REMOVAL OF HYDROFLUORIC ACID FROM LIQUID STREAMS, INCLUDING FLUORIDE SALT PRECIPITATION

RELATED APPLICATIONS

This application claims priority under 35 U.S.C. § 119(e) to U.S. Provisional Patent Application No. 63/565,224, filed March 14, 2024, and entitled "Removal of Hydrofluoric Acid from Liquid Streams," and to U.S. Provisional Patent Application No. 63/565,450, filed March 14, 2024, and entitled "Removal of Hydrofluoric Acid from Liquid Streams, Including Fluoride Salt Precipitation," each of which is incorporated herein by reference in its entirety for all purposes.

TECHNICAL FIELD

Methods and related systems for treating hydrofluoric acid-containing streams are provided.

BACKGROUND

Hydrofluoric acid poses safety and environmental problems. Therefore, improved methods and related system for treating hydrofluoric acid-containing mixtures are desirable.

SUMMARY

Methods and related systems for treating hydrofluoric acid-containing streams are provided. The hydrofluoric acid-containing stream may be, for example, an aqueous wastewater stream from an industrial process such as a semiconductor manufacturing process. The pH of the stream may be adjusted such that a relatively high percentage of the hydrofluoric acid (HF) molecules in the stream are deprotonated to form fluoride ions. In some instances, at least a portion the pH-adjusted stream forms part of (or all of) an inlet stream that is transported to a membrane separator. The membrane separator may produce a retentate outlet stream with a higher concentration of fluoride ions than the inlet stream and a permeate outlet stream containing a portion of liquid from the inlet stream. The methods may include additional treatments, such as removing other species present in the hydrofluoric acid-containing stream, such as silica.

The subject matter of the present invention involves, in some cases, interrelated products, alternative solutions to a particular problem, and/or a plurality of different uses of one or more systems and/or articles.

In one aspect, a method for treating a hydrofluoric acid (HF)-containing stream is provided. In some embodiments, the method comprises adjusting a pH of an aqueous stream comprising HF molecules present at a concentration of greater than or equal to 100 mg/L, such that at least 50 mole percent (mol%) of the HF molecules are deprotonated to form dissolved fluoride ions (F^-), thereby forming a pH-adjusted stream; and transporting a first membrane separator retentate inlet stream to a retentate side of a first membrane separator such that: a first membrane separator retentate outlet stream exits the retentate side of the first membrane separator, the first membrane separator retentate outlet stream having concentration of dissolved fluoride ions that is greater than a concentration of dissolved fluoride ions of the first membrane separator retentate inlet stream, and at least a portion of liquid from the first membrane separator retentate inlet stream is transported from the retentate side of the first membrane separator, through a semi-permeable membrane of the first membrane separator, to a permeate side of the first membrane separator where the portion of liquid forms some or all of a first membrane separator permeate outlet stream that is transported out of the permeate side of the first membrane separator; wherein the first membrane separator retentate inlet stream comprises at least a portion of the pH-adjusted stream.

In another aspect, a system for managing an aqueous effluent with high concentration of fluoride is provided. In some embodiments, the system comprises an inlet for receiving an aqueous effluent with high concentration of fluoride; a first treatment assembly, the first treatment assembly including: a first treatment assembly input configured to receive the aqueous effluent from the inlet; a first treatment unit configured to increase pH level of the aqueous effluent to arrive at a treated aqueous effluent; and a first treatment assembly output configured to provide the treated aqueous effluent to a first filtration assembly; a first filtration assembly, the first filtration assembly including: a first filtration assembly input configured to receive the treated aqueous effluent from the first treatment assembly; a first filtration unit configured to filter pollutants and/or contaminants from the treated aqueous effluent to arrive at a first permeate and a first reject water; and a first filtration assembly output configured to

provide the first permeate to a second filtration assembly and the first reject water to a collection assembly; a second filtration assembly, the second filtration assembly including: a second filtration assembly input configured to receive the first permeate from the first filtration assembly; a second filtration unit configured to filter impurities from the first permeate to arrive at a second permeate and a second reject water; and a second filtration assembly output configured to provide the second permeate to a polishing assembly and the second reject water to a collection assembly; a polishing assembly, the polishing assembly including: a polishing assembly input configured to receive the second permeate from a second filtration assembly; a polishing unit configured to remove impurities from the second permeate to arrive at a first final output and a third reject water; and a polishing assembly output configured to provide the first final output and the third reject water to a collection assembly; a collection assembly, the collection assembly including: a collection assembly input configured to receive the first reject water, second reject water and/or third reject water; a collection unit configured to collect the first reject water, second reject water and/or third reject water; and a collection assembly output configured to provide the collected first reject water, second reject water and/or third reject water to a second treatment assembly; a second treatment assembly, the second treatment assembly including: a second treatment assembly input configured to receive the collected first reject water, second reject water and/or third reject water from the collection assembly; a second treatment unit configured to precipitate fluoride and silica in the collected first reject water, second reject water and/or third reject water to arrive at a first treated reject water; and a second treatment assembly output configured to provide the first treated reject water to a sedimentation assembly; a sedimentation assembly, the sedimentation assembly including: a sedimentation assembly input configured to receive the first treated reject water from the second treatment assembly; a sedimentation unit configured to sediment impurities in the first treated reject water to arrive at an effluent discharge and a calcium fluoride sludge; and a sedimentation assembly output configured to provide a first liquid output to a reaction assembly; a reaction assembly, the reaction assembly including: a reaction assembly input configured to receive the first liquid output from the sedimentation assembly; a reaction unit configured to remove impurities in the first liquid output to arrive at a second liquid output; and a reaction assembly output configured to provide the

second liquid output to a clarifier assembly; a clarifier assembly, the reaction assembly including: a clarifier assembly input configured to receive the second liquid output from the reaction assembly output; a clarifier assembly unit to remove solids in the second liquid output to arrive at an effluent discharge and a calcium fluoride sludge; and a clarifier assembly output configured to provide the calcium fluoride sludge to a filter press assembly; and a filter press assembly, the filter press assembly including: a filter press assembly input configured to receive the calcium fluoride sludge from the sedimentation assembly output and the clarifier assembly output; a filter press assembly unit to remove liquid from the calcium fluoride sludge; and a filter press assembly output to provide a second final output.

In another aspect, methods for managing an aqueous effluent with high concentration of fluoride are provided. In some embodiments, the method comprises receiving an aqueous effluent with high concentration of fluoride; treating the aqueous effluent with high concentration of fluoride to increase pH level of the aqueous effluent to arrive at a treated aqueous effluent; filtering the treated aqueous effluent to arrive at a first permeate and a first reject water; filtering the first permeate to arrive at a second permeate and a second reject water; polishing the second permeate to arrive at a first final output and a third reject water; collecting the first reject water, the second reject water and the third reject water in a collection unit; treating the collected first reject water, second reject water and/or third reject water by precipitating fluoride and/or silica in the collected first reject water, second reject water and/or third reject water to arrive at a first treated reject water; sedimenting impurities in the first treated reject water to arrive at a first liquid output and calcium fluoride sludge; reacting the first liquid output to arrive at a second liquid output; removing solids in the second liquid output to arrive at an effluent discharge and a calcium fluoride sludge; and removing liquid from the calcium fluoride sludge to arrive at a second final output.

Other advantages and novel features of the present invention will become apparent from the following detailed description of various non-limiting embodiments of the invention when considered in conjunction with the accompanying figures. In cases where the present specification and a document incorporated by reference include conflicting and/or inconsistent disclosure, the present specification shall control.

BRIEF DESCRIPTION OF THE DRAWINGS

Non-limiting embodiments of the present invention will be described by way of example with reference to the accompanying figures, which are schematic and are not intended to be drawn to scale. In the figures, each identical or nearly identical component illustrated is typically represented by a single numeral. For purposes of clarity, not every component is labeled in every figure, nor is every component of each embodiment of the invention shown where illustration is not necessary to allow those of ordinary skill in the art to understand the invention. In the figures:

FIG. 1 is a schematic diagram of an example of a system for treating a hydrofluoric acid-containing stream comprising a pH adjustment vessel and a membrane separator, according to some embodiments;

FIG. 2 is a schematic diagram of an example of a system for treating a hydrofluoric acid-containing stream comprising a pH adjustment vessel, a first membrane separator, and a second membrane separator, according to some embodiments;

FIG. 3 is a schematic diagram of an example of a system for treating a hydrofluoric acid-containing stream comprising a pH adjustment vessel and a membrane separator configured to recycle a portion of a retentate outlet stream, according to some embodiments;

FIG. 4 is a schematic diagram of an example of a system for treating a hydrofluoric acid-containing stream comprising a pH adjustment vessel, a coagulation vessel, a flocculation vessel, a solids separation vessel, a filtration assembly, and a membrane, according to some embodiments;

FIG. 5A is a schematic illustration of a single-membrane membrane separator, according to some embodiments;

FIG. 5B is a schematic illustration of a membrane separator comprising multiple semi-permeable membranes fluidically connected in parallel, according to some embodiments;

FIG. 5C is a schematic illustration of a membrane separator comprising multiple semi-permeable membranes fluidically connected in series, according to some embodiments;

FIG. 6 is a schematic illustration of an example of a system for treating a hydrofluoric acid-containing stream, according to some embodiments; and

FIG. 7 is a schematic illustration a method for treating a hydrofluoric acid-containing stream, according to some embodiments.

DETAILED DESCRIPTION

Methods and related systems for treating hydrofluoric acid-containing streams are provided. The hydrofluoric acid-containing stream may be, for example, an aqueous wastewater stream from an industrial process such as a semiconductor manufacturing process. The pH of the stream may be adjusted such that a relatively high percentage of the hydrofluoric acid (HF) molecules in the stream are deprotonated to form fluoride ions. In some instances, at least a portion the pH-adjusted stream forms part of (or all of) an inlet stream that is transported to a membrane separator. The membrane separator may produce a retentate outlet stream with a higher concentration of dissolved fluoride ions than the inlet stream and a permeate outlet stream containing a portion of liquid from the inlet stream. The methods may include additional treatments, such as removing other species present in the hydrofluoric acid-containing stream, such as silica.

Certain processes produce liquid streams comprising hydrofluoric acid. As one example, some industrial processes (such as microelectronics/semiconductor production processes) produce aqueous streams with hydrofluoric acid. For example, such processes may produce hydrofluoric acid-containing wastewater. The presence of hydrofluoric acid in such streams can pose an environmental and/or safety danger. Therefore, it can be desirable to treat such streams to separate the hydrofluoric acid (e.g., by removal and/or conversion to other species). One approach to removing hydrofluoric acid is chemical precipitation. For example, calcium chloride and/or calcium hydroxide may be added to a liquid stream comprising hydrofluoric acid to induce formation of solid calcium fluoride (e.g., as a precipitate and/or sludge). However, it has been realized in the context of this disclosure that the use of chemical agents to induce precipitation may lead to presence of residual calcium ions in the treated liquid stream, which may be undesirable under certain circumstances. Accordingly, aspects of this disclosure are directed to methods and systems for the separation of hydrofluoric acid from liquid streams (e.g., aqueous streams such as wastewater streams) using little to no

chemical fluoride precipitating agents (e.g., calcium containing precipitating agents). For example, some embodiments involve use of membrane-based separation techniques (e.g., osmotic separation) to concentrate fluoride and produce liquid permeates with reduced fluoride content.

Methods (e.g., for removing and/or recovering HF or fluoride ions) and related systems are generally described. FIGS. 1-4 show schematic illustrations of system 100, which is an example of a system in which certain methods described herein may be carried out. The systems of this disclosure may comprise a single membrane separator or a plurality of membrane separators.

Some embodiments comprise treating an aqueous stream comprising HF molecules. Examples of types of aqueous streams that can be treated according to the methods and using the systems of this disclosure are described in more detail below. Referring again to FIGS. 1-4, aqueous stream 20 may be fed into system 100 for treatment.

In some embodiments, at least 50 wt%, at least 75 wt%, at least 90 wt%, at least 95 wt%, at least 98 wt%, at least 99 wt%, at least 99.9 wt%, or more (e.g., all) of the liquid of the aqueous stream is water. The aqueous stream may comprise a relatively large amount of hydrofluoric acid. Hydrofluoric acid is a weak acid, and so an aqueous solution of hydrofluoric acid will have both the conjugate acid (HF molecules) and conjugate base (fluoride ions) present at the same time. At equilibrium, the relative ratio of the concentration of HF molecules to fluoride ions in the aqueous solution is influenced by the pH of the aqueous solution. This relationship can be represented in general for monobasic weak acids as the following:

$$\mathrm{pH} = \mathrm{p}K_\mathrm{a} + \log_{10}\left(\frac{[\mathrm{Base}]}{[\mathrm{Acid}]}\right) \qquad \text{Eq. [1]}$$

In Eq. [1], the $\mathrm{p}K_\mathrm{a}$ corresponds to that of the weak acid, [Acid] is the molar concentration of the conjugate acid, and [Base] is the molar concentration of the conjugate base. The $\mathrm{p}K_\mathrm{a}$ of HF in water is 3.17. By rearranging Eq. [1], one can determine the concentration of HF molecules as it relates to the concentration of fluoride ions using Eq. 2a or the concentration of fluoride ions as it relates to the concentration of HF molecules using Eq. 2b:

$$[HF] = [F^-](10^{3.17-pH}) \quad \text{Eq. [2a]}$$

$$[F^-] = [HF](10^{pH-3.17}) \quad \text{Eq. [2b]}$$

In Eq. [2a] and Eq. [2b], [HF] is the molar concentration of HF molecules, and $[F^-]$ is the molar concentration of fluoride ions.

The aqueous stream may comprise HF molecules in a relatively large amount. The large amount of HF may be due, for example, to the aqueous stream being an effluent from an industrial process such as HF-etching (e.g., of semiconductor materials). In some embodiments, the aqueous stream comprises HF molecules that are present at a concentration of greater than or equal to 100 mg/L, greater than or equal to 150 mg/L, greater than or equal to 200 mg/L, greater than or equal to 350 mg/L, and/or up to 500 mg/L, up to 750 mg/L, up to 1000 mg/L, up to 2000 mg/L, or greater. Combinations of these ranges are possible.

In some embodiments, the pH of the aqueous stream comprising the HF molecules is adjusted. The adjustment in pH may be performed such that at least some of the HF molecules in the aqueous stream are deprotonated to form dissolved fluoride ions. The pH adjustment may form a pH-adjusted stream. For example, in FIGS. 1-4, aqueous stream 20 enters pH-adjustment vessel 25, where the pH of aqueous stream 20 is adjusted, thereby forming pH-adjusted stream 101. It has been realized in the context of this disclosure that converting some or all of the HF molecules to fluoride ions can promote more effective removal of the hydrofluoric acid from the aqueous stream (e.g., during wastewater treatment). As a non-limiting example, it is believed that, when employing membrane-based separation techniques (e.g., with the membrane separator below), the negatively charged fluoride ions are more readily rejected by the semi-permeable membrane than are the neutral HF molecules. Accordingly, by converting some or all of the HF molecules to dissolved fluoride ions, the rejection of fluoride ions by the membrane separator may be improved, which can promote greater separation efficiency.

In some embodiments, the adjustment of the pH of the aqueous stream is an increase of the pH. As discussed above in the context of Equations [1], [2a], and [2b], an increase in the pH of a solution comprising dissolved HF molecules and their conjugate

base fluoride molecules results in a relative increase in the molar concentration of fluoride ions and a relative decrease in the concentration of HF molecules as some HF molecules are deprotonated. In some embodiments, the pH adjustment is performed such that greater than or equal to 50 mole percent (mol%), greater than or equal to 75 mol%, greater than or equal to 90 mol%, greater than or equal to 95 mol%, greater than or equal to 98 mol%, greater than or equal to 99 mol%, greater than or equal to 99.9 mol%, greater than or equal to 99.99 mol%, or more of the HF molecules are deprotonated. The percentage of HF molecules that are deprotonated can be determined by measuring the pH and the fluoride content of both the aqueous stream and the resulting pH-adjusted stream to determine the molar concentration of HF and dissolved fluoride ions in each stream. The pH can be determined using any suitable pH meter. The fluoride content can be determined, for example, by taking a sample of each stream, completely converting all HF molecules to fluoride ions (e.g., by performing an acid-base titration) and then performing a potentiometric titration to determine the fluoride concentration. Equations [1], [2a], and [2b] above can be used to calculate the molar concentrations of HF molecules and fluoride ions once the pH and total fluoride content is known.

In some embodiments, the pH of the aqueous solution is increased by exposing the aqueous stream to one or more chemical agents. For example, the aqueous solution may be exposed to a base. The base may include a strong base and/or a weak base that is strong enough to deprotonate HF. Examples of chemical agents that may be used include, but are not limited to sodium hydroxide, potassium hydroxide, sodium carbonate, sodium bicarbonate, potassium carbonate, and/or potassium bicarbonate. In some embodiments, the chemical agent is a base that is strong enough to deprotonate HF but does not increase hardness of water. In some embodiments, the base comprises sodium hydroxide or potassium hydroxide, as these are examples of bases that can promote deprotonation without increasing hardness. In some embodiments, less than 10 wt% (e.g., less than 5 wt%, less than 2 wt%, less than 1 wt%, less than 0.1 wt% or none) of the base is calcium hydroxide, calcium bicarbonate, magnesium hydroxide, or magnesium hydroxide, as these bases may undesirably contribute to hardness of the resulting solution. The chemical agent may be exposed to the aqueous solution as a solid (e.g., pellets or powder), or as a liquid (e.g., dissolved in a solvent such as water).

