloric acid.

5 12. The method of claim 11, where the hydrochloric acid includes the hydrochloric acid stream from the bipolar membrane electrodialysis unit.

13. The method of claim 1, further comprising dechlorinating the precipitated slurry or the reduced pH permeate.

10 14. The method of claim 13, where the dechlorinating includes contacting the precipitated slurry or the reduced pH permeate with carbon.

15. The method of claim 1, further comprising returning the NF reject to the precipitating.

15 16. The method of claim 1, where the seawater reverse osmosis membrane further provides low salt water to a brackish water reverse osmosis membrane.

17. The method of claim 1, further comprising using at least a portion of the sodium chloride concentrate for hydraulic fracturing.

18. The method of claim 1, where the oxidant includes sodium hypochlorite.

20 19. The method of claim 18, further comprising combining the sodium hypochlorite with the hydrochloric acid stream and then with sodium chlorite.

20. The method of claim 1, further comprising removing barium from the hydrocarbon produced water.

21. The method of claim 1, where the nanofiltration membrane unit includes a nanofiltration membrane having a molecular cut-off range of about 300 g/mol.

22. A method of processing hydrocarbon produced water, the method comprising:

deoiling the hydrocarbon produced water to provide a deoiled feed stream;

introducing an oxidant to the deoiled feed stream to provide an oxidized feed stream;

transferring the oxidized feed stream to a partially complete precipitation and to a substantially complete precipitation;

where the substantially complete precipitation precipitates the oxidized feed stream to provide a precipitated slurry, and

the partially complete precipitation precipitates the oxidized feed stream to remove from 10% to 95% by weight of total hardness in the oxidized feed stream to provide a less-concentrated precipitated slurry;

passing the precipitated slurry from the complete precipitation through a first tubular membrane filter unit to produce a permeate;

passing the less-concentrated precipitated slurry from the partially completed precipitation through a second tubular membrane filter unit to produce a hydraulic fracturing brine;

reducing the pH of the permeate to provide a reduced pH permeate;

passing the reduced pH permeate through a first nanofiltration membrane unit to produce a NF permeate and a NF reject;

passing the NF permeate to an electrolysis cell, where the electrolysis cell provides the oxidant.

23. The method of claim 22, where the deoiling includes recovering a hydrocarbon fraction from the produced water.

24. The method of claim 22, where the electrolysis cell is undivided or divided.

5 25. The method of claim 22, where the substantially complete precipitation and the partially complete precipitation include adding lime and sodium hydroxide to the oxidized feed stream.

26. The method of claim 22, further comprising stoichiometrically overdosing the precipitated slurry with a precipitation agent selected from
10 lime, soda ash, caustic soda, and combinations thereof.

27. The method of claim 22, where the first tubular membrane filter unit and the second tubular membrane filter unit comprise a semipermeable tubular membrane having a pore size of less than 1 micron.

28. The method of claim 27, further comprising cleaning the
15 semipermeable tubular membranes with a cleaning solution selected from hydrochloric acid, sodium hypochlorite, and combinations thereof.

29. The method of claim 22, further comprising removing and dewatering solids from the second tubular membrane filter unit.

30. The method of claim 22, where the reducing the pH of the permeate
20 includes contacting the permeate with hydrochloric acid.

31. The method of claim 22, further comprising dechlorinating the precipitated slurry or the reduced pH permeate .

32. The method of claim 31, where the dechlorinating includes contacting the precipitated slurry or the reduced pH permeate with carbon.

33. The method of claim 22, further comprising returning the NF reject to the substantially complete precipitation.

34. The method of claim 22, further comprising using at least a portion of the hydraulic fracturing brine for hydraulic fracturing.

5 35. The method of claim 22, where the oxidant includes sodium hypochlorite.

36. The method of claim 22, further comprising removing barium from the hydrocarbon produced water.

37. The method of claim 22, where the nanofiltration membrane unit
10 includes a nanofiltration membrane having a molecular cut-off range of about 300 g/mol.

38. The method of claim 22, further comprising:

transferring the NF permeate to a first electrodialysis device including univalent anion and univalent cation membranes and electrodes to produce
15 a first diluate depleted in sodium chloride and a first sodium chloride concentrate;

passing the first diluate to the electrolysis cell;

passing at least a portion of the first sodium chloride concentrate to a bipolar membrane electrodialysis unit; and

20 generating a hydrochloric acid stream and a sodium hydroxide stream from the bipolar membrane electrodialysis unit.