In some embodiments in which the pH of the aqueous stream is increased during the pH adjustment, the pH of the aqueous stream is increased by at least 0.3, at least 0.5 at least 1, at least 2, at least 3, at least 4, or more. In some embodiments in which the pH of the aqueous stream is increased during the pH adjustment, the pH of the aqueous stream is increased by a value that is less than or equal to 7, less than or equal to 6, less than or equal to 5, or less. Combinations of these ranges are possible. The increase in the pH can be determined taking the difference in the pH of the pH-adjusted stream and the aqueous stream.

In some embodiments, the pH of the aqueous stream prior to the pH adjustment is greater than or equal to 0, greater than or equal to 1, greater than or equal to 2, greater than or equal to 3, or greater. In some embodiments, the pH of the aqueous stream prior to the pH adjustment is less than or equal to 11, less than or equal to 5, less than or equal to 4, or less. In some embodiments, the pH of the aqueous stream prior to the pH adjustment is less than or equal to 5, less than or equal to 4, or less. Combinations of these ranges are possible.

In some embodiments, the pH of the pH-adjusted stream is sufficiently high such that an adequate percentage of the hydrofluoric acid is in its deprotonated state (as fluoride ions) (e.g., to promote efficient downstream membrane-based separation). In some embodiments, the pH of the pH-adjusted stream is low enough such that other potentially deleterious phenomena do not occur. For example, the aqueous stream may comprise positively charged protic contaminants for which downstream separation would be less efficient if the pH were increased to such an extent that a significant percentage of the positively charged protic contaminants were deprotonated to form neutral contaminants, which may be harder to separate using membrane-based separators. As a non-limiting illustrative example, the aqueous stream may comprise ammonium cations (commonly known to be present in certain wastewater streams due to the longstanding use of ammonia in removing silica), the removal of which in downstream separation processes would be less efficient if the pH were increased to such an extent that a significant percentage of the positively charged ammonium cations were deprotonated to form neutral ammonia (NH_3), which may be harder to separate using membrane-based separators. In some embodiments, the pH of the pH-adjusted stream is greater than or equal to 5.5, greater than or equal to 5.8, greater than or equal to 6, or greater. In some

embodiments, the pH of the pH-adjusted stream is less than or equal to 6.8, less than or equal to 6.5, or less. Combinations of these ranges (e.g., greater than or equal to 5.5 and less than or equal to 6.8, or greater than or equal to 5.5 and less than or equal to 6.5) are possible.

As noted above, in some, but not necessarily all embodiments, the pH adjustment is performed in a pH-adjustment vessel (e.g., pH-adjustment vessel 25). Any of a variety of vessels may be used, such as a tank and/or a flow reactor. The pH-adjustment vessel may be fluidically connected to a source of the aqueous stream (e.g., a source of wastewater effluent). The pH-adjustment vessel may be further configured to receive the chemical agent (e.g., solid base and/or base in a liquid state). The pH-adjustment vessel may be fluidically connected to one or more downstream components of the system. For example, in FIGS. 1-4, pH-adjustment vessel 25 is fluidically connected (directly or indirectly) to retentate side 103 of first membrane separator 102, such that at least a portion (e.g., at least 5 wt%, at least 10 wt%, at least 20 wt%, at least 50 wt%, at least 80 wt%, at least 90 wt%, at least 95 wt%, at least 99 wt%, or more) of the output of the pH-adjustment vessel (e.g., pH-adjusted stream 101) forms some or all of first membrane separator retentate inlet stream 105. As discussed in more detail below, one or more additional treatments and/or separation processes may be performed on pH-adjusted stream 101 before it reaches the retentate side 103 of first membrane separator 102, such as the removal of one or more contaminants such as dissolved and/or colloidal silica.

Some embodiments comprise transporting a first membrane separator retentate inlet stream to a retentate side of a first membrane separator. A membrane separator refers to a collection of components including one or more semi-permeable membranes configured to perform a membrane-based separation process (e.g., an osmotic process, a filtration process, or a combination thereof) on at least one input stream and produce at least one output stream. The first membrane separator may comprise at least one semi-permeable membrane defining a permeate side of the first membrane separator and a retentate side of the first membrane separator. Each membrane separator described herein may include further sub-units such as, for example, individual semi-permeable membrane modules (e.g., in the form of cartridges), valving, fluidic conduits, and the like. As described in more detail below, each membrane separator can include a single semi-permeable membrane or multiple semi-permeable membranes. In some

embodiments, a single membrane separator can include multiple sub-units (e.g., multiple modules such as multiple cartridges) that may or may not share a common container.

In some embodiments, the first membrane separator retentate inlet stream comprises at least a portion of the pH-adjusted stream. In some embodiments, the first membrane separator retentate inlet stream (which may comprise at least a portion (e.g., at least 5 wt%, at least 10 wt%, at least 20 wt%, at least 50 wt%, at least 80 wt%, at least 90 wt%, at least 95 wt%, at least 99 wt%, or more) of the pH-adjusted stream, optionally with one or more other streams) is transported to a retentate side of a first membrane separator such that a first membrane separator retentate outlet stream exits the retentate side of the first membrane separator, the first membrane separator retentate outlet stream having concentration of dissolved fluoride ions that is greater (e.g., by a factor of at least 1.03, at least 1.035, at least 1.05, at least 1.10, at least 1.25, at least 1.40, at least 1.50, at least 2, at least 3, at least 4, at least 5, at least 10, and/or up to 20, up to 50, or greater) than the concentration of dissolved fluoride ions of the first membrane separator retentate inlet stream. For example, referring again to FIGS. 1-4, first membrane separator 102 may comprise at least one semi-permeable membrane defining retentate side 103 and permeate side 104, and first membrane separator retentate inlet stream 105 may be transported to retentate side 103 such that first membrane separator retentate outlet stream 106 exits retentate side 103. In some embodiments, such as those shown in FIGS. 1-4, first membrane separator retentate inlet stream 105 comprises at least a portion of pH-adjusted stream 101. This step may be performed such that first membrane separator retentate outlet stream 106 has a concentration of dissolved fluoride ions that is greater than the concentration of dissolved fluoride ions of first membrane separator retentate inlet stream 105, according to some embodiments. For example, this step may be performed such that first membrane separator retentate outlet stream 106 has a concentration of the fluoride ions that is increased with respect to the concentration of first membrane separator retentate inlet stream 105 (e.g., by a factor of at least 1.03, at least 1.035, at least 1.05, at least 1.10, at least 1.25, at least 1.40, at least 1.50, at least 2, at least 3, at least 4, at least 5, at least 10, and/or up to 20, up to 50, or greater). In some embodiments, a hydraulic pressure is applied (e.g., to facilitate transport of liquid and/or solute from the retentate side to the permeate side). For example, the hydraulic pressure may be applied the retentate side of the first membrane separator during at least a portion

of time during which the at least a portion of liquid from the first membrane separator retentate inlet stream is transported from the retentate side of the first membrane separator, through the semi-permeable membrane of the first membrane separator, to the permeate side of the first membrane separator. In some embodiments, the system is operated such that the first membrane separator retentate inlet stream has a hydraulic pressure of at least 200 psi (at least 1.38×10^3 kPa), at least 500 psi (at least 3.45×10^3 kPa), at least 750 psi (at least 5.17×10^3 kPa), at least 1000 psi (at least 6.90×10^3 kPa), and/or up to 1500 psi (up to 1.03×10^4 kPa), up to 2000 psi (up to 1.38×10^4 kPa), or more.

In some embodiments, at least a portion (e.g., at least 5 wt%, at least 10 wt%, at least 20 wt%, at least 50 wt%, at least 80 wt%, and/or up to 90 wt%, up to 95 wt%, up to 99 wt%, or more) of liquid (e.g., water) from the first membrane separator retentate inlet stream is transported from the retentate side of the first membrane separator, through a semi-permeable membrane of the first membrane separator, to a permeate side of the first membrane separator. Referring again to FIGS. 1-4, for example, at least a portion of liquid from first membrane separator retentate inlet stream 105 may be transported from retentate side 103, through a semi-permeable membrane, to permeate side 104. Liquid transported from the retentate side to the permeate side of the first membrane separator may form some or all of a first membrane separator permeate outlet stream (e.g., first membrane separator permeate outlet stream 107 in FIGS. 1-4), which may be discharged from the system (e.g., as relatively pure liquid such as relatively pure water).

In some, but not necessarily all embodiments, a portion (e.g., at least 5 wt%, at least 10 wt%, at least 20 wt%, at least 50 wt%, at least 80 wt%, and/or up to 85 wt%, up to 90 wt%, or more) of fluoride ions from the first membrane separator retentate inlet stream is transported from the retentate side of the first membrane separator, through a semi-permeable membrane of the first membrane separator, to a permeate side of the first membrane separator. However, in some embodiments, little or none (e.g., less than or equal to 10 wt%, less than or equal to 5 wt%, less than or equal to 2 wt%, less than or equal to 1 wt%, less than or equal to 0.1 wt%, or less) of the fluoride ions from the first membrane separator retentate inlet stream is transported from the retentate side of the first membrane separator, through a semi-permeable membrane of the first membrane separator, to a permeate side of the first membrane separator.

In some embodiments, one or more membrane separators (e.g., the first membrane separator) is operated as an osmotic separator. For example, in some embodiments, the semi-permeable membrane is an osmotic membrane. Transport of solvent (e.g., water) through osmotic membrane(s) of membrane separators can be achieved via a transmembrane net driving force (i.e., a net driving force through the thickness of the membrane(s)), according to certain embodiments. Generally, the transmembrane net driving force ($\Delta\chi$) is expressed as:

$$\Delta\chi = \Delta P - \Delta\Pi = (P_1 - P_2) - (\Pi_1 - \Pi_2) \quad [3]$$

wherein P_1 is the hydraulic pressure on the retentate side of the osmotic membrane, P_2 is the hydraulic pressure on the permeate side of the osmotic membrane, Π_1 is the osmotic pressure of the stream on the retentate side of the osmotic membrane, and Π_2 is the osmotic pressure of the stream on the permeate side of the osmotic membrane. ($P_1 - P_2$) can be referred to as the transmembrane hydraulic pressure difference, and (Π_1 - Π_2) can be referred to as the transmembrane osmotic pressure difference.

Those of ordinary skill in the art are familiar with the concept of osmotic pressure. The osmotic pressure of a particular liquid is an intrinsic property of the liquid. The osmotic pressure can be determined in a number of ways, with the most efficient method depending upon the type of liquid being analyzed. For certain solutions with relatively low molar concentrations of ions, osmotic pressure can be accurately measured using an osmometer. In other cases, the osmotic pressure can simply be determined by comparison with solutions with known osmotic pressures. For example, to determine the osmotic pressure of an uncharacterized solution, one could apply a known amount of the uncharacterized solution on one side of a non-porous, semi-permeable, osmotic membrane and iteratively apply different solutions with known osmotic pressures on the other side of the osmotic membrane until the differential pressure through the thickness of the membrane is zero.

The osmotic pressure (Π) of a solution containing n solubilized species may be estimated as:

$$\Pi = \sum_{j=1}^{n} i_j M_j RT \quad [4]$$

wherein i_j is the van't Hoff factor of the j^{th} solubilized species, M_j is the molar concentration of the j^{th} solubilized species in the solution, R is the ideal gas constant, and T is the absolute temperature of the solution. Equation [4] generally provides an accurate

estimate of osmotic pressure for liquid with low concentrations of solubilized species (e.g., concentrations at or below between about 4 wt% and about 6 wt%). For many liquids comprising solubilized species, at species concentrations above around 4-6 wt%, the increase in osmotic pressure per increase in salt concentration is greater than linear (e.g., slightly exponential).

As mentioned above, one type of osmotic separation technique that can be performed using the membrane separators of this disclosure, according to some embodiments, is reverse osmosis. Reverse osmosis generally occurs when the osmotic pressure on the retentate side of the osmotic membrane is greater than the osmotic pressure on the permeate side of the osmotic membrane, and a pressure is applied to the retentate side of the osmotic membrane such that the hydraulic pressure on the retentate side of the osmotic membrane is sufficiently greater than the hydraulic pressure on the permeate side of the osmotic membrane such that the osmotic pressure difference is overcome and liquid (e.g., a solvent such as water) is transported from the retentate side of the osmotic membrane to the permeate side of the osmotic membrane. Generally, such situations result when the transmembrane hydraulic pressure difference (P_1-P_2) is greater than the transmembrane osmotic pressure difference (Π_1 - Π_2) such that liquid (e.g., a solvent such as water) is transported from the retentate side of the osmotic membrane to the permeate side of the osmotic membrane (rather than having liquid be transported from the permeate side of the osmotic membrane to the retentate side of the osmotic membrane, which would be energetically favored in the absence of the pressure applied to the retentate side of the osmotic membrane). In some embodiments, the first membrane separator is operated to perform reverse osmosis.

Some embodiments comprise transporting a second membrane separator retentate inlet stream to a retentate side of a second membrane separator. The second membrane separator may comprise at least one semi-permeable membrane defining a permeate side of the second membrane separator and a retentate side of the second membrane separator.

In some embodiments, the second membrane separator retentate inlet stream (which may comprise at least a portion (e.g., at least 5 wt%, at least 10 wt%, at least 20 wt%, at least 50 wt%, at least 80 wt%, at least 90 wt%, at least 95 wt%, at least 99 wt%, or more) of the first membrane separator retentate outlet stream, optionally with one or

more other streams) is transported to a retentate side of the second membrane separator such that a second membrane separator retentate outlet stream exits the retentate side of the second membrane separator, the second membrane separator retentate outlet stream having a concentration of dissolved fluoride ions that is greater (e.g., by a factor of at least 1.03, at least 1.035, at least 1.05, at least 1.10, at least 1.25, at least 1.40, at least 1.50, at least 2, at least 3, at least 4, at least 5, at least 10, and/or up to 20, up to 50, or greater) than the concentration of dissolved fluoride ions of the second membrane separator retentate inlet stream. For example, referring again to FIG. 2, second membrane separator 108 may comprise at least one semi-permeable membrane defining retentate side 109 and permeate side 110, and second membrane separator retentate inlet stream 111 may be transported to retentate side 109 such that second membrane separator retentate outlet stream 112 exits retentate side 109. In some embodiments, such as those shown in FIG. 2, second membrane separator retentate inlet stream 111 comprises at least a portion of first membrane separator retentate outlet stream 106. This step may be performed such that second membrane separator retentate outlet stream 112 has a concentration of dissolved fluoride ions that is greater than the concentration of dissolved fluoride ions of second membrane separator retentate inlet stream 111, according to some embodiments. For example, this step may be performed such that second membrane separator retentate outlet stream 112 has a concentration of dissolved fluoride ions that is increased with respect to the concentration of dissolved fluoride ions of second membrane separator retentate inlet stream 111 (e.g., e.g., by a factor of at least 1.03, at least 1.035, at least 1.05, at least 1.10, at least 1.25, at least 1.40, at least 1.50, at least 2, at least 3, at least 4, at least 5, at least 10, and/or up to 20, up to 50, or greater). In some embodiments, a hydraulic pressure is applied (e.g., to facilitate transport of liquid and/or solute (e.g., fluoride ions) from the retentate side to the permeate side). In some embodiments, the system is operated such that the second membrane separator retentate inlet stream has a hydraulic pressure that is at least 50%, at least 75%, at least 90%, at least 95%, or more of the pressure of the first membrane separator retentate inlet stream. In some embodiments, the system is operated such that the second membrane separator retentate inlet stream has a hydraulic pressure of at least 200 psi (at least 1.38×10^3 kPa), at least 500 psi (at least 3.45×10^3 kPa), at least 750 psi (at least 5.17×10^3

kPa), at least 1000 psi (at least 6.90×10^3 kPa), and/or up to 1500 psi (up to 1.03×10^4 kPa), up to 2000 psi (up to 1.38×10^4 kPa), or more.

In some embodiments, at least a portion (e.g., at least 5 wt%, at least 10 wt%, at least 20 wt%, at least 50 wt%, at least 80 wt%, and/or up to 90 wt%, up to 95 wt%, up to 99 wt%, or more) of liquid (e.g., water) from the second membrane separator retentate inlet stream is transported from the retentate side of the second membrane separator, through a semi-permeable membrane of the second membrane separator, to a permeate side of the second membrane separator. Referring again to FIG. 2, for example, at least a portion of liquid from second membrane separator retentate inlet stream 111 may be transported from retentate side 109, through a semi-permeable membrane, to permeate side 110. Liquid transported from the retentate side to the permeate side of the second membrane separator may form some (e.g., at least 5 wt%, at least 10 wt%, at least 20 wt%, at least 50 wt%, at least 80 wt%, at least 90 wt%, at least 95 wt%, at least 99 wt%, or more) or all of the liquid of a second membrane separator permeate outlet stream (e.g., second membrane separator permeate outlet stream 113 in FIG. 2).

In some, but not necessarily all embodiments, at least a portion (e.g., at least 5 wt%, at least 10 wt%, at least 20 wt%, at least 50 wt%, at least 80 wt%, and/or up to 85%, up to 90%, or more) of the fluoride ions from the second membrane separator retentate inlet stream is transported from the retentate side of the second membrane separator, through the semi-permeable membrane of the second membrane separator, to the permeate side of the second membrane separator. Referring again to FIG. 2and 6, for example, in some embodiments at least a portion of the fluoride ions from second membrane separator retentate inlet stream 111 may be transported from retentate side 109, through a semi-permeable membrane, to permeate side 110. The fluoride ions transported from the retentate side to the permeate side of the second membrane separator may form some (e.g., at least 5 wt%, at least 10 wt%, at least 20 wt%, at least 50 wt%, at least 80 wt%, at least 90 wt%, at least 95 wt%, at least 99 wt%, or more) or all of any solute present in the second membrane separator permeate outlet stream (e.g., second membrane separator permeate outlet stream 113 in FIG. 2). However, in some embodiments, little or none (e.g., less than or equal to 10 wt%, less than or equal to 5 wt%, less than or equal to 2 wt%, less than or equal to 1 wt%, less than or equal to 0.1 wt%, or less) of the fluoride ions from the second membrane separator retentate inlet

stream is transported from the retentate side of the second membrane separator, through a semi-permeable membrane of the second membrane separator, to a permeate side of the second membrane separator.

The amount of fluoride ions that may pass through the semi-permeable membrane of the second membrane separator may depend on any of a variety of parameters such as the fluoride ion concentration in the second membrane separator retentate inlet stream, the permeability of the membrane with respect to fluoride ions, the water permeability of the membrane, the temperature, and/or a magnitude of hydraulic pressure of the second membrane separator retentate inlet stream. In some embodiments, at least a portion of liquid and fluoride ions from the second membrane separator retentate inlet stream is transported from the retentate side of the second membrane separator, through the semi-permeable membrane of the second membrane separator, to the permeate side of the second membrane separator.

While FIGS. 1-4 show one or two membrane separators, it should be understood that a different number of membrane separators can be employed in the system and used in the methods of this disclosure. For example, a system comprising a plurality of membrane separators may have at least one, at least two, at least three, at least four, at least five, at least ten, and least twenty, or more membrane separators configured as described in this disclosure. For example, some embodiments comprise transporting a third membrane separator retentate inlet stream to a retentate side of a third membrane separator. The third membrane separator may comprise at least one semi-permeable membrane defining a permeate side of the third membrane separator and a retentate side of the third membrane separator. The third membrane separator retentate inlet stream may comprise at least a portion of the second membrane separator retentate outlet stream.

In some embodiments, at least a portion of a stream exiting one or more membrane separator is recirculated and fed back into a membrane separator (e.g., an upstream membrane separator). Such recycle processes may allow for relatively high amounts of liquid to be removed by the system (in some instances using fewer system components) and/or for relatively high recovery rates and/or efficiencies compared to some embodiments in which no such recycle occurs.

As one example of a recycle process, in some embodiments the first membrane separator retentate inlet stream comprises at least a portion (e.g., at least 5 wt%, at least 10 wt%, at least 20 wt%, at least 50 wt%, at least 80 wt%, at least 90 wt%, at least 95 wt%, at least 99 wt%, or more) of the first membrane separator retentate outlet stream. The first membrane separator retentate inlet stream may comprise at least a portion of the first membrane separator retentate outlet stream during at least a period of time (e.g., an entirety or a subset of time) during operation of the first membrane separator as part of the methods described in this disclosure. As an illustrative example, the embodiment shown in FIG. 3 shows a portion of first membrane separator retentate outlet stream 106 being transported back to first membrane separator retentate inlet stream 105 as recycle stream 119. Recycle stream 119 may be combined with pH-adjusted stream 101 to form at least part of first membrane separator retentate inlet stream 105. However, in some embodiments, such as during certain of the batch processes described below, the recycle stream comprising at least a portion of the first membrane separator retentate outlet stream is not mixed with the pH-adjusted stream prior to or during incorporation of that portion of the first membrane separator retentate outlet stream into the first membrane separator retentate inlet stream. For example, in some embodiments, during at least a period of time during the liquid removal process, the first membrane separator retentate inlet stream comprises at least a portion of the first membrane separator retentate outlet stream, but less than or equal to 20 wt%, less than or equal to 10 wt%, less than or equal to 5 wt%, less than or equal to 2 wt%, less than or equal to 1 wt%, less than or equal to 0.1 wt%, or none of the first membrane separator retentate inlet stream is from the pH-adjusted stream during that period of time.

In some embodiments, a hydraulic pressure of the recycle stream is increased (e.g., by a factor of greater than or equal to 1.05, greater than or equal to 1.1, greater than or equal to 1.2, greater than or equal to 1.5, greater than or equal to 2, greater than or equal to 5, and/or up to 10, up to 20, or more) prior to becoming part of the first membrane separator retentate inlet stream. Such an increase in pressure can be accomplished using any of a variety of techniques, such as using a pump. In some instances, the recycle process involving the first membrane separator (e.g., incorporating a portion of the first membrane separator retentate outlet stream into the first membrane separator retentate inlet stream) is performed in a batch manner. In some embodiments,

the recycle process is performed in a continuous manner. In some embodiments, the recycle process is performed using a semi-batch process. Batch operation, semi-batch operation, and continuous operation of membrane separators are generally known. During batch operation, a hydraulic pressure of the membrane separator retentate inlet stream is increased over time during operation, as quantities of streams are fed to the retentate side inlet stream. A difference between batch and semi-batch operation in this context is that during semi-batch operation, at least some mixing of the recycle stream (e.g., a portion of the first membrane separator retentate outlet stream) and the pH-adjusted stream feeding the first membrane separator retentate inlet stream occurs. Batch or semi-batch operation of a process involving a membrane separator (e.g., a recycle process) can reduce the amount of energy required to operate the membrane separator by gradually increasing the concentration (and in some instances the hydraulic pressure) of the membrane separator retentate inlet stream rather than maintaining an entirety of the membrane separator's streams at a high pressure, as is generally the case during continuous operation. Such a reduction in energy usage may allow for fluoride ion (and in some instances silica) concentration with greater energy efficiency.

As noted elsewhere, one or more additional contaminants in the aqueous stream fed to the system may be removed. For example, at least a portion of the pH-adjusted stream may be subjected to one or more additional treatment steps before being transported to the retentate side of the first membrane separator (e.g., as part of or all of the first membrane separator retentate inlet stream). In some embodiments, the pH-adjusted stream comprises silica (SiO_2). At least some (e.g., at least 50 wt%, at least 75 wt%, at least 90 wt%, at least 95 wt%, at least 98 wt%, at least 99 wt%, at least 99.9 wt%) or all of the silica in the pH-adjusted stream (e.g., immediately after the pH-adjustment) may be, for example, dissolved and/or colloidal silica. In some embodiments, at least a portion (e.g., at least 50 wt%, at least 75 wt%, at least 90 wt%, at least 95 wt%, at least 98 wt%, at least 99 wt%, at least 99.9 wt%) of the dissolved and/or colloidal silica in the pH-adjusted stream is subjected to coagulation. For example, in FIG. 4, at least a portion of pH-adjusted stream 101 (shown as stream 101a) may be transported to coagulation vessel 26 (e.g., a tank or flow reactor), where that portion may be exposed to one or more coagulants (either as a solid or as part of a liquid solution), thereby producing portion 101b containing at least some of the coagulated silica. The

coagulation vessel may be fluidically connected to an outlet of the pH adjustment vessel. The coagulation vessel may be further configured to receive the coagulant (e.g., in a solid and/or liquid state). The coagulation vessel may be fluidically connected to one or more downstream components of the system. For example, in FIG 4, coagulation vessel 26 is fluidically connected (indirectly) to retentate side 103 of first membrane separator 102.

In some embodiments, the coagulant comprises an inorganic coagulant. Non-limiting examples of inorganic coagulants include, but are not limited to, iron chloride, ferric sulfate, sodium aluminate, aluminum chlorohydrate, polyaluminum chloride, magnesium chloride, and/or magnesium oxide. Organic coagulant such as polyamine may also be used in addition or instead of an inorganic coagulant. It has been realized in the context of this disclosure that some coagulants such as ferric chloride and ferric sulfate can be used in relatively low pH ranges, which may be beneficial for certain pH adjusted streams, as discussed above. The amount of coagulant used may be sufficiently high so as to induce the desired amount of coagulation of the silica.

In some embodiments, at least some (e.g., at least 50 wt%, at least 75 wt%, at least 90 wt%, at least 95 wt%, at least 98 wt%, at least 99 wt%, at least 99.9 wt%) or all of the coagulated silica in the pH-adjusted stream (e.g., immediately after the coagulation process) is subjected to flocculation. For example, in FIG. 4, at least a portion of pH-adjusted stream 101 (shown as stream 101b) may be transported from coagulation vessel 26 to flocculation vessel 27 (e.g., a tank or flow reactor), where that portion may be exposed to one or more flocculants (either as a solid or as part of a liquid solution), thereby producing portion 101c containing at least some of the flocs of silica formed. The flocculation vessel may be fluidically connected to an outlet of the coagulation vessel. The flocculation vessel may be further configured to receive the flocculant (e.g., in a solid and/or liquid state). The flocculation vessel may be fluidically connected to one or more downstream components of the system. For example, in FIG 4, coagulation vessel 27 is fluidically connected (indirectly) to retentate side 103 of first membrane separator 102.

In some embodiments, the flocculent comprises a polymer. In some embodiments, the flocculent comprises a polyelectrolyte. A polyelectrolyte generally refers to a polymer comprising a plurality of repeat units that comprise a group that

dissociates into a cation and an anion in an aqueous solution. It is believed that addition of the polyelectrolyte to the aqueous stream may promote the formation of flocs through bridging.

In some embodiments, the polyelectrolyte comprises an anionic polymer. The anion polymer may have a negative charge after dissociation in solution. In some embodiments, the polyelectrolyte comprises a non-ionic polymer. A non-ionic polymer may have a neutral charge after dissociation in solution.

In some embodiments, the polyelectrolyte is a homopolymer. In certain embodiments, the polyelectrolyte is a. In some such embodiments, the polyelectrolyte is an alternative copolymer, a periodic copolymer, a statistic copolymer, a block copolymer, and/or a grafted copolymer.

In some embodiments, the polyelectrolyte comprises polyacrylamide. According to some embodiments, the polyelectrolyte comprises a non-ionic polyacrylamide. In certain embodiments, the non-ionic polyacrylamide is a homopolymer (e.g., comprising only polyacrylamide repeat units). In some embodiments, the polymer comprises an anionic polymer. According to some embodiments, the polyelectrolyte comprises an anionic polyacrylamide. In certain embodiments, the anionic polyacrylamide is a copolymer. In some embodiments, for example, the anionic polyacrylamide comprises acrylamide repeat units and one or more additional types of repeat units (e.g., acrylate repeat units).

In some embodiments, the flocculant comprises a natural polymer (e.g., polysaccharides such as starch and its constituents, different types of gums, alginic acid, cellulose and its derivatives, dextran, glycogen). Other examples of polymer flocculants that may be used include, but are not limited to polyethylene oxide (PEO), polydiallyl dimethyl ammonium chloride (polyDADMAC), polyacrylic acid and its derivatives, polystyrene sulfonic acid (PSSA), and any other suitable flocculants.

In some embodiments, at least some (e.g., at least 50 wt%, at least 75 wt%, at least 90 wt%, at least 95 wt%, at least 98 wt%, at least 99 wt%, at least 99.9 wt%) or all of the floc and/or agglomerated silica in the pH-adjusted stream (e.g., immediately after the flocculation process) is subjected to a solids separation process. For example, in FIG. 4, at least a portion of pH-adjusted stream 101 (shown as stream 101c) may be transported from flocculation vessel 27 to solids separation vessel 28, thereby producing

stream 101d containing less flocculated and/or agglomerated silica than stream 101c entering solids separation vessel 28. Solids separation vessel 28 may also produce stream 160 comprising concentrated solid silica that is in the form of sludge, or which is subsequently converted to sludge via downstream processing. The solids separation vessel may be fluidically connected to an outlet of the flocculation vessel. The solids separation vessel may be fluidically connected to one or more downstream components of the system. For example, in FIG 4, solids separation vessel 28 is fluidically connected (indirectly) to retentate side 103 of first membrane separator 102.

The solids separation vessel be in any of a variety of configurations. In some embodiments, the solids separation vessel comprises a gravity-based settling vessel. In certain embodiments, the gravity-based settling vessel comprises a clarifier. The clarifier can be configured such that at least a portion of floc within a stream in the clarifier settle within the clarifier.

In certain embodiments, the clarifier is a lamella clarifier (e.g., an inclined-plate clarifier). A lamella clarifier generally refers to a vessel comprising a plurality of inclined plates. In operation, a stream may enter the lamella clarifier, and floc within the stream may settle on one or more of the inclined plates of the lamella clarifier. In some cases, floc may begin to accumulate on the inclined plates, and as the weight of the accumulated flocs increases, the flocs may slide down the inclined plates to the bottom of the clarifier. In certain cases, collection hoppers may be located at the bottom of the clarifier, collecting the settling flocs as a solids-containing stream. In some cases, a sludge removal device (e.g., a sludge scraper) may scrape the bottom of the clarifier to remove sludge from the clarifier. In some embodiments, at least a portion of the removed sludge may exit the clarifier as part of the solids-containing stream. A clarified stream comprising fewer contaminants may exit through the top of the clarifier. Non-limiting examples of suitable clarifiers include a Hydro-Flo ClariMax™ inclined plate clarifier and a Slant Plate Clarifier (M.W. Watermark).

Other non-limiting examples of solids separation vessels include, for example, a hydrocyclone (e.g., a de-oiling hydrocyclone), a corrugated plate interceptor, an adsorption media filter, a coalescing media filter, a membrane filter, an induced gas flotation (IGF) separator, and/or a skimmer.

In some embodiments, at least some (e.g., at least 50 wt%, at least 75 wt%, at least 90 wt%, at least 95 wt%, at least 98 wt%, at least 99 wt%, at least 99.9 wt%) or all of the pH-adjusted stream (e.g., as the clarified stream output by the solids separation vessel) is subjected to a filtration process. For example, in FIG. 4, at least a portion of pH-adjusted stream 101 (shown as stream 101d) may be transported from solids separation vessel 28 to filtration assembly 29, thereby producing stream 101e containing filtered pH-adjusted stream. Stream 101e may form some or all of first membrane separator retentate inlet stream 105. The solids separation vessel may be fluidically connected to an outlet of the solids separation vessel. The filtration assembly may also be fluidically connected to one or more downstream components of the system. For example, in FIG 4, filtration assembly 29 is fluidically connected to retentate side 103 of first membrane separator 102.

The filtration assembly may be in any of a variety of configurations. In some embodiments, the filtration assembly comprises one or more semi-permeable membranes defining a retentate side and a permeate side. The permeate side of the filtration assembly may be fluidically connected to the retentate side of the first membrane separator. In some embodiments, the filtration assembly comprises an ultrafiltration unit. In some embodiments, the filtration assembly comprises a reverse osmosis unit (e.g., a polishing reverse osmosis unit). In some embodiments, the filtration assembly comprises an ultrafiltration unit followed by a reverse osmosis unit configured to receive at least some of the permeate produced by ultrafiltration unit. The first membrane separator may be configured to receive at least a portion of the permeate output from the reverse osmosis unit.

In some embodiments, a pressure of any of the streams described herein can be increased via one or more additional components, such as one or more booster pumps. In some embodiments, a pressure of any of the streams described herein can be decreased via one or more additional components, such as one or more additional valves and/or energy recovery devices. In some embodiments, a membrane separator described herein further comprises one or more heating, cooling, or other concentration or dilution mechanisms or devices.

The membrane separators described herein (e.g., the first membrane separator, the second membrane separator, the third membrane separator) can each include a single semi-permeable membrane or a plurality of semi-permeable membranes.

FIG. 5A is a schematic illustration of membrane separator 200A, in which a single semi-permeable membrane is used to separate permeate side 204 from retentate side 206. Membrane separator 200A can be operated by transporting retentate inlet stream 210 across retentate side 206. At least a portion of a liquid (e.g., a solvent) and, in some instances, solute within retentate inlet stream 210 can be transported across semi-permeable membrane 202 to permeate side 204. This can result in the formation of retentate outlet stream 212, which can include a higher concentration of solute than is contained within retentate inlet stream 210, as well as permeate outlet stream 214. Permeate outlet stream 214 can correspond to the liquid (e.g., solvent) and, in some instances, solute, of retentate inlet stream 210 that was transported from retentate side 206 to permeate side 204.

In some embodiments, a membrane separator (e.g., the first membrane separator, the second membrane separator, the third membrane separator) comprises a plurality of semi-permeable membranes connected in parallel. One example of such an arrangement is shown in FIG. 5B. In FIG. 5B, membrane separator 200B comprises three semi-permeable membranes 202A, 202B, and 202C arranged in parallel. Retentate inlet stream 210 is split into three sub-streams, with one sub-stream fed to retentate side 206A of semi-permeable membrane 202A, another sub-stream fed to retentate side 206B of semi-permeable membrane 202B, and yet another sub-stream fed to retentate side 206C of semi-permeable membrane 202C. Membrane separator 200B can be operated by transporting the retentate inlet sub-streams across the retentate sides of the semi-permeable membranes. At least a portion of a liquid (e.g., a solvent), and, in some instances, solute, within retentate inlet stream 210 can be transported across each of semi-permeable membranes 202A, 202B, and 202C to permeate sides 204A, 204B, and 204C, respectively. This can result in the formation of three retentate outlet sub-streams, which can be combined to form retentate outlet stream 212. Retentate outlet stream 212 can include a higher concentration of solute than is contained within retentate inlet stream 210. Permeate outlet stream 214 can also be formed (from three permeate outlet sub-streams). Permeate outlet stream 214 can correspond to the liquid (e.g., solvent),

and, in some instances, solute of retentate inlet stream 210 that was transported from retentate sides 206A-206C to permeate sides 204A-204C.

While FIG. 5B shows three semi-permeable membranes connected in parallel, other embodiments could include 2, 4, 5, or more semi-permeable membranes connected in parallel.