39. The method of claim 22, further comprising:

passing a portion of the hydraulic fracturing brine through a second nanofiltration membrane to produce a second NF permeate and a second NF
25 reject;

transferring the second NF reject to the partially complete precipitation; and

transferring the second NF permeate to a second electrodialysis device including univalent anion and univalent cation membranes and electrodes
5 to produce a second diluate depleted in sodium chloride and a second sodium chloride concentrate.

40. The method of claim 39, further comprising transferring the second diluate to a seawater reverse osmosis membrane to provide freshwater.

1/8

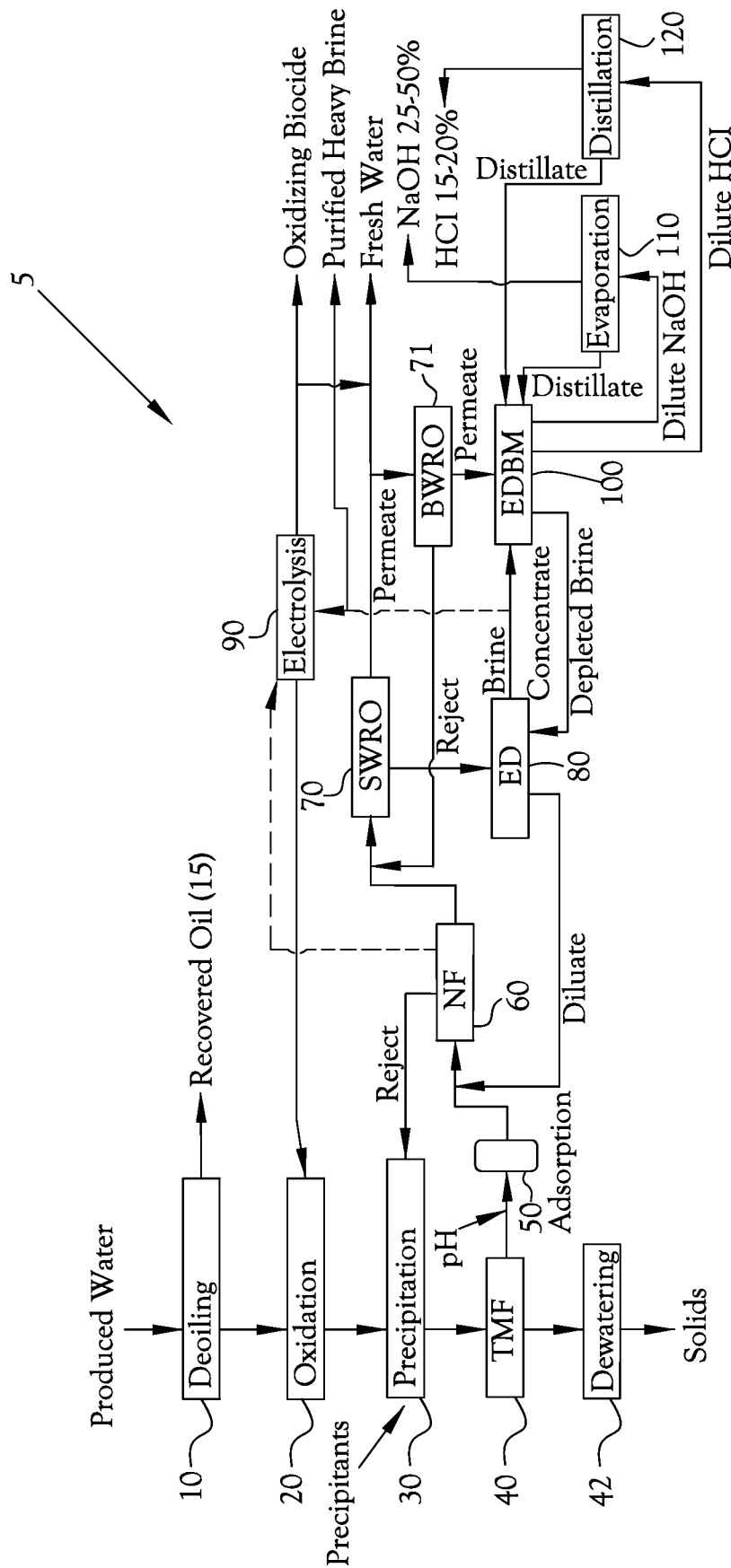
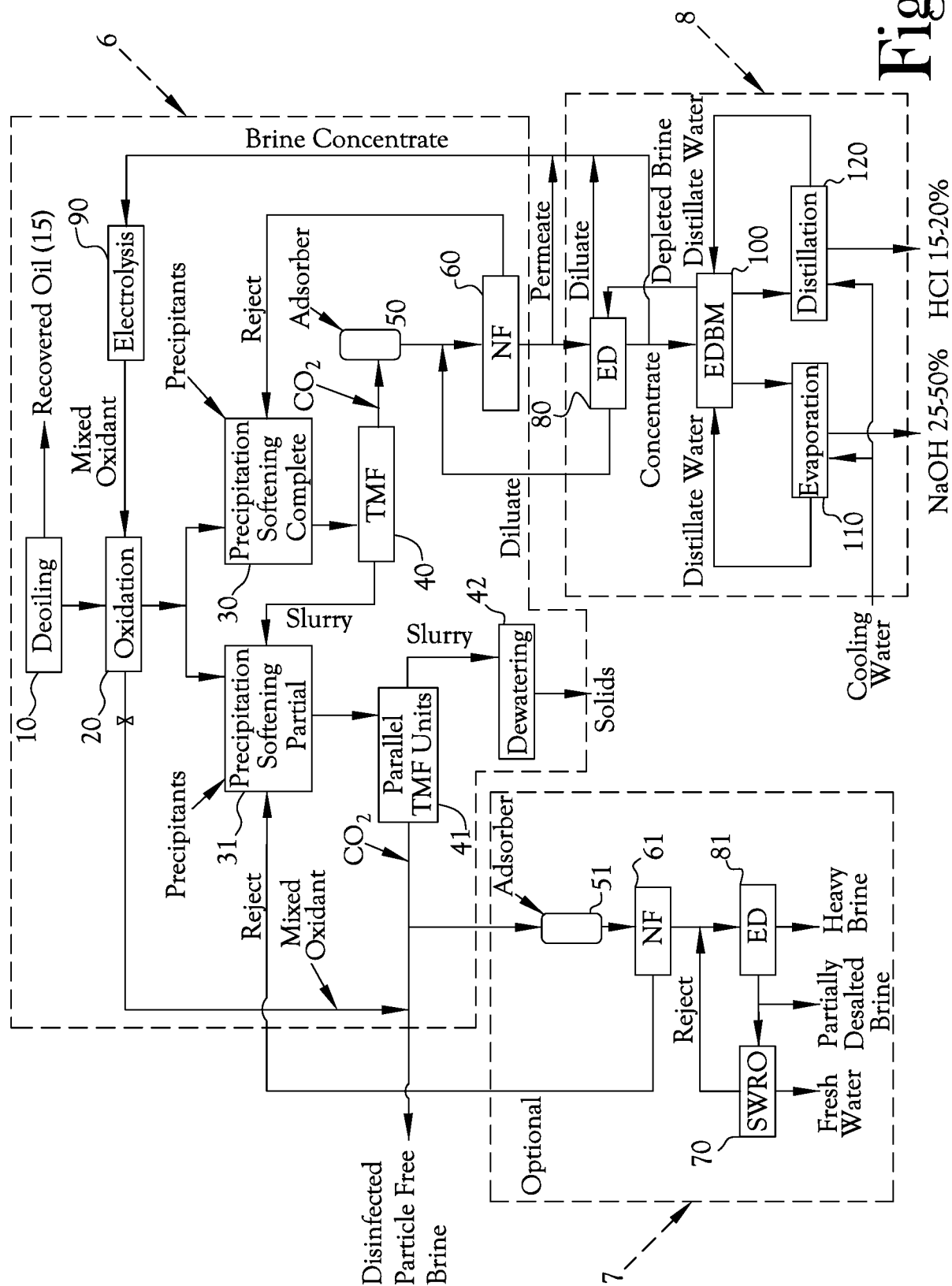