In some embodiments, a membrane separator (e.g., the first membrane separator, the second membrane separator) comprises a plurality of semi-permeable membranes connected in series. One example of such an arrangement is shown in FIG. 5C. In FIG. 5C, membrane separator 200C comprises three semi-permeable membranes 202A, 202B, and 202C arranged in series. In FIG. 5C, retentate inlet stream 210 is first transported to retentate side 206A of semi-permeable membrane 202A. At least a portion of a liquid (e.g., a solvent), and, in some instances, solute, within retentate inlet stream 210 can be transported across semi-permeable membrane 202A to permeate side 204A of semi-permeable membrane 202A. This can result in the formation of permeate outlet stream 214 and first intermediate retentate stream 240 that is transported to retentate side 206B of semi-permeable membrane 202B. At least a portion of a liquid (e.g., a solvent), and, in some instances, solute, within first intermediate retentate stream 240 can be transported across semi-permeable membrane 202B to permeate side 204B of semi-permeable membrane 202B. This can result in the formation of permeate outlet stream 250 and second intermediate retentate stream 241 that is transported to retentate side 206C of semi-permeable membrane 202C. At least a portion of a liquid (e.g., a solvent), and, in some instances, solute within second intermediate retentate stream 241 can be transported across semi-permeable membrane 202C to permeate side 204C of semi-permeable membrane 202C. This can result in the formation of permeate outlet stream 251 and retentate outlet stream 212.

While FIG. 5C shows three semi-permeable membranes connected in series, other embodiments could include 2, 4, 5, or more semi-permeable membranes connected in series.

For membrane separators comprising a plurality of semi-permeable membranes, parameters such as rejection percentage, recovery, and salt passage percentage at standard conditions for the membrane separators are calculated by performing a mass balance on the entire membrane separator. This means that all initial retentate streams

for the membrane separator would be added and considered together, all final permeate outlet streams for the membrane separator would be added and considered together, and all final retentate outlet streams for the membrane separator would be added and considered together. For example, as mentioned above, in FIG. 5B, membrane separator 200B comprises three semi-permeable membranes 202A, 202B, and 202C arranged in parallel. Accordingly, calculation of the composition of the retentate inlet stream of membrane separator 200B for the purpose of calculating parameters such as the rejection percentage, recovery, and salt passage percentage at standard conditions for membrane separator 200B would involve taking measurements of retentate inlet stream 210 prior to it being split into the three inlet sub-streams fed to retentate sides 206A, 206B, and 206C of semi-permeable membranes 202A, 202B, and 202C, respectively. Similarly, calculation of the composition of the retentate outlet stream of membrane separator 200B for the purpose of calculating parameters such as the rejection percentage, recovery, and salt passage percentage at standard conditions for membrane separator 200B would involve taking measurements of retentate outlet stream 212, which is a combination of the three outlet sub-streams from retentate sides 206A, 206B, and 206C from semi-permeable membranes 202A, 202B, and 202C, respectively. Also similarly, calculation of the composition of the permeate outlet stream of membrane separator 200B for the purpose of calculating parameters such as the rejection percentage, recovery, and salt passage percentage at standard conditions would involve taking measurements of permeate outlet stream 214, which is a combination of the three outlet sub-streams from permeate sides 204A, 204B, and 204C from semi-permeable membranes 202A, 202B, and 202C, respectively.

As another example of the calculation of parameters corresponding to a membrane separator comprising a plurality of semi-permeable membranes, reference is made to membrane separator 200C in FIG. 5C. Membrane separator 200C comprises three semi-permeable membranes 202A, 202B, and 202C arranged in series. Accordingly, calculation of the composition of the retentate inlet stream of membrane separator 200C for the purpose of calculating parameters such as the rejection percentage, recovery, and salt passage percentage at standard conditions for membrane separator 200C would involve taking measurements of retentate inlet stream 210 prior to it entering semi-permeable membrane 202A because semi-permeable membrane 202A is

the initial semi-permeable membrane in the series. Similarly, calculation of the composition of the retentate outlet stream of membrane separator 200C for the purpose of calculating parameters such as the rejection percentage, recovery, and salt passage percentage at standard conditions for membrane separator 200C would involve taking measurements of retentate outlet stream 212 exiting semi-permeable membrane 202C because semi-permeable membrane 202C is the final semi-permeable membrane in the series with respect to the retentate outlet streams, thereby making retentate outlet stream 212 the final retentate outlet stream of membrane separator 200C. Calculation of the composition of the permeate outlet stream of membrane separator 200C for the purpose of calculating parameters such as the rejection percentage, recovery, and salt passage percentage at standard conditions would involve taking measurements of a combination of permeate outlet streams 214, 250, and 251 exiting semi-permeable membranes 202A, 202B, and 202C respectively. In addition, in some embodiments, a given membrane separator could include multiple semi-permeable membranes connected in parallel as well as multiple semi-permeable membranes connected in series.

In some embodiments, the first membrane separator comprises a plurality of semi-permeable membranes. In some such embodiments, the plurality of semi-permeable membranes within the first membrane separator are connected in series. In some such embodiments, the plurality of semi-permeable membranes within the first membrane separator are connected in parallel. In certain embodiments, the first membrane separator comprises a plurality of membranes a first portion of which are connected in series and another portion of which are connected in parallel.

In some embodiments, the second membrane separator comprises a plurality of semi-permeable membranes. In some such embodiments, the plurality of semi-permeable membranes within the second membrane separator are connected in series. In some such embodiments, the plurality of semi-permeable membranes within the second membrane separator are connected in parallel. In certain embodiments, the second membrane separator comprises a plurality of membranes a first portion of which are connected in series and another portion of which are connected in parallel.

As mentioned above, each membrane separator of the system may comprise at least one semi-permeable membrane. In general, a semi-permeable membrane is a barrier that allows some components of a mixture to pass through while blocking at least

some of other components (e.g., blocking all of another component, or reducing the relative rate of permeation of another component). For example, a semi-permeable membrane may block some molecules in a liquid solution from passing through while allowing others to pass through. In some instances, a semi-permeable membrane blocks some molecules and permits other molecules to pass through based on their molecular weight and/or charge. As noted above, a semi-permeable membrane can be used for osmotic processes. For example, the semi-permeable membrane may be an osmotic membrane. An osmotic membrane may be capable of producing an osmotic pressure difference between solutions on either side of the membrane upon application of a hydraulic pressure difference across the two sides of the membrane. For example, if an osmotic membrane is placed between two solutions of identical composition such that there is initially no osmotic pressure difference across the membrane, application of a hydraulic pressure difference across the osmotic membrane may allow for transport of components from one side of the membrane to the other such that an osmotic pressure difference across the two sides of the membrane is established. Semi-permeable membranes may also be used for nanofiltration processes. Semi-permeable membranes may be configured for osmotic processes, nanofiltration processes, and/or processes in which separation is achieved based on a combination of nanofiltration and osmotic mechanisms (e.g., based on, for example, the molecular weight cutoff of the membranes, pore sizes of the membranes, the nature of the mixtures to which they are exposed, and a magnitude of applied hydraulic pressure).

The semi-permeable membrane medium can comprise, for example, a metal, a ceramic, a polymer (e.g., polyamides, polyethylenes, polyesters, poly(tetrafluoroethylene), polysulfones, polycarbonates, polypropylenes, poly(acrylates)), and/or composites or other combinations of these. The semi-permeable membranes generally allow for the selective transport of solvent (e.g., water) through the membrane, where solvent is capable of being transmitted through the membrane while solute (e.g., solubilized species such as solubilized ions) are inhibited from being transported through the membrane. Examples of commercially available semi-permeable membranes that can be used in association with certain of the embodiments described herein include, but are not limited to, those commercially available from Dow Water and Process Solutions (e.g., FilmTec^{TM} membranes), Hydranautics, GE Osmonics, Suez, LG,

Toyobo, Microdyn, and Toray Membrane, among others known to those of ordinary skill in the art.

In some embodiments, the semi-permeable membrane(s) of the first membrane separator and/or the second membrane separator has an average pore size of greater than or equal to 0.0001 microns, greater than or equal to 0.001 microns, greater than or equal to 0.002 microns or greater. In some embodiments, the semi-permeable membrane of the first membrane separator and/or the second membrane separator has an average pore size of less than or equal to 0.01 microns, less than or equal to 0.005 microns, or less. Combinations of these ranges (e.g., greater than or equal to 0.0001 microns and less than or equal to 0.01 microns) are possible.

In some embodiments (such as some embodiments in which the first membrane separator receives a permeate inlet stream), the semi-permeable membrane(s) of the second membrane separator has an average pore size that is greater than that of the semi-permeable membrane(s) of the first membrane separator (e.g., by a factor of at least 1.05, at least 1.1, at least 1.2, at least 1.5, at least 2, at least 3, at least 5, or more). The average pore size of the semi-permeable membrane may affect any of a variety of the parameters discussed below, such as solute permeability, water permeability, salt passage, rejection, and/or recovery. Average pore size can be determined, for example, using mercury intrusion porosimetry.

In some embodiments, the semi-permeable membrane of a membrane separator of this disclosure has an average molecular weight cutoff (MWCO) that is sufficiently high such that a desired amount of liquid and/or solute (and/or type of solute) can pass through during operation of the system. In some embodiments, the semi-permeable membrane(s) of the first membrane separator and/or the second membrane separator, has an average MWCO of greater than or equal to 50 Daltons, greater than or equal to 75 Daltons, greater than or equal to 100 Daltons, greater than or equal to 150 Daltons, or greater. In some embodiments, the semi-permeable membrane of a membrane separator of this disclosure has an average molecular weight cutoff (MWCO) that is sufficiently low such that a desired amount of solute (and/or type of solute) is rejected such that an effective separation is performed. In some embodiments, the semi-permeable membrane(s) of the first membrane separator and/or the second membrane separator has an average MWCO of less than or equal to 400 Daltons, less than or equal to 300

Daltons, less than or equal to 250 Daltons, less than or equal to 200 Daltons, or less. Combinations of these ranges (e.g., greater than or equal to 50 Daltons and less than or equal to 400 Daltons, greater than or equal to 50 Daltons and less than or equal to 250 Daltons) are possible. The average MWCO of a membrane refers to the lowest molecular weight solute in which 90% of the solute is retained by the membrane.

In some embodiments, the semi-permeable membrane(s) of the second membrane separator has an average MWCO that is greater than that of the semi-permeable membrane(s) of the first membrane separator (e.g., by a factor of at least 1.05, at least 1.1, at least 1.2, at least 1.5, at least 2, at least 3, at least 5, and/or up to 10, up to 20, or more). The average MWCO of the semi-permeable membrane may affect any of a variety of the parameters discussed below, such as solute permeability, salt passage, rejection, and/or recovery.

The solute (e.g., fluoride ion) permeability of each membrane separator may be chosen based on any of a variety of design criteria such as desired purity of permeate, desired hydraulic pressure to be used, and nature of incoming influent (e.g., solute concentration of incoming influent). The solute permeability of a membrane separator can be calculated from the solute flux through the membrane and the respective concentrations of solute on either side using equation [5] below:

$$J_S = B(C_R - C_P) \quad [5]$$

In the above equation, J_s represents the ion flux, C_R represents the concentration of solute on the retentate side of the membrane, C_P represents the concentration of solute on the permeate side of the membrane, and B represents the solute permeability. Solute permeability is dependent on the species of solute in the retentate inlet stream and the concentrations on either side of the membrane.

In some embodiments, the solute permeabilities of the first membrane separator and the second membrane separator (and, if present a third membrane separator, a fourth membrane separator, or more) during operation of the method are chosen to afford good, consistent performance across all membrane separators by accounting for differences in concentrations of their respective retentate inlet streams. In some embodiments, the solute permeability of the first membrane separator during the step of transporting the first membrane separator retentate inlet stream to the retentate side of the first membrane separator is different than the solute permeability of the second membrane separator

during the step of transporting the second membrane separator retentate inlet stream to the retentate side of the second membrane separator. The difference in solute permeabilities between the first membrane separator and the second membrane separator may be due, at least in part, to use of different semi-permeable membranes in the first and second membrane separators (e.g., having different pore sizes, MWCOs, and/or surface chemistries). In some embodiments, the solute permeability of the first membrane separator during the step of transporting the first membrane separator retentate inlet stream to the retentate side of the first membrane separator and the solute permeability of the second membrane separator during the step of transporting the second membrane separator retentate inlet stream to the retentate side of the second membrane separator are at least 5% different, at least 10% different, at least 20% different, at least 50% different, and/or up to 100% different or more different from each other.

In some embodiments, the solute permeability of the second membrane separator during the step of transporting the second membrane separator retentate inlet stream to the retentate side of the second membrane separator is greater than the solute permeability of the first membrane separator during the step of transporting the first membrane separator retentate inlet stream to the retentate side of the first membrane separator (e.g., by a factor of at least 1.05, at least 1.1, at least 1.2, at least 1.5, at least, 2, at least, 3, at least 5, or more). In some embodiments, the first membrane separator has a solute permeability of 0 during operation of the first membrane separator. In this context, the solute permeability refers to the permeability of all total solute in the streams. However, in some embodiments, the relationships between permeabilities of the first and second membrane separators hold for one or more specific solute species described in this disclosure, such as solubilized NaCl and/or solubilized fluoride ions.

When calculating the percentage difference between two values (unless specified otherwise herein), the percentage calculation is made using the value that is larger in magnitude as the basis. To illustrate, if a first value is V_1, and a second value is V_2 (which is larger than V_1), the percentage difference ($V_{\%Diff}$) between V_1 and V_2 would be calculated as:

$$V_{\%Diff} = \frac{V_2 - V_1}{V_2} \times 100\% \quad [6]$$

and the first and second values would be said to be within X% of each other if $V_{\%Diff}$ is X% or less, and the first and second values would be said to be at least X% different than each other if $V_{\%Diff}$ is X% or more.

Water permeability can be calculated from the water flux, pressure differential and osmotic differential, as shown below in equation [7]:

$$J_W = A(\Delta P - \Delta \pi) \quad [7]$$

In the above equation [7], J_w represents the flux of water through the membrane, ΔP represents the hydraulic pressure differential across the membrane, $\Delta \pi$ represents the osmotic pressure differential across the membrane, and A represents the water permeability.

The salt passage percentage at standard conditions of each membrane separator may be chosen based on any of a variety of design criteria such as desired purity of permeate, desired hydraulic pressure to be used, and nature of incoming influent (e.g., solute type and/or concentration of incoming influent). The salt passage percentage at standard conditions of a membrane separator is an intrinsic property of the separator based on the quantity of salt, as a percentage, which passes through the semi-permeable membrane(s) from the retentate side to the permeate side of the membrane separator under defined reference conditions. The salt passage percentage at standard conditions of a membrane separator can be determined using the standardized test described in ASTM D4516-19a.

In some embodiments, the salt passages at standard conditions of the first membrane separator and the second membrane separator (and, if present a third membrane separator, a fourth membrane separator, or more) used in in the operation of the method are chosen to afford good, consistent performance across all membrane separators by accounting for differences in concentrations of their respective retentate inlet streams. In some embodiments, the salt passage percentage at standard conditions of the first membrane separator is different than the salt passage percentage at standard conditions of the second membrane separator. The difference in salt passages at standard conditions between the first membrane separator and the second membrane separator may be due, at least in part, to use of different semi-permeable membranes in the first and second membrane separators (e.g., having different pore sizes, MWCOs, and/or surface chemistries). In some embodiments, the salt passage percentage at standard

conditions of the first membrane separator and the salt passage percentage at standard conditions of the second membrane separator are at least 5% different, at least 10% different, at least 20% different, at least 50% different, and/or up to 100% different or more different from each other. In some embodiments, the salt passage percentage at standard conditions of the second membrane separator is greater than the salt passage percentage at standard conditions of the first membrane separator (e.g., by a factor of at least 1.05, at least 1.1, at least 1.2, at least 1.5, at least, 2, at least, 3, at least 5, and/or up to 10, up to 20, or more).

In some embodiments, the salt passage percentage at standard conditions of the first membrane separator and/or the second membrane separator membrane separator are independently greater than or equal to 0%, greater than or equal to 1%, greater than or equal to 2%, greater than or equal to 5%, greater than or equal to 10%, greater than or equal to 15%, greater than or equal to 20%, greater than or equal to 50%, greater than or equal to 75%, and/or up to 80%, up to 85%, up to 90%, or greater. In some embodiments, the first membrane separator has a relatively low salt passage percentage at standard conditions. Such a low salt passage percentage at standard conditions may be useful in embodiments in which the first membrane separator is operated as a high-rejection reverse osmosis separator. In some embodiments, the first membrane separator has a salt passage percentage at standard conditions of less than or equal to 10%, less than or equal to 5%, less than or equal to 2%, less than or equal to 1%, less than or equal to 0.1%, or less. In some embodiments, the second membrane separator has a relatively low salt passage percentage at standard conditions. Such a low salt passage percentage at standard conditions may be useful in embodiments in which the second membrane separator is operated as a high-rejection reverse osmosis separator. In some embodiments, the second membrane separator has a salt passage percentage at standard conditions of less than or equal to 10%, less than or equal to 5%, less than or equal to 2%, less than or equal to 1%, less than or equal to 0.1%, or less.

Intrinsic properties of a semi-permeable membrane such as salt passage percentage at standard conditions, pore size, and/or MWCO can be selected based on supplier specifications for commercially-obtained membranes, by controlling the synthesis of membranes, and/or by physically and/or chemically modifying existing membranes (e.g., commercially obtained membranes). As an example of the latter, in

some embodiments, a set of identical membranes may be obtained commercially (or prepared synthetically). A first subset of the membranes may be used without further modification. A second subset may be subjected to a first type of modification procedure (e.g., chemical treatment) that enlarges the pores of the membranes and/or modifies the surface chemistry of the membranes in such a way that the intrinsic salt passage (salt passage percentage at standard conditions), average pore size, and/or MWCO is increased. In such a way, the first subset of membranes could be incorporated into the first membrane separator and the second subset of membranes into the second membrane separator. Each of the first membrane separator and the second membrane separator may then have a differing salt passage percentage at standard conditions and, in use, differing permeabilities, rejections, and recoveries.