Fig.1

Fig. 2



3/8

Niobrara/DJ Basin Coil Water Test Result Summary

Parameter (ppm unless noted)	As Received	Pretreated	Desalted	% Removed
pH	7.69	8.6	9.6	----
Conductivity ($\mu\text{S}/\text{cm}$)	31600	26211	223	99.29
TDS	16600	14001	115	99.30
Total Hardness (CaCO_3)	200	14	ND	>99.99
Aluminum	4.78	ND	NA	>99.99
Calcium	53.9	3.25	NA	93.97
Iron	22.7	ND	NA	>99.99
Magnesium	11.4	2.93	NA	74.29
Boron	9.33	NA	6.0	35.69
Barium	1.69	0.0602	NA	96.43
Manganese	ND	ND	NA	-----
Strontium	6.47	0.598	NA	90.75
Sulfate	189	ND	NA	>99.99
Silicon	19.0	NA	0.0698	99.63
Silica (SiO_2)	40.7	NA	0.149	99.63
TSS	264	ND	NA	>99.99
TOC	2860	493	3.46	99.87
Oil & Grease	180	ND	NA	>99.99

ND – Not Detected at or above the reporting limit

NA – Not Analyzed

Fig.3

4/8

Table 2
Niobrara/DJ Basin Flowback Test Result Summary

Parameter (ppm unless noted)	As Received	Pretreated	Desalted	% Removed
pH	6.97	8.56	9.98	-----
Conductivity (μ S/cm)	22800	18130	223	99.02
TDS	17300	10200	52	99.69
Total Hardness (as CaCO ₃)	600	25	ND	>99.99
Aluminum	11.6	ND	NA	>99.99
Calcium	205	7.22	NA	96.47
Iron	34.1	ND	NA	>99.99
Magnesium	2620	1.44	NA	99.94
Boron	17.6	NA	1.44	91.81
Barium	4.56	0.0688	NA	98.49
Manganese	ND	ND	NA	-----
Strontium	19.9	1.23	NA	93.81
Sulfate	243	ND	NA	>99.99
Silicon	48.5	NA	0.0439	99.90
Silica (SiO ₂)	104	NA	0.0939	99.90
TSS	ND	ND	NA	-----
TOC	4440	NA	159	96.41

ND – Not Detected at or above the reporting limit

NA – Not Analyzed

Fig.4

5/8

Niobrara/DJ Basin Produced Water Test Result Summary

Parameter (ppm unless noted)	As Received	Pretreated	Desalted	% Removed
pH	6.095	7.55	6.67	-----
Conductivity (μ S/cm)	35500	28250	306	99.14
TDS	23900	16700	200	99.16
Total Hardness (CaCO ₃)	1010	<1	ND	>99.99
Aluminum	0.0596	ND	ND	>99.99
Calcium	316	1.12	ND	>99.99
Iron	203	ND	ND	>99.99
Magnesium	45.7	0.491	NA	98.92
Boron	21.1	NA	1.53	92.75
Barium	16.3	0.0717	NA	99.56
Manganese	2.16	ND	ND	>99.99
Strontium	51.7	0.375	NA	99.27
Silicon	41.9	NA	0.0289	99.93
Silica (SiO ₂)	89.6	NA	0.0618	99.93
TSS	540	ND	ND	>99.99
TOC	1130	7.91	2.43	99.78
Sulfate	ND	ND	NA	-----

ND – Not Detected at or above the reporting limit

NA – Not Analyzed

Fig.5

6/8

Permian Basin Produced Water Test Result Summary

Parameter (ppm)	Influent	Pretreated	Concentrate
TDS	51,900	44,279	200,000
Total Hardness (as CaCO ₃)	2,300	ND	ND
Aluminum	ND	ND	ND
Barium	1.39	0.0385	ND
Beryllium	ND	ND	ND
Calcium	754	0.870	ND
Copper	ND	ND	ND
Iron	ND	ND	ND
Magnesium	175	0.870	ND
Manganese	ND	ND	ND
Strontium	265	1.11	1.38
Sulfate	NA	ND	NA

ND – Not Detected at or above the reporting limit

NA – Not Analyzed

Fig.6

7/8

Ardmore Basin Produced Water Test Result Summary

Parameter (ppm unless noted)	Influent	Pretreated	Desalted	Removal (%)
pH	6.2	11.5	7.22	-----
Conductivity (μ S/cm)	121000	100000	<1	>99.99
TDS	89000	73200	ND	>99.99
Total Hardness (CaCO ₃)	19,223	ND	NA	>99.99
Aluminum	10.5	ND	NA	>99.99
Calcium	5230	3.01	NA	99.94
Iron	5.81	ND	NA	>99.99
Magnesium	1,560	0.776	NA	99.95
Barium	120	0.09	NA	99.92
Manganese	1.28	ND	NA	>99.99
Strontium	285	0.281	NA	99.90