In some embodiments, the semi-permeable membrane comprises cross-links. For example, the membrane may be a cross-linked polyamide membrane. In some embodiments, the semi-permeable membrane comprises an active layer which comprises the cross-links (e.g., a cross-linked polyamide active layer). One way in which a semi-permeable membrane of can be modified (e.g., such that the intrinsic salt passage, average pore size, and/or MWCO is increased) is via disruption of at least some (e.g., at least 0.01 mole percent (mol%), at least 0.1 mol%, at least 0.2 mol%, at least 0.5 mol%, at least 1 mol%, at least 2 mol%, at least 5 mol%, and/or up to 10 mol%, up to 20 mol%, or more) of the cross-links of the membrane. For example, cross-links (e.g., of polyamide chains) of the membrane may be disrupted via physical treatment (e.g., thermal treatment and/or mechanical disruption) and/or chemical treatment (e.g., via treatment with a chemical reagent and/or ultraviolet or visible light). Chemical treatment may result in chemical disruption (e.g., via breaking of chemical bonds due to a chemical reaction, breaking of noncovalent interactions such as hydrogen bonding) of at least some (e.g., at least 0.1 mole percent (mol%), at least 0.2 mol%, at least 0.5 mol%, at least 1 mol%, at least 2 mol%, at least 5 mol%, and/or up to 10 mol%, up to 20 mol%, or more) of the cross-links. In some embodiments in which the semi-permeable membrane comprises cross-links (e.g., as part of an active layer), the semi-permeable membrane comprises a cross-linked polymeric material derived from monomers. In some such embodiments, fewer than or equal to 99.9 mol% (e.g., fewer than or equal to 99 mol%, fewer than or equal to 98 mol%, fewer than or equal to 95 mol%, and/or as few as 90

mol%, as few as 80 mol%, or fewer) of the monomers participate in at least one cross-link (e.g., due at least in part to disruption such as chemical disruption).

One example of a way in which at least some cross-links may be disrupted is by treating at least a portion of the membrane with a chemical reagent tending to break covalent and/or noncovalent bonds within the cross-links of the membrane. In some embodiments, the chemical reagent comprises an oxidant. One example of a potential oxidant for use with at least some membranes (e.g., polyamide membranes) is hypochlorite (ClO^-). The hypochlorite may be provided as a solution comprising sodium hypochlorite (NaClO). The cross-links of the membrane may be disrupted by exposing at least a portion of the membrane to the chemical reagent (e.g., an oxidant such as hypochlorite). The duration of the exposure and/or the amount of chemical reagent (e.g., concentration of reagent in a solution contacting the membrane) may be selected based on a desired extent of disruption of the cross-links of the membrane. The desired extent of disruption of the cross-links of the membrane may in turn be based at least on a desired permeability of the semi-permeable membrane under certain conditions, a desired average pore size, and/or a desired MWCO.

The presence and extent of disrupted cross-links may be determined by examination of the semi-permeable membrane. For example, the loss of cross-links due to chemical disruption may be detected and quantified by observing the presence and/or number of certain atoms or moieties (e.g., terminal functional groups) associated with the chemical dissociation of the cross-links being considered. The presence and/or number of such certain atoms or moieties may be observed using, for example spectroscopic techniques such as infrared (IR) spectroscopy (e.g., Fourier-Transform Infrared (FTIR) spectroscopy) or X-ray photoelectron spectroscopy (XPS). For example, XPS can be used to determine deviations from atomic ratios of certain atoms compared to ratios that would be expected in the absence of disruption of cross-linking. As an illustrative example, a partially oxidized polyamide membrane can be measured by determining the atomic ratio of oxygen to nitrogen using XPS. When polyamide is fully crosslinked, all oxygen atoms and nitrogen atoms in the polyamide polymer form amide groups, resulting in a 1:1 atomic ratio of oxygen to nitrogen. In a fully linear polyamide (thereby lacking cross-links), a free carboxyl group is present for every two amide groups, so the atomic ratio of oxygen to nitrogen is 2:1. Measurements of atomic ratio values between

1:1 and 2:1 can be used to determine extent of disruption of partially-oxidized polyamide accordingly. For example, an atomic ratio of oxygen to nitrogen of 1.5:1 in a polyamide membrane would indicate that 50 mol% of the crosslink are disrupted.

The rejection of each membrane separator may be chosen based on any of a variety of design criteria such as desired purity of permeate, desired hydraulic pressure to be used, and nature of incoming influent (e.g., solute concentration of incoming influent). The rejection, R, of a membrane separator can be calculated from C_R (the concentration of solute on the retentate side of the membrane) and C_P (the concentration of solute on the permeate side of the membrane) and expressed as a percentage using Equation [8] below:

$$R = [1 - (C_P/C_R)] * 100 \quad [8]$$

In some embodiments, the rejections (R) of the first membrane separator and the second membrane separator (and, if present the third membrane separator, the fourth membrane separator, or more) during operation of the method are chosen to afford good, consistent performance across all membrane separators by accounting for differences in concentrations of their respective retentate inlet streams. In some embodiments, the rejection of the first membrane separator for at least one solute (or all solutes) (e.g., the solute during the step of transporting the first membrane separator retentate inlet stream to the retentate side of the first membrane separator) is different than a rejection of the second membrane separator for the for at least one solute (e.g., fluoride ions, or all solutes) (e.g., the solute during the step of transporting the second membrane separator retentate inlet stream to the retentate side of the second membrane separator). The difference in rejections between the first membrane separator and the second membrane separator may be due, at least in part, to use of different semi-permeable membranes in the first and second membrane separators (e.g., having different pore sizes, MWCOs, and/or surface chemistries).

In some embodiments, the rejection of the first membrane separator for at least one solute (e.g., fluoride ions, or all solute) (e.g., the solute during the step of transporting the first membrane separator retentate inlet stream to the retentate side of the first membrane separator) and the rejection of the second membrane separator for at least one solute (e.g., fluoride ions, or all solute) (e.g., the solute during the step of transporting the second membrane separator retentate inlet stream to the retentate side of

the second membrane separator) are at least 5% different, at least 10% different, at least 20% different, at least 50% different, and/or up to 100% different, or more different from each other. In some embodiments, the rejection of the second membrane separator for at least one solute (e.g., fluoride ions, or all solutes) (e.g., the solute during the step of transporting the second membrane separator retentate inlet stream to the retentate side of the second membrane separator) is less than that of the first membrane separator for the at least one solute e.g., fluoride ions, (or all solutes) (e.g., the solute during the step of transporting the first membrane separator retentate inlet stream to the retentate side of the second membrane separator) (e.g., by at least 5%, at least 10%, at least 20%, at least 50%, at least 75%, at least 90%, or more).

In some embodiments, the rejection for at least one solute (e.g., fluoride ions, or all solutes) (e.g., the solute during the step of transporting the first membrane separator retentate inlet stream to the retentate side of the first membrane separator) of the first membrane separator is greater than or equal to 10%, greater than or equal to 15%, greater than or equal to 20%, greater than or equal to 50%, greater than or equal to 75%, greater than or equal to 80%, greater than or equal to 85%, greater than or equal to 90%, greater than or equal to 95%, greater than or equal to 98%, greater than or equal to 99%, greater than or equal to 99.9%, or greater. In some embodiments, the rejection for at least one solute (e.g., fluoride ions, or all solutes) (e.g., the solute during the step of transporting the first membrane separator retentate inlet stream to the retentate side of the first membrane separator) of the first membrane separator is less than or equal to 100%, less than or equal to 99%, less than or equal to 95%, less than or equal to 90%, less than or equal to 85%, less than or equal to 80%, less than or equal to 75%, less than or equal to 60%, less than or equal to 50%, or less. Combinations of these ranges (e.g., greater than or equal to 10% and less than or equal to 100%) are possible.

In some embodiments, the rejection for at least one solute (e.g., fluoride ions, or all solutes) (e.g., the solute during the step of transporting the first membrane separator retentate inlet stream to the retentate side of the first membrane separator) of the first membrane separator and/or the second membrane separator are, independently, greater than or equal to 10%, greater than or equal to 15%, greater than or equal to 20%, greater than or equal to 50%, greater than or equal to 75%, greater than or equal to 90%, greater than or equal to 95%, or greater. In some embodiments, the rejection for at least one

solute e.g., fluoride ions, (or all solutes) (e.g., the solute during the step of transporting the first membrane separator retentate inlet stream to the retentate side of the first membrane separator) of the second membrane separator is less than or equal to greater than or equal to 95%, less than or equal to 90%, less than or equal to 85%, less than or equal to 80%, less than or equal to 75%, less than or equal to 60%, less than or equal to 50%, or less. Combinations of these ranges (e.g., greater than or equal to 10% and less than or equal to 95%) are possible.

The systems and methods described herein can be used to process a variety of aqueous streams. Generally, the aqueous stream comprises water and at least one solute (also referred to herein as a solubilized species). According to certain embodiments, the aqueous stream comprises solubilized ions as a solute. The solubilized ion(s) may originate, for example, from a salt that has been dissolved in the liquid (e.g., solvent(s)) of the aqueous stream. A solubilized ion is generally an ion that has been solubilized to such an extent that the ion is no longer ionically bonded to a counter-ion. The aqueous stream can comprise any of a variety of solutes (e.g., solubilized ions) including, but not limited to, Na^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Cl^-, ammonia cations, carbonate anions, bicarbonate anions, sulfate anions, bisulfate anions, and/or silica. In some embodiments, an aqueous stream comprises at least one solubilized monovalent cation (i.e., a cation with a redox state of +1 when solubilized). For example, in some embodiments, an aqueous stream comprises Na^+ and/or K^+. In certain embodiments, an aqueous stream comprises at least one monovalent anion (i.e., an anion having redox state of -1 when solubilized). For example, in some embodiments, an aqueous stream comprises Cl^- and/or Br^-. In some embodiments, an aqueous stream comprises at least one monovalent cation and at least one monovalent anion. In some embodiments, an aqueous stream comprises one or more divalent cations (i.e., a cation with a redox state of +2 when solubilized) and/or one or more divalent anions (i.e., an anion with a redox state of –2 when solubilized). Cations and/or anions having other valencies may also be present in aqueous streams), in some embodiments.

In some embodiments, the total concentration of solubilized ions in the aqueous stream is relatively high. One advantage associated with certain embodiments is that initial aqueous streams with relatively high solubilized ion concentrations can be treated without the use of energy intensive methods. In certain embodiments, the total

concentration of solubilized ions in the aqueous stream transported into the system is at least 60,000 ppm, at least 80,000 ppm, or at least 100,000 ppm (and/or, in some embodiments, up to 200,000, up to 500,000 ppm, or more). Aqueous streams with solubilized ion concentrations outside these ranges could also be used.

In some embodiments, the aqueous stream is derived from any of a variety of types of wastewater. In some embodiments, the aqueous stream can be derived water used in or wastewater resulting from mining processes, wastewater from semiconductor manufacturing, wastewater from textile manufacturing, wastewater from pharmaceutical manufacturing, and/or the effluent of a chemical process.

It should be understood that, in the present disclosure, the word "purified" (and, similarly, "pure" and "purify") is used to describe any liquid that contains the component of interest in a higher percentage than is contained within a reference stream, and does not necessarily require that the liquid be 100% pure. That is to say, a "purified" stream can be partially or completely purified. As a non-limiting example, a water stream may be made up of 80 wt% water but could still be considered "purified" relative to an aqueous stream that is made up of 50 wt% water. Of course, it should also be understood that, in some embodiments, the "purified" stream could be made up of only (or substantially only) the component of interest. For example, a "purified" water stream could be made up of substantially only water (e.g., water in an amount of at least 98 wt%, at least 99 wt%, or more, or at least 99.9 wt%) and/or could be made up of only water (i.e., 100 wt% water).

In some embodiments, the systems described herein can be used to achieve a relatively high level of purification. In some embodiments, the solute concentration in the first membrane separator and/or the second membrane separator retentate outlet streams is at least 1%, at least 2%, at least 5%, at least 10%, at least 25%, at least 50%, at least 100%, at least 200% higher, on a mass basis, than the concentration of the solute in the aqueous stream. As would be understood by one of ordinary skill in the art, an increase in concentration is measured relative to the lower concentration. For example, if the solute concentration in the first membrane separator retentate inlet stream is 35 grams/L, and the solute concentration in the first membrane separator retentate outlet stream is 38.5 grams/L, then the solute concentration in the first membrane separator retentate outlet stream is 10% higher, on a mass basis, than the solute concentration in

first membrane separator retentate inlet stream (because the difference, 3.5 grams/L, is 10% of the lower value (i.e., 10% of 35 grams/L)).

As used herein, two elements are in fluidic communication with each other (or, equivalently, in fluid communication with each other) when fluid may be transported from one of the elements to the other of the elements without otherwise altering the configurations of the elements or a configuration of an element between them (such as a valve). Two conduits connected by an open valve (thus allowing for the flow of fluid between the two conduits) are considered to be in fluidic communication with each other. In contrast, two conduits separated by a closed valve (thus preventing the flow of fluid between the conduits) are not considered to be in fluidic communication with each other.

As used herein, two elements are fluidically connected to each other when they are connected such that, under at least one configuration of the elements and any intervening elements, the two elements are in fluidic communication with each other. Two membrane separators connected by a valve and conduits that permit flow between the membrane separators in at least one configuration of the valve would be said to be fluidically connected to each other. To further illustrate, two membrane separators that are connected by a valve and conduits that permit flow between the membrane separators in a first valve configuration but not a second valve configuration are considered to be fluidically connected to each other both when the valve is in the first configuration and when the valve is in the second configuration. In contrast, two membrane separators that are not connected to each other (e.g., by a valve, another conduit, or another component) in a way that would permit fluid to be transported between them under any configuration would not be said to be fluidically connected to each other. Elements that are in fluidic communication with each other are always fluidically connected to each other, but not all elements that are fluidically connected to each other are necessarily in fluidic communication with each other.

Various components are described herein as being fluidically connected. Fluidic connections may be either direct fluidic connections or indirect fluidic connections. Generally, a direct fluidic connection exists between a first region and a second region (and the two regions are said to be directly fluidically connected to each other) when they are fluidically connected to each other and when the composition of the fluid at the

second region of the fluidic connection has not substantially changed relative to the composition of the fluid at the first region of the fluidic connection (i.e., no fluid component that was present in the first region of the fluidic connection is present in a weight percentage in the second region of the fluidic connection that is more than 5% different from the weight percentage of that component in the first region of the fluidic connection). As an illustrative example, a stream that connects first and second unit operations, and in which the pressure and temperature of the fluid is adjusted but the composition of the fluid is not altered, would be said to directly fluidically connect the first and second unit operations. If, on the other hand, a separation step is performed and/or a chemical reaction is performed that substantially alters the composition of the stream contents during passage from the first component to the second component, the stream would not be said to directly fluidically connect the first and second unit operations. In some embodiments, a direct fluidic connection between a first region and a second region can be configured such that the fluid does not undergo a phase change from the first region to the second region. In some embodiments, the direct fluidic connection can be configured such that at least 50 wt% (or at least 75 wt%, at least 90 wt%, at least 95 wt%, or at least 98 wt%) of the fluid (e.g., liquid) in the first region is transported to the second region via the direct fluidic connection. Any of the fluidic connections described herein may be, in some embodiments, direct fluidic connections. In other cases, the fluidic connections may be indirect fluidic connections.

In some embodiments, the retentate side of the first membrane separator is fluidically connected to the retentate side of the second membrane separator. Such a fluidic connection may facilitate transport of at least a portion of the first membrane separator retentate side outlet stream from the retentate side of the first membrane separator (e.g., from a retentate side outlet of the first membrane separator) to the retentate side of the second membrane separator (e.g., by forming some or all of a second membrane separator retentate inlet stream that enters a retentate side inlet of the second membrane separator). In some embodiments, the retentate side of the first membrane separator is directly fluidically connected to the retentate side of the second membrane separator.

U.S. Patent Application Publication No. 2023-0001355, published on January 5, 2023, filed as U.S. Patent Application No. 17/305,289, on July 2, 2021, and entitled

"Membranes with Controlled Porosity for Serial Filtration," is incorporated herein by reference in its entirety for all purposes. U.S. Patent Application No. 18/315,130, filed on May 10, 2023, and entitled "Liquid Separation Using Solute-Permeable Membranes and Related Systems," is incorporated herein by reference in its entirety for all purposes.

Example embodiments of a system for managing an aqueous stream with high concentration of fluoride (e.g., system 300)

FIG. 6 illustrates an example embodiment of a system (e.g., system 300) for managing an aqueous effluent. The aqueous effluent may be an aqueous effluent containing high concentration of fluoride, or the like. As described in the present disclosure, system 300 is configurable or configured to perform such management by performing one or more of a variety functions, actions, and/or processes using one or more of the elements described in the present disclosure.

In an example embodiment, system 300 is configurable or configured to manage an aqueous effluent with high concentration of fluoride. The aqueous effluent may contain not only high concentration of fluoride also other elements, impurities and solids. System 300 includes inlet 301, or the like, configurable or configured to receive the aqueous effluent into the system. For example, inlet 301 may receive the aqueous effluent from waterways, pipes, or the like, that connects from an area, catchment area, pond, and/or industrial wastewater generated from, but not limited to, semiconductor industry, and any other industries that may generate similar industrial wastewater. Inlet 301 may also be and/or include a collection area, tank, or the like. In such an example, the aqueous effluent to be treated may be collected, fed and/or stored prior to feeding the aqueous effluent into the system.

System 300 further includes first treatment assembly 302, or the like. First treatment assembly 302 may be configurable or configured to perform a variety of functions, including treating the aqueous effluent. First treatment assembly 302 may include a first treatment assembly input, or the like, configurable or configured to receive the aqueous effluent provided by inlet 301. First treatment assembly 302 also includes a treatment unit, or the like. The first treatment unit may be configurable or configured to increase pH level of the aqueous effluent so as to produce a treated aqueous effluent. Generally, the pH level of the aqueous effluent with high concentration of fluoride is

low. The present disclosure provides that an alkaline agent is added to the aqueous effluent with high concentration of fluoride to adjust the level of pH of the aqueous effluent. By adding an alkaline agent, the pH of the aqueous effluent is increased to pH 6.0 to pH 7.0. The aqueous effluent, when treated at an alkali pH level, allows higher rejections of fluoride from the aqueous effluent. Examples of suitable alkaline agents that may be used in the present disclosure includes, but not limited to, sodium hydroxide, sodium carbonate, calcium carbonate, magnesium hydroxide, potassium hydroxide and any other suitable alkaline agents which may be used. First treatment assembly 302 may also include a first treatment assembly output, or the like, configurable or configured to provide the treated aqueous effluent to a first filtration assembly.

System 300 also includes first filtration assembly 303, or the like. First filtration assembly 303 may be configurable or configured to perform a variety of functions, including filtering the aqueous effluent. First filtration assembly 303 includes a first filtration assembly input configured to receive the treated aqueous effluent from first treatment assembly 302. First filtration assembly 303 may include a first filtration unit, or the like, that is configurable or configured to filter pollutants and/or contaminants from the treated aqueous effluent to arrive at a first permeate and a first reject water. Examples of pollutants and/or contaminants that may be filtered includes particulate matter, sediments, solids, and any suspended matters such as colloidal silica. The first filtration unit may include a filtration unit or system, or the like. The filtration unit may be or include, but is not limited to, an automatic backwash filter system, an ultrafiltration system, a cartridge filtration system, a multimedia filtration system, a membrane cartridge filtration system, and any other suitable filtration systems which may be used. First filtration assembly 303 may also include a first filtration assembly output that is configurable or configured to provide the first permeate to a second filtration assembly and the first reject water to a collection assembly.

System 300 further includes second filtration assembly 304, or the like. Second filtration assembly 304 may be configurable or configured to perform a variety of functions, including filtering the first permeate. The second filtration assembly includes a second filtration assembly input configured to receive the first permeate from the first filtration assembly. Second filtration assembly 304 may include a second filtration unit, or the like, that is configurable or configured to filter impurities from the first permeate

to arrive at a second permeate and a second reject water. Examples of pollutants and/or contaminants that may be filtered includes particulate matter, sediments, solids, and any suspended matter such as colloidal silica. The second filtration unit may include a filtration unit or system, or the like. The filtration unit or system may be or include, but is not limited to, an automatic backwash filter system, an ultrafiltration system, a cartridge filtration system, a multimedia filtration, a membrane cartridge filtration, and any other suitable filtration systems which may be used. The second filtration assembly 303 may also include a second filtration assembly output that is configurable or configured to provide the second permeate to a polishing assembly and/or a third filtration assembly and the second reject water to a collection assembly.

In some embodiments, system 300 may further comprise of third filtration assembly 312, or the like. Third filtration assembly 312 may be configurable or configured to perform a variety of functions, including filtering the second permeate. The third filtration assembly includes a third filtration assembly input configured to receive the second permeate from the second filtration assembly. Third filtration assembly 312 may include a third filtration unit, or the like, that is configurable or configured to filter impurities from the second permeate to arrive at a third permeate. Examples of pollutants and/or contaminants that may be filtered includes particulate matter, sediments, solids, and any suspended matter such as colloidal silica. The third filtration unit may include a filtration unit or system, or the like. The filtration unit or system may be or include, but is not limited to, an automatic backwash filter system, an ultrafiltration system, a cartridge filtration system, a multimedia filtration, a membrane cartridge filtration, and any other suitable filtration systems which may be used. Third filtration assembly 312 may also include a third filtration assembly output that is configurable or configured to provide the third permeate to polishing assembly 305.

System 300 further includes polishing assembly 305, or the like. Polishing assembly 305 may be configurable or configured to perform a variety of functions, including removing impurities from liquid. Polishing assembly 305 includes a polishing assembly input that is configurable or configured to receive the second permeate from a second filtration assembly. In some embodiments, polishing assembly 305 is configurable or configured to receive the third permeate from third filtration assembly 312. Polishing assembly 305 may include a polishing unit, or the like. The polishing unit

may be configurable or configured to remove impurities from the second permeate to arrive at a first final output and a third reject water. The first polishing unit may be and/or include conventional nanofiltration (NF) membranes, brackish water reverse osmosis (BWRO) membranes, seawater reverse osmosis (SWRO) membranes, electrodialysis reversal, forward osmosis and/or any other suitable membranes which may be used. In an example, the polishing unit may be configurable or configured to remove remaining impurities, including suspended solids, particles, organics and dissolved solids, to produce clean first final output which may include water products that has no and/or significantly reduced concentration of fluoride. The clean or pure water products are subsequently safely disposed into a water source in the environment, reused in the treatment system where applicable and/or used in any other suitable applications. Polishing assembly 305 may also include a polishing assembly output configurable or configured to provide the third reject water to collection assembly 306 and the first final output for further processing or applications.

System 300 also includes collection assembly 306, or the like. Collection assembly 306 may be configurable or configured to perform a variety of functions, including collecting the reject water. Collection assembly 306 includes a collection assembly output that is configurable or configured to receive the first reject water, second reject water and/or third reject water. The first reject water, second reject water and/or third reject water are reject water from the first filtration assembly, the second filtration assembly and the polishing assembly respectively. The collection unit may be configurable or configured to collect the first reject water, second reject water and/or third reject water. Collection assembly 306 may also include a collection assembly output configurable or configured to provide the collected reject water to a second treatment assembly.

System 300 includes second treatment assembly 307, or the like. Second treatment assembly 307 may be configurable or configured to perform a variety of functions, including treating a reject water that is selected from the first reject water, second reject water and/or third reject water. Second treatment assembly 307 includes a second treatment assembly input configured to receive the collected first reject water, second reject water and/or third reject water from the collection assembly. Second treatment assembly 307 may include a second treatment unit configured to precipitate

fluoride and/or to coagulate silica in the collected first reject water, second reject water and/or third reject water to arrive at a first treated reject water. In an example, the second treatment unit is configurable or configured to treat the reject water selected from the first reject water, the second reject water and the third reject water collected from various stages in the system as described in the present disclosure. In some embodiments, the reject water to be treated in second treatment assembly 307 may also be selected from one or more wastewater streams or any other sources including, but not limited to, wastewater stream with high concentration of copper, wastewater stream with high concentration of silica, wastewater stream with high alkalinity, wastewater stream with high concentration of sulfate, local scrubber recyclable system, or a combination thereof.

The reject water in second treatment assembly 307 may be treated by precipitating the fluoride that is present in the reject water to form a calcium fluoride sludge. The precipitation may be performed using agents such as, but not limited to, calcium chloride, calcium hydroxide, sodium hydroxide and/or a combination thereof. The method also includes treating the collected first reject water, second reject water and/or third reject water by precipitating fluoride and/or silica in the collected first reject water, second reject water and/or third reject water to arrive at a first treated reject water. The fluoride in the first reject water, second reject water and/or third reject water may be precipitated using agents such as, but not limited to, calcium chloride, calcium hydroxide, sodium hydroxide, aluminum sulfate and/or a combination thereof. The amount or concentration of precipitating agents to be used in the treatment varies depending on the amount or concentration of fluoride in the collected first reject water, second reject water and/or third reject water, the pH of the collected first reject water, second reject water and/or third reject water, and others.

In an example, calcium hydroxide is used as the precipitating agent to precipitate the fluoride that is present in a reject water or effluent during treatment. The amount or concentration of calcium hydroxide used is 2920 mg/l. In another example, a combination of calcium hydroxide and calcium chloride is used to precipitate the fluoride that is present in a reject water. The combination of calcium hydroxide and calcium chloride includes 800 mg/l of calcium hydroxide and 2350 mg/l of calcium chloride. In these methods, the calcium (Ca) compound from the calcium hydroxide and/or and calcium chloride reacts with the fluoride present in the reject water or effluent

to form of insoluble calcium fluoride (sludge) to remove the fluorine which may be removed downstream. With these methods, the amount or concentration fluoride in the reject water or effluent is reduced significantly and efficiently to a desired level for safe disposal. See Table 1.

Table 1 : The concentration of fluoride before and after treatment using precipitating agents.

Parameters	**Fluoride concentration before treatment (ppm)**	**Fluoride concentration after treatment (ppm)**
Treated with calcium hydroxide	372	9.02
Treated with calcium hydroxide and calcium chloride	372	7.02

Further, the collected first reject water, second reject water and/or third reject water in second treatment assembly 307 may be treated by coagulating the silica that is present in the reject water. The coagulation may be performed using agents such as, but not limited to, ferric chloride, sodium aluminate, sodium hydroxide and any other suitable agents which may be used. In an example, ferric chloride, or any other suitable agents, is used as the coagulating agent to coagulate the silica that is present in a reject water or effluent during treatment. The amount or concentration of coagulating agents to be used in the treatment varies depending on the amount or concentration of silica in the collected first reject water, second reject water and/or third reject water, and others. In an example, ferric chloride is used as the coagulating agent to coagulate the silica that is present in a reject water or effluent during treatment. The amount or concentration of ferric chloride used is 50 mg/l to 300 mg/l. Although the results of the above exemplary embodiments are achieved from bench scale experiments, it is understood that similar or same parameters can be applied and similar or same results can be achieved on a pilot scale using raw industrial wastewater in a wastewater treatment plant. Second treatment assembly 307 may also include a second treatment assembly output configured to provide the first treated reject water to a sedimentation assembly and/or a third treatment assembly.

In some embodiments, system 300 may further include third treatment assembly 313, or the like. Third treatment assembly 313 may be configurable or configured to perform a variety of functions, including further treating the first treated reject water. Second treatment assembly 307 includes a third treatment assembly input configurable or configured to receive the first treated reject water from the second treatment assembly. Third treatment assembly 313 may include a third treatment unit configurable or configured to further precipitate fluoride and/or coagulate silica that is present in the first treated reject water to arrive at a second treated reject water. In some embodiments, the third treatment unit is configurable or configured to treat the first treated reject water from second treatment assembly 307 as described in the present disclosure. Although the process of treating the reject water by precipitating the fluoride and/or silica that is present in the reject water is performed in second treatment assembly 307, there may be further fluoride and/or silica that is still present in the first treated reject water. The first treated reject water in third treatment assembly 313 may be treated by precipitating the fluoride that is still present in the first treated reject water. The precipitation may be performed using but not limited to, calcium chloride, calcium hydroxide, sodium hydroxide and/or a combination thereof as described in the present disclosure. In another embodiment, the first treated reject water in third treatment assembly 313 may be treated by coagulating the silica that is present in the first treated reject water. The coagulation may be performed using but not limited to, ferric chloride, sodium aluminate, sodium hydroxide and any other suitable agents which may be used as described in the present disclosure. Third treatment assembly 313 may also include a third treatment assembly output configurable or configured to provide the second treated reject water to a sedimentation assembly.

System 300 includes sedimentation assembly 308, or the like. Sedimentation assembly 308 may be configurable or configured to perform a variety of functions, including sedimenting impurities in a treated reject water. Sedimentation assembly 308 includes a sedimentation assembly input configurable or configured to receive the first treated reject water from the second treatment assembly. Sedimentation assembly 308 may include a sedimentation unit configurable or configured to sediment impurities in the first treated reject water to arrive at a first liquid output and calcium fluoride sludge. In some embodiments, the sedimentation assembly input may be configurable or

configured to receive the second treated reject water from third treatment assembly 313 to sediment impurities in the second treated reject water. Similarly, sedimentation assembly 308 may include a sedimentation unit configurable or configured to sediment impurities in the second treated reject water to arrive at a first liquid output and a calcium fluoride sludge. Examples of suitable sedimentation system that may be used in the present disclosure includes, but not limited to, horizontal flow tank, multi-layer tank, settling tank, tube settler, conical bottom tanks, and any other sedimentation system which may be used. In an example, the impurities such as calcium fluoride (e.g., calcium fluoride sludge), which forms the heavier particles or solids in the first treated reject water and/or second treated reject water, are allowed to settle to the base of the sedimentation unit. As such, the sedimentation of the calcium fluoride sludge provides a first liquid output which is free or substantially free of calcium fluoride sludge. Other impurities such as calcium carbonate, calcium sulphate, calcium phosphate, and silica may be present in minor quantities together with the calcium fluoride (sludge). Sedimentation assembly 308 may also include a sedimentation assembly output configurable or configured to provide the first liquid output to reaction assembly 309. Further, the sedimentation assembly output is configurable or configured to provide the calcium fluoride sludge from the sedimentation process to filter press assembly 311. In some embodiments, the sedimentation assembly output configurable or configured to provide the calcium fluoride sludge from the sedimentation process to holding tank 314.

The system further includes reaction assembly 309, or the like. Reaction assembly 309 may be configurable or configured to perform a variety of functions, including removing solid impurities in the first liquid output. Reaction assembly 309 includes a reaction assembly input configurable or configured to receive the first liquid output from the sedimentation assembly. The reaction assembly may include a reaction unit configurable or configured to remove solids in the first liquid output to arrive at a second liquid output and a calcium fluoride sludge. In an example, the first liquid output may be treated in the reaction unit to remove the remaining impurities (e.g., calcium fluoride sludge, calcium carbonate, calcium sulphate, calcium phosphate, and silica) that are still present in the first liquid output via coagulation and flocculation. Examples of suitable coagulants that may be used in the present disclosure includes, but not limited to, inorganic coagulants (e.g., aluminum sulfate, aluminum chloride, sodium aluminate,

ferric chloride, ferric sulfate, etc.), organic coagulants (e.g., polyamines, etc.), and any other suitable coagulants. Examples of suitable flocculants that may be used in the present disclosure includes, but not limited to, natural polymers (e.g., polysaccharides, mainly starch and its constituents, different types of gums, alginic acid, cellulose and its derivatives, dextran, glycogen, etc.), polyacrylamide (PAM) and polyethylene oxide (PEO), polydiallyl dimethyl ammonium chloride (polyDADMAC), polyacrylic acid and its derivatives, polystyrene sulfonic acid (PSSA), and any other suitable flocculants. Reaction assembly 309 may also include a reaction assembly output configurable or configured to provide the second liquid output to clarifier assembly 310.

The system includes clarifier assembly 310, or the like. Clarifier assembly 310 may be configurable of configured to perform a variety of functions, including removing solids in the second liquid output. Clarifier assembly 310 includes a clarifier assembly input configurable or configured to receive the second liquid output from the reaction assembly output. Clarifier assembly 310 may further include a clarifier assembly unit configured or configurable to remove impurities in the second liquid output to arrive at an effluent discharge and a calcium fluoride sludge. Clarifier assembly 310 may also include a clarifier assembly output configurable or configured to provide the effluent discharge to be discharged. Examples of suitable clarifiers that may be used in the present disclosure, but not limited to, high rate solid contact clarifier, lamella clarifier, and any other clarifiers that may be used. The effluent discharge may be an effluent that is free or substantially free of fluoride concentration and other impurities. The effluent at this stage is expected to meet the standard requirements for safe discharge into the environment and/or to be reused in the or alternative treatment system where applicable and/or to be used in any other suitable applications.

The system includes filter press assembly 311, or the like. Filter press assembly 311 may be configurable or configured to perform a variety of functions, including removing liquid in the calcium fluoride sludge. Filter press assembly 311 includes a filter press assembly input configurable or configured to receive the calcium fluoride sludge from the sedimentation assembly output and/or the clarifier assembly output. In some embodiments, the filter press assembly input may be configurable or configured to receive the calcium fluoride sludge from holding tank 314. Filter press assembly 311 may further include a filter press assembly unit configurable or configured to remove

liquid from the calcium fluoride sludge. Filter presses are commonly used to provide sludge dewatering by applying high pressure or pressing the sludge between a plurality of porous plates. The liquid (e.g., water) is being forced out of the calcium fluoride sludge when high pressure is applied. Filter press assembly 311 may also include a filter press assembly output to provide the second final output. The second final output (e.g., clean or other water products) may or may not be treated further before being safely disposed into a water source in the environment. The second final output may also be reused in the treatment system where applicable and/or used in any other suitable applications. Further, the calcium fluoride sludge obtained through the filter press assembly is comprised of 75% calcium fluoride.

The system may further include holding tank assembly 314, or the like. The holding tank assembly may be configurable or configured to perform a variety of function, including collecting the calcium fluoride sludge. Holding tank 314 includes a holding tank assembly input configurable or configured to receive the calcium fluoride sludge from the sedimentation assembly and/or the clarifier assembly. Holding tank assembly 314 may further include a holding tank assembly unit configurable or configured to collect the calcium fluoride sludge from the sedimentation assembly and/or the clarifier assembly. The holding tank assembly unit may be further configurable or configured to treat the calcium fluoride sludge with a polymer. Examples of suitable polymers that may be used in the present disclosure include, but not limited to, natural polymers (e.g., polysaccharides, mainly starch and its constituents, different types of gums, alginic acid, cellulose and its derivatives, dextran, glycogen, etc.), polyacrylamide (PAM) and polyethylene oxide (PEO), polydiallyl dimethyl ammonium chloride (polyDADMAC), polyacrylic acid and its derivatives, polystyrene sulfonic acid (PSSA), and any other suitable polymers. Holding tank assembly 314 may also include a holding tank assembly output configurable or configured to provide the calcium fluoride sludge to filter press assembly 311.