ND – Not Detected at or above the reporting limit

NA – Not Analyzed

Fig.7

8/8

Williston Basin Produced Water Test Result Summary

Parameter (ppm unless noted)	Influent	Pretreated	Desalted	Removal (%)
pH	5.98	6.96	7.10	-----
Conductivity (μ S/cm)	240000	200000	<1	>99.99
TDS	331000	176000	ND	>99.99
TSS	954	ND	NA	>99.99
Total Hardness, mg/L (CaCO ₃)	44000	<5	NA	>99.98
Aluminum	1.57	ND	NA	>99.99
Boron	141	73.6	NA	47.8
Calcium	16200	6.14	NA	99.96
Chloride	118000	163000	NA	>99.99
Iron	39	ND	NA	>99.99
Magnesium	447	0.520	NA	99.98
Barium	6.7	0.128	NA	98.08
Manganese	6.71	ND	NA	>99.99
Silica (SiO ₂)	13.7	16.2	NA	-----
Silicon	6.39	7.58	NA	-----
Sodium	78900	66000	NA	>99.99
Strontium	1020	0.698	NA	99.93
Sulfate	884	15.2	NA	98.28

ND - Not Detected at or above the reporting limit

NA - Not Analyzed

Fig.8

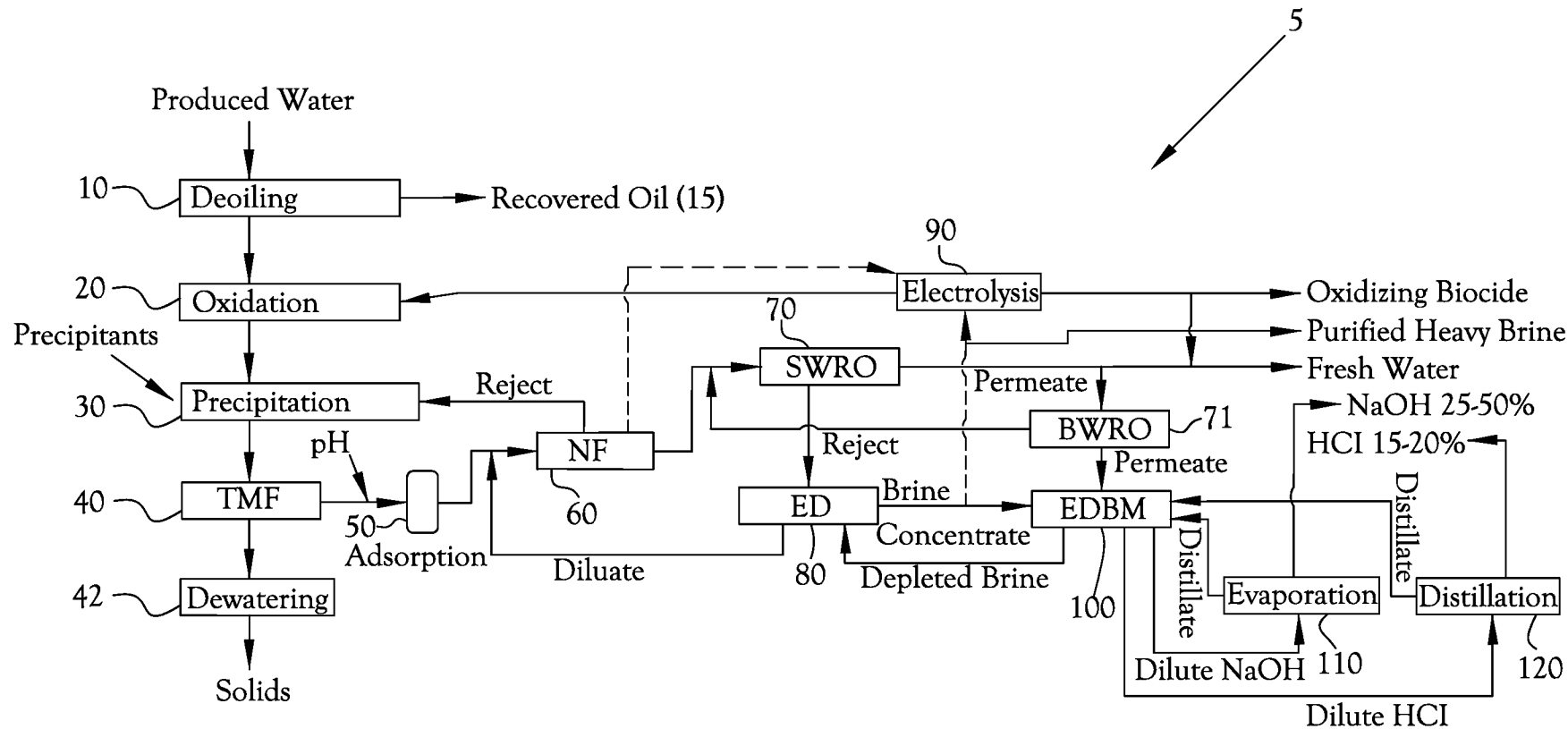


Fig.1