Example embodiments of a method for managing an aqueous effluent with high concentration of fluoride (e.g., method 400).

FIG. 7 illustrates an example embodiment of a system (e.g., method 400) for managing an aqueous effluent. The aqueous effluent may be an aqueous effluent

containing high concentration of fluoride, or the like. One or more actions of method may be performed by one or more elements as described in the present disclosure.

In an example embodiment, method 400 provides a method for managing an aqueous effluent. The method includes receiving an aqueous effluent with high concentration of fluoride, or the like 402. The aqueous effluent may contain not only high concentration of fluoride but also other elements, impurities and solids. The aqueous effluent may be received by inlet 301, or the like, configurable or configured to receive the aqueous effluent into the system. For example, the aqueous effluent may be received by inlet 301 into the system from a waterway, pipes, or the like, that connects from an area, catchment area, pond, and/or industrial wastewater generated from, but not limited to, semiconductor industry, and any other industries that may generate similar industrial wastewater. Inlet 301 may also be and/or include a collection area, tank, or the like. In such an example, the aqueous effluent to be treated may be collected, fed and/or stored prior to feeding the aqueous effluent into the system.

The method also includes treating the aqueous effluent with high concentration of fluoride to increase pH level of the aqueous effluent to arrive at treated aqueous effluent 404. The aqueous effluent may be treated in first treatment assembly 302, or the like. First treatment assembly 302 may include a first treatment assembly input, or the like, configurable or configured to receive the aqueous effluent provided by inlet 301. First treatment assembly 302 also includes a treatment unit, or the like. The first treatment unit may be configurable or configured to increase pH level of the aqueous effluent so as to produce a treated aqueous effluent. First treatment assembly 302 may also include a first treatment assembly output, or the like, configurable or configured to provide the treated aqueous effluent to a first filtration assembly. The pH level of the aqueous effluent with high concentration of fluoride is low. In an embodiment, the method provides adding an alkaline agent to the aqueous effluent with high concentration of fluoride to adjust the level of pH of the aqueous effluent. By adding an alkaline agent, the pH of the aqueous effluent is increased to pH 6.0 to pH 7.0. The aqueous effluent, when treated at an alkali pH level, allows higher rejections of fluoride from the aqueous effluent. Examples of suitable alkaline agents that may be used in the present disclosure includes, but not limited to, sodium hydroxide, sodium carbonate,

calcium carbonate, magnesium hydroxide, potassium hydroxide and any other suitable alkaline agents which may be used.

The method includes filtering the treated aqueous effluent to arrive at a first permeate and first reject water 406. The treated aqueous effluent may be filtered by first filtration assembly 303, or the like. First filtration assembly 303 may be configurable or configured to perform a variety of functions, including filtering the aqueous effluent. First filtration assembly 303 includes a first filtration assembly input configurable or configured to receive the treated aqueous effluent from first treatment assembly 302. First filtration assembly 303 may include a first filtration unit, or the like, that is configurable or configured to filter pollutants and/or contaminants from the treated aqueous effluent to arrive at a first permeate and a first reject water. In an embodiment, the treated aqueous effluent may be filtered by the first filter unit to filter or remove impurities including, but not limited to, particulate matter, sediments, solids, and any suspended matters such as colloidal silica. In an example embodiment, the treated aqueous effluent may be filtered by a first filtration unit may include a filtration unit or system, or the like. The first filtration unit may be or includes, but is not limited to, an automatic backwash filter system, an ultrafiltration system, a cartridge filtration system, a multimedia filtration, a membrane cartridge filtration, and any other suitable filtration systems which may be used. First filtration assembly 303 may also include a first filtration assembly output that is configurable or configured to provide the first permeate to second filtration assembly 304 and the first reject water to collection assembly 306.

The method includes filtering the first permeate to arrive at a second permeate and second reject water 408. The first permeate may be filtered by second filtration assembly 304, or the like. Second filtration assembly 304 includes a first filtration assembly input configurable or configured to receive the first permeate from the first filtration assembly 303. Second filtration assembly 304 may include a second filtration unit, or the like, that is configurable or configured to filter impurities from the first permeate to arrive at a second permeate and a second reject water. In an embodiment, the first permeate may be filtered by the second filter unit to filter or remove impurities including, but not limited to, particulate matter, sediments, solids, and any suspended matters such as colloidal silica. In an example embodiment, the first permeate may be filtered by a second filtration unit that includes a filtration unit or system, or the like. The

second filtration unit may be, but is not limited to, an automatic backwash filter system, an ultrafiltration system, a cartridge filtration system, a multimedia filtration, a membrane cartridge filtration, and any other suitable filtration systems which may be used. Second filtration assembly 304 may also include a second filtration assembly output that is configurable or configured to provide the second permeate to polishing assembly 305 and the second reject water to collection assembly 306.

In some embodiments, method 400 may further comprise of filtering the second permeate to arrive at a third permeate and second reject water 424. The second permeate may be filtered by third filtration assembly 312, or the like. Third filtration assembly 312 includes a third filtration assembly input configurable or configured to receive the second permeate from second filtration assembly 304. Third filtration assembly 312 may include a third filtration unit, or the like, that is configurable or configured to filter impurities from the second permeate to arrive at a third permeate and a third reject water. In some embodiments, the second permeate may be filtered by the third filter unit to filter or remove impurities including, but not limited to, particulate matter, sediments, solids, and any suspended matters such as colloidal silica. In an example embodiment, the second permeate may be filtered by a third filtration unit that includes a filtration unit or system, or the like. The third filtration unit may be, but is not limited to, an automatic backwash filter system, an ultrafiltration system, a cartridge filtration system, a multimedia filtration, a membrane cartridge filtration, and any other suitable filtration systems which may be used. Third filtration assembly 312 may also include a third filtration assembly output that is configurable or configured to provide the third permeate to polishing assembly 305.

The method also includes polishing the second permeate to arrive at a first final output and third reject water 410. In some embodiments, the method also includes polishing the third permeate received from third filtration assembly 312 to arrive at a first final output and third reject water 410. The second and/or third permeate may be polished by polishing assembly 305, or the like. Polishing assembly 305 includes a polishing assembly input that is configurable or configured to receive the second permeate from a second filtration assembly. In some embodiments, polishing assembly 305 may also include a polishing assembly input that is configurable or configured to receive the third permeate from a third filtration assembly. Polishing assembly 305 may

include a polishing unit, or the like. The polishing unit may be configurable or configured to remove impurities from the second permeate and/or the third permeate to arrive at a first final output and a third reject water. The first polishing unit may be and/or include conventional nanofiltration (NF) membranes, brackish water reverse osmosis (BWRO) membranes, sea water reverse osmosis (SWRO) membranes, electrodialysis reversal, forward osmosis and/or any other suitable membranes which may be used. In an example, the polishing unit may be configurable or configured to remove remaining impurities, including suspended solids, particles, organics and dissolved solids, to produce clean first final output which may include water products that has no and/or significantly reduced concentration of fluoride. The clean or pure water products are subsequently safely disposed into a water source in the environment, reused in the treatment system where applicable and/or used in any other suitable applications. Polishing assembly 305 may also include a polishing assembly output configurable or configured to provide the third reject water to collection assembly 306 and the first final output for further processing or applications.

Method 400 includes collecting the first reject water, the second reject water and third reject water 412. The first reject water, the second reject water and the third reject water may be collected in collection assembly 306, or the like. Collection assembly 306 includes a collection assembly output that is configurable or configured to receive the first reject water, second reject water and/or third reject water. The first reject water, second reject water and/or third reject water are reject water that is collected from the first filtration assembly, the second filtration assembly and the polishing assembly respectively. The collection unit may be configurable or configured to collect the first reject water, second reject water and/or third reject water. Collection assembly 306 may also include a collection assembly output configurable or configured to provide the collected reject water to a second treatment assembly.

Method 400 further includes treating the collected first reject water, second reject water and/or third reject water by precipitating fluoride and/or silica in the collected first reject water, second reject water and/or third reject water to arrive at first treated reject water 414. The collected first reject water, second reject water and/or third reject water is treated in second treatment assembly 307, or the like. Second treatment assembly 307 includes a second treatment assembly input configured to receive the collected first reject

water, second reject water and/or third reject water from the collection assembly. Second treatment assembly 307 may include a second treatment unit configured to precipitate fluoride and/or silica in the collected first reject water, second reject water and/or third reject water to arrive at a first treated reject water. In an example, the reject water selected from the first reject water, the second reject water and/or the third reject water collected from various stages in the system as described in the present disclosure is treated in the second treatment unit. In some embodiments, the reject water to be treated in second treatment assembly 307 may also be selected from one or more wastewater streams or any other sources including, but not limited to, wastewater stream with high concentration of copper, wastewater stream with high concentration of silica, wastewater stream with high alkalinity, wastewater stream with high concentration of sulfate, local scrubber recyclable system, or a combination thereof.

The reject water as collected in second treatment assembly 307 is treated by precipitating the fluoride that is present in the reject water to form a calcium fluoride sludge. The calcium fluoride (sludge) may be precipitated using agents such as, but not limited to, calcium chloride, calcium hydroxide, sodium hydroxide and/or a combination thereof. The method also includes treating the collected first reject water, second reject water and/or third reject water by precipitating fluoride and/or silica in the collected first reject water, second reject water and/or third reject water to arrive at a first treated reject water. The fluoride in the first reject water, second reject water and/or third reject water may be precipitated using agents such as, but not limited to, calcium chloride, calcium hydroxide, sodium hydroxide, aluminum sulfate and/or a combination thereof. The amount or concentration of precipitating agents to be used in the treatment varies depending on the amount or concentration of fluoride in the collected first reject water, second reject water and/or third reject water, the pH of the collected first reject water, second reject water and/or third reject water, and others.

In an example, calcium hydroxide is used as the precipitating agent to precipitate the fluoride that is present in a reject water or effluent during treatment. The amount or concentration of calcium hydroxide used is 2920 mg/l. In another example, a combination of calcium hydroxide and calcium chloride is used to precipitate the fluoride that is present in a reject water. The combination of calcium hydroxide and calcium chloride includes 800 mg/l of calcium hydroxide and 2350 mg/l of calcium

chloride. In these methods, the calcium (Ca) compound from the calcium hydroxide and/or and calcium chloride reacts with the fluoride present in the reject water or effluent to form of insoluble calcium fluoride (sludge) to remove the fluorine which may be removed downstream. With these methods, the amount or concentration fluoride in the reject water or effluent is reduced significantly and efficiently to a desired level for safe disposal. See Table 2.

Table 2 : The concentration of fluoride before and after treatment using precipitating agents.

Parameters	**Fluoride concentration before treatment (ppm)**	**Fluoride concentration after treatment (ppm)**
Treated with calcium hydroxide	372	9.02
Treated with calcium hydroxide and calcium chloride	372	7.02

Further, the collected first reject water, second reject water and/or third reject water in second treatment assembly 307 may be treated by coagulating the silica that is present in the reject water. The coagulation may be performed using agents such as, but not limited to, ferric chloride, sodium aluminate, sodium hydroxide and any other suitable agents which may be used. In an example, ferric chloride, or any other suitable agents, is used as the coagulating agent to coagulate the silica that is present in a reject water or effluent during treatment. The amount or concentration of coagulating agents to be used in the treatment varies depending on the amount or concentration of silica in the collected first reject water, second reject water and/or third reject water, and others. In an example, ferric chloride is used as the coagulating agent to coagulate the silica that is present in a reject water or effluent during treatment. The amount or concentration of ferric chloride used is 50 mg/l to 300 mg/l. Although the results of the above exemplary embodiments are achieved from bench scale experiments, it is understood that similar or same parameters can be applied and similar or same results can be achieved on a pilot scale using raw industrial wastewater in a wastewater treatment plant. Second treatment assembly 307 may also include a second treatment assembly output configured to provide the first treated reject water to a sedimentation assembly.

In some embodiments, method 400 may further include treating the first treated reject water 426. The first treated reject water may be treated in third treatment assembly 313. Second treatment assembly 307 includes a third treatment assembly input configurable or configured to receive the first treated reject water from the second treatment assembly. Third treatment assembly 313 may include a third treatment unit configurable or configured to further precipitate fluoride and/or silica that is present in the first treated reject water to arrive at a second treated reject water. In some embodiments, the first treated reject water from second treatment assembly 307 as described in the present disclosure is being treated in the third treatment unit. Although the process of treating the reject water by precipitating the fluoride and/or silica that is present in the reject water is performed in second treatment assembly 307, there may be further fluoride and/or silica that may be still present in the first treated reject water. The first treated reject water in third treatment assembly 313 may be treated by precipitating the fluoride that is still present in the first treated reject water. The precipitation may be performed using but not limited to, calcium chloride, calcium hydroxide, sodium hydroxide and/or a combination thereof as described in the present disclosure. In another embodiment, the first treated reject water in third treatment assembly 313 may be treated by coagulating the silica that is present in the first treated reject water. The coagulation may be performed using but not limited to, ferric chloride, sodium aluminate, sodium hydroxide and any other suitable agents which may be used as described in the present disclosure. Third treatment assembly 313 may also include a third treatment assembly output configurable or configured to provide the second treated reject water to a sedimentation assembly.

Method 400 includes sedimenting impurities in the first treated reject water to arrive at a first liquid output and calcium fluoride sludge 416. The first treated reject water may be sedimented in sedimentation assembly 308. Sedimentation assembly 308 includes a sedimentation assembly input configurable or configured to receive the first treated reject water from the second treatment assembly. Sedimentation assembly 308 may include a sedimentation unit configurable or configured to sediment impurities in the first treated reject water to arrive at a first liquid output and calcium fluoride sludge. In some embodiments, the sedimentation assembly input may be configurable or configured to receive the second treated reject water from third treatment assembly 313

to sediment impurities in the second treated reject water. Similarly, sedimentation assembly 308 may include a sedimentation unit configurable or configured to sediment impurities in the second treated reject water to arrive at a first liquid output and a calcium fluoride sludge. Examples of suitable sedimentation system that may be used in the present disclosure includes, but not limited to, horizontal flow tank, multi-layer tank, settling tank, tube settler, conical bottom tanks, and any other sedimentation system which may be used. In an example, the impurities such as calcium fluoride (e.g., calcium fluoride sludge), which forms the heavier particles or solids in the first treated reject water and/or second treated reject water, are allowed to settle to the base of the sedimentation unit. As such, the sedimentation of the calcium fluoride sludge provides a first liquid output which is free or substantially free of calcium fluoride sludge. Other impurities such as calcium carbonate, calcium sulphate, calcium phosphate, and silica may be present in minor quantities together with the calcium fluoride (sludge). Sedimentation assembly 308 may also include a sedimentation assembly output configurable or configured to provide the first liquid output to reaction assembly 309. Further, the sedimentation assembly output is configurable or configured to provide the calcium fluoride sludge from the sedimentation process to filter press assembly 311. In some embodiments, the sedimentation assembly output configurable or configured to provide the calcium fluoride sludge from the sedimentation process to holding tank assembly 314.

Method 400 includes reacting the first liquid output to arrive at a second liquid output 418. The first liquid output may be reacted with selected agents (e.g., flocculants) in reaction assembly 309, or the like. Reaction assembly 309 includes a reaction assembly input configurable or configured to receive the first liquid output from the sedimentation assembly. The reaction assembly may include a reaction unit configurable or configured to remove solids in the first liquid output to arrive at a second liquid output and a calcium fluoride sludge. In an example, the first liquid output may be treated in the reaction unit to remove the remaining impurities (e.g., calcium fluoride sludge, calcium carbonate, calcium sulphate, calcium phosphate, and silica) that are still present in the first liquid output via coagulation and flocculation. Examples of suitable coagulants that may be used in the present disclosure includes, but not limited to, inorganic coagulants (e.g., aluminum sulfate, aluminum chloride, sodium aluminate, ferric chloride, ferric

sulfate, etc.), organic coagulants (e.g., polyamines, etc.), and any other suitable coagulants. Examples of suitable flocculants that may be used in the present disclosure includes, but not limited to, natural polymers natural polymers (e.g., polysaccharides, mainly starch and its constituents, different types of gums, alginic acid, cellulose and its derivatives, dextran, glycogen, etc.), polyacrylamide (PAM) and polyethylene oxide (PEO), polydiallyl dimethyl ammonium chloride (polyDADMAC), polyacrylic acid and its derivatives, polystyrene sulfonic acid (PSSA), and any other suitable flocculants. Reaction assembly 309 may also include a reaction assembly output configurable or configured to provide the second liquid output to clarifier assembly 310.

Method 400 also includes removing solids in the second liquid output to arrive at an effluent discharge and calcium fluoride sludge 420. The solids in the second liquid output may be removed in clarifier assembly 310, or the like. Clarifier assembly 310 includes a clarifier assembly input configurable or configured to receive the second liquid output from the reaction assembly output. Clarifier assembly 310 may further include a clarifier assembly unit configured or configurable to remove impurities in the second liquid output to arrive at an effluent discharge and a calcium fluoride sludge. Clarifier assembly 310 may also include a clarifier assembly output configurable or configured to provide the effluent discharge to be discharged. Examples of suitable clarifiers that may be used in the present disclosure, but not limited to, high rate solid contact clarifier, lamella clarifier, and any other clarifiers that may be used. The effluent discharge may be an effluent that is free or substantially free of fluoride concentration and other impurities. The effluent at this stage is expected to meet the standard requirements for safe discharge into the environment and/or to be reused in the or alternative treatment system where applicable and/or to be used in any other suitable applications.

Method 400 also includes removing liquid from the calcium fluoride sludge to arrive at second final output 422. The liquid in the calcium fluoride sludge may be removed using filter press assembly 311, or the like. Filter press assembly 311 may be configurable or configured to perform a variety of functions, including removing liquid in the calcium fluoride sludge. Filter press assembly 311 includes a filter press assembly input configurable or configured to receive the calcium fluoride sludge from the sedimentation assembly output and/or the clarifier assembly output. In some

embodiments, the filter press assembly input may be configurable or configured to receive the calcium fluoride sludge from holding tank assembly 314. Filter press assembly 311 may further include a filter press assembly unit configurable or configured to remove liquid from the calcium fluoride sludge. Filter presses are commonly used to provide sludge dewatering by applying high pressure or pressing the sludge between a plurality of porous plates. The liquid (e.g., water) is being forced out of the calcium fluoride sludge when high pressure is applied. Filter press assembly 311 may also include a filter press assembly output to provide the second final output. The second final output (e.g., clean or other water products) may or may not be treated further before being safely disposed into a water source in the environment. The second final output may also be reused in the treatment system where applicable and/or used in any other suitable applications. Further, the calcium fluoride sludge obtained through the filter press assembly is comprised of 75% calcium fluoride.

In some embodiments, method 400 may further include collecting calcium fluoride sludge 428. The calcium fluoride sludge may be collected in holding tank assembly 314. Holding tank assembly 314 includes a holding tank assembly input configurable or configured to receive the calcium fluoride sludge from sedimentation assembly 308 and/or clarifier assembly 310. Holding tank assembly 314 may further include a holding tank assembly unit configurable or configured to collect the calcium fluoride sludge provided from sedimentation assembly 308 and/or clarifier assembly 310. The calcium fluoride sludge is then further treated with a polymer. Examples of suitable polymers that may be used in the present disclosure include, but not limited to, natural polymers (e.g., polysaccharides, mainly starch and its constituents, different types of gums, alginic acid, cellulose and its derivatives, dextran, glycogen, etc.), polyacrylamide (PAM) and polyethylene oxide (PEO), polydiallyl dimethyl ammonium chloride (polyDADMAC), polyacrylic acid and its derivatives, polystyrene sulfonic acid (PSSA), and any other suitable polymers. Holding tank assembly 314 may also include a holding tank assembly output configurable or configured to provide the calcium fluoride sludge to filter press assembly 311.

U.S. Provisional Patent Application No. 63/565,224, filed March 14, 2024, and entitled “Removal of Hydrofluoric Acid from Liquid Streams,” and U.S. Provisional Patent Application No. 63/565,450, filed March 14, 2024, and entitled “Removal of

Hydrofluoric Acid from Liquid Streams, Including Fluoride Salt Precipitation," are each incorporated herein by reference in its entirety for all purposes.

While several embodiments of the present invention have been described and illustrated herein, those of ordinary skill in the art will readily envision a variety of other means and/or structures for performing the functions and/or obtaining the results and/or one or more of the advantages described herein, and each of such variations and/or modifications is deemed to be within the scope of the present invention. More generally, those skilled in the art will readily appreciate that all parameters, dimensions, materials, and configurations described herein are meant to be exemplary and that the actual parameters, dimensions, materials, and/or configurations will depend upon the specific application or applications for which the teachings of the present invention is/are used. Those skilled in the art will recognize, or be able to ascertain using no more than routine experimentation, many equivalents to the specific embodiments of the invention described herein. It is, therefore, to be understood that the foregoing embodiments are presented by way of example only and that, within the scope of the appended claims and equivalents thereto, the invention may be practiced otherwise than as specifically described and claimed. The present invention is directed to each individual feature, system, article, material, and/or method described herein. In addition, any combination of two or more such features, systems, articles, materials, and/or methods, if such features, systems, articles, materials, and/or methods are not mutually inconsistent, is included within the scope of the present invention.

As used herein in the specification and in the claims, the phrase "at least a portion" means some or all. "At least a portion" may mean, in accordance with certain embodiments, at least 1 wt%, at least 2 wt%, at least 5 wt%, at least 10 wt%, at least 25 wt%, at least 50 wt%, at least 75 wt%, at least 90 wt%, at least 95 wt%, or at least 99 wt%, and/or, in certain embodiments, up to 100 wt%.

The indefinite articles "a" and "an," as used herein in the specification and in the claims, unless clearly indicated to the contrary, should be understood to mean "at least one."

The phrase "and/or," as used herein in the specification and in the claims, should be understood to mean "either or both" of the elements so conjoined, i.e., elements that are conjunctively present in some cases and disjunctively present in other cases. Other

elements may optionally be present other than the elements specifically identified by the "and/or" clause, whether related or unrelated to those elements specifically identified unless clearly indicated to the contrary. Thus, as a non-limiting example, a reference to "A and/or B," when used in conjunction with open-ended language such as "comprising" can refer, in one embodiment, to A without B (optionally including elements other than B); in another embodiment, to B without A (optionally including elements other than A); in yet another embodiment, to both A and B (optionally including other elements); etc.

As used herein in the specification and in the claims, "or" should be understood to have the same meaning as "and/or" as defined above. For example, when separating items in a list, "or" or "and/or" shall be interpreted as being inclusive, i.e., the inclusion of at least one, but also including more than one, of a number or list of elements, and, optionally, additional unlisted items. Only terms clearly indicated to the contrary, such as "only one of" or "exactly one of," or, when used in the claims, "consisting of," will refer to the inclusion of exactly one element of a number or list of elements. In general, the term "or" as used herein shall only be interpreted as indicating exclusive alternatives (i.e. "one or the other but not both") when preceded by terms of exclusivity, such as "either," "one of," "only one of," or "exactly one of." "Consisting essentially of," when used in the claims, shall have its ordinary meaning as used in the field of patent law.

As used herein in the specification and in the claims, the phrase "at least one," in reference to a list of one or more elements, should be understood to mean at least one element selected from any one or more of the elements in the list of elements, but not necessarily including at least one of each and every element specifically listed within the list of elements and not excluding any combinations of elements in the list of elements. This definition also allows that elements may optionally be present other than the elements specifically identified within the list of elements to which the phrase "at least one" refers, whether related or unrelated to those elements specifically identified. Thus, as a non-limiting example, "at least one of A and B" (or, equivalently, "at least one of A or B," or, equivalently "at least one of A and/or B") can refer, in one embodiment, to at least one, optionally including more than one, A, with no B present (and optionally including elements other than B); in another embodiment, to at least one, optionally including more than one, B, with no A present (and optionally including elements other than A); in yet another embodiment, to at least one, optionally including more than one,

A, and at least one, optionally including more than one, B (and optionally including other elements); etc.

Unless clearly indicated to the contrary, concentrations and percentages described herein are on a mass basis.

As used herein, "wt%" is an abbreviation of weight percentage. As used herein, "at%" is an abbreviation of atomic percentage.

Some embodiments may be embodied as a method, of which various examples have been described. The acts performed as part of the methods may be ordered in any suitable way. Accordingly, embodiments may be constructed in which acts are performed in an order different than illustrated, which may include different (e.g., more or less) acts than those that are described, and/or that may involve performing some acts simultaneously, even though the acts are shown as being performed sequentially in the embodiments specifically described above.

Use of ordinal terms such as "first," "second," "third," etc., in the claims to modify a claim element does not by itself connote any priority, precedence, or order of one claim element over another or the temporal order in which acts of a method are performed, but are used merely as labels to distinguish one claim element having a certain name from another element having a same name (but for use of the ordinal term) to distinguish the claim elements.

In the claims, as well as in the specification above, all transitional phrases such as "comprising," "including," "carrying," "having," "containing," "involving," "holding," and the like are to be understood to be open-ended, i.e., to mean including but not limited to. Only the transitional phrases "consisting of" and "consisting essentially of" shall be closed or semi-closed transitional phrases, respectively, as set forth in the United States Patent Office Manual of Patent Examining Procedures, Section 2111.03.

CLAIMS

What is claimed is:

1. A method for treating a hydrofluoric acid (HF)-containing stream, comprising:

adjusting a pH of an aqueous stream comprising HF molecules present at a concentration of greater than or equal to 100 mg/L, such that at least 50 mole percent (mol%) of the HF molecules are deprotonated to form dissolved fluoride ions (F^-), thereby forming a pH-adjusted stream; and

transporting a first membrane separator retentate inlet stream to a retentate side of a first membrane separator such that:

a first membrane separator retentate outlet stream exits the retentate side of the first membrane separator, the first membrane separator retentate outlet stream having concentration of dissolved fluoride ions that is greater than a concentration of dissolved fluoride ions of the first membrane separator retentate inlet stream, and

at least a portion of liquid from the first membrane separator retentate inlet stream is transported from the retentate side of the first membrane separator, through a semi-permeable membrane of the first membrane separator, to a permeate side of the first membrane separator where the portion of liquid forms some or all of a first membrane separator permeate outlet stream that is transported out of the permeate side of the first membrane separator;

wherein the first membrane separator retentate inlet stream comprises at least a portion of the pH-adjusted stream.

2. The method of claim 1, wherein a hydraulic pressure is applied to the retentate side of the first membrane separator during at least a portion of time during which the at least a portion of liquid from the first membrane separator retentate inlet stream is transported from the retentate side of the first membrane separator, through the semi-permeable membrane of the first membrane separator, to the permeate side of the first membrane separator.

3. The method of any one of claims 1-2, wherein the first membrane separator is operated as a reverse osmosis membrane separator during the transporting.

4. The method of any one of claims 1-3, wherein the pH-adjusted stream comprises dissolved and/or colloidal silica (SiO_2), and wherein the method further comprises coagulating at least a portion of the dissolved and/or colloidal silica.

5. The method of claim 4, wherein the coagulating comprises treating at least a portion of the pH-adjusted stream with an inorganic coagulant.

6. The method of claim 5, wherein the inorganic coagulant comprises iron chloride and/or ferric sulfate.

7. The method of any one of claims 1-6, wherein the pH of the pH-adjusted stream is greater than or equal to 5.5.

8. The method of any one of claims 1-7, wherein the pH of the pH-adjusted stream is less than or equal to 6.8.

9. The method of any one of claims 1-8, wherein the first membrane separator retentate inlet stream comprises at least a portion of the first membrane separator retentate outlet stream during at least a portion of the method, thereby establishing a recycle process.

10. The method of claim 9, wherein the recycle process is a batch or semi-batch process.

11. The method of claim 10, wherein the recycle process is a semi-batch process.

12. The method of any one of claims 1-11, wherein the first membrane separator has a rejection for fluoride ions of greater than or equal to 90%.

13. The method of any one of claims 1-12, further comprising transporting a second membrane separator retentate inlet stream comprising at least a portion of the first membrane separator retentate outlet stream to a retentate side of a second membrane separator such that:

a second membrane separator retentate outlet stream exits the retentate side of the second membrane separator, the second membrane separator retentate outlet stream having a concentration of dissolved fluoride ions that is greater than a concentration of dissolved fluoride ions in the second membrane separator retentate inlet stream, and

at least a portion of liquid from the second membrane separator retentate inlet stream is transported from the retentate side of the second membrane separator, through a semi-permeable membrane of the second membrane separator, to a permeate side of the second membrane separator where the portion of liquid forms some or all of a second membrane separator permeate outlet stream that is transported out of the permeate side of the second membrane separator.

14. The method of claim 13, wherein the transporting the second membrane separator retentate inlet stream to the retentate side of the second membrane separator is performed such that at least a portion of the dissolved fluoride ions from the second membrane separator retentate inlet stream are transported from the retentate side of the second membrane separator, through a semi-permeable membrane of the second membrane separator, to a permeate side of the second membrane separator where the portion of dissolved fluoride ions forms some of the second membrane separator permeate outlet stream that is transported out of the permeate side of the second membrane separator.

15. The method of any one of claims 13-14, wherein a salt passage percentage at standard conditions of the second membrane separator is greater than a salt passage percentage at standard conditions of the first membrane separator, wherein the salt passage percentage at standard conditions is determined using ASTM D4516-19a.

16. The method of claim 15, wherein the second membrane separator has a salt passage percentage at standard conditions that is greater than that of the first membrane separator by a factor of at least 1.05.

17. The method of any one of claims 13-16, wherein the second membrane separator has a rejection for fluoride ions on the retentate side that is less than that of the first membrane separator.

18. The method of any one of claims 13-17, wherein the second membrane separator has a rejection for fluoride ions on the retentate side that is less than that of the first membrane separator by at least 5%.

19. The method of any one of claims 13-18, wherein the first membrane separator and/or the second membrane separator has a rejection for fluoride ions of less than or equal to 95%.

20. The method of any one of claims 13-19, wherein the first membrane separator and/or the second membrane separator has a rejection for fluoride ions of greater than or equal to 10%.

21. A system for managing an aqueous effluent with high concentration of fluoride, the system comprising:

an inlet for receiving an aqueous effluent with high concentration of fluoride;

a first treatment assembly, the first treatment assembly including:

a first treatment assembly input configured to receive the aqueous effluent from the inlet;

a first treatment unit configured to increase pH level of the aqueous effluent to arrive at a treated aqueous effluent; and

a first treatment assembly output configured to provide the treated aqueous effluent to a first filtration assembly;

a first filtration assembly, the first filtration assembly including:

a first filtration assembly input configured to receive the treated aqueous effluent from the first treatment assembly;

a first filtration unit configured to filter pollutants and/or contaminants from the treated aqueous effluent to arrive at a first permeate and a first reject water; and

a first filtration assembly output configured to provide the first permeate to a second filtration assembly and the first reject water to a collection assembly;

a second filtration assembly, the second filtration assembly including:

a second filtration assembly input configured to receive the first permeate from the first filtration assembly;

a second filtration unit configured to filter impurities from the first permeate to arrive at a second permeate and a second reject water; and

a second filtration assembly output configured to provide the second permeate to a polishing assembly and the second reject water to a collection assembly;

a polishing assembly, the polishing assembly including:

a polishing assembly input configured to receive the second permeate from a second filtration assembly;

a polishing unit configured to remove impurities from the second permeate to arrive at a first final output and a third reject water; and

a polishing assembly output configured to provide the first final output and the third reject water to a collection assembly;

a collection assembly, the collection assembly including:

a collection assembly input configured to receive the first reject water, second reject water and/or third reject water;

a collection unit configured to collect the first reject water, second reject water and/or third reject water; and

a collection assembly output configured to provide the collected first reject water, second reject water and/or third reject water to a second treatment assembly;

a second treatment assembly, the second treatment assembly including:

a second treatment assembly input configured to receive the collected first reject water, second reject water and/or third reject water from the collection assembly;

a second treatment unit configured to precipitate fluoride and silica in the collected first reject water, second reject water and/or third reject water to arrive at a first treated reject water; and

a second treatment assembly output configured to provide the first treated reject water to a sedimentation assembly;

a sedimentation assembly, the sedimentation assembly including:

a sedimentation assembly input configured to receive the first treated reject water from the second treatment assembly;

a sedimentation unit configured to sediment impurities in the first treated reject water to arrive at an effluent discharge and a calcium fluoride sludge; and

a sedimentation assembly output configured to provide a first liquid output to a reaction assembly;

a reaction assembly, the reaction assembly including:

a reaction assembly input configured to receive the first liquid output from the sedimentation assembly;

a reaction unit configured to remove impurities in the first liquid output to arrive at a second liquid output; and

a reaction assembly output configured to provide the second liquid output to a clarifier assembly;

a clarifier assembly, the reaction assembly including:

a clarifier assembly input configured to receive the second liquid output from the reaction assembly output;

a clarifier assembly unit to remove solids in the second liquid output to arrive at an effluent discharge and a calcium fluoride sludge; and

a clarifier assembly output configured to provide the calcium fluoride sludge to a filter press assembly; and

a filter press assembly, the filter press assembly including:

a filter press assembly input configured to receive the calcium fluoride sludge from the sedimentation assembly output and the clarifier assembly output;

a filter press assembly unit to remove liquid from the calcium fluoride sludge; and

a filter press assembly output to provide a second final output.

22. The system of claim 21, wherein the first treatment unit is configured to increase the pH level of the aqueous effluent with high concentration of fluoride to pH 6.0 to pH 7.0.

23. The system of claim 22, wherein the pH level of the aqueous effluent with high concentration of fluoride may be increased using one or more alkaline agents including sodium hydroxide, sodium carbonate, calcium carbonate, magnesium hydroxide, and potassium hydroxide.

24. The system of claim 21, wherein the first filtration unit includes at least one of the following:

an automatic backwash filter system;

an ultrafiltration system;

a cartridge filtration system;

a multimedia filtration ; and/or

a membrane cartridge filtration system.

25. The system of claim 21, wherein the second filtration unit includes at least one of the following:

an automatic backwash filter system;

an ultrafiltration system;

a cartridge filtration system;

a multimedia filtration; and/or

a membrane cartridge filtration system.

26. The system of claim 21, further comprising a third filtration assembly, the third filtration assembly including:

a third filtration assembly input configured to receive the second permeate from the second filtration assembly;

a third filtration unit configured to filter solid impurities from the second permeate to arrive at a third permeate and a third reject water; and

a third filtration assembly output configured to provide the third permeate to a polishing assembly and the third reject water to the collection assembly.

27. The system of claim 26, wherein the third filtration unit includes at least one of the following:

an automatic backwash filter system;

an ultrafiltration system;

a cartridge filtration system;

a multimedia filtration; and/or

a membrane cartridge filtration system.

28. The system of claim 21, wherein the polishing unit includes one of the following:

nanofiltration membranes;

brackish water reverse osmosis;

seawater reverse osmosis membranes;

electrodialysis reversal; and/or

forward osmosis.

29. The system of claim 21, further comprising the collection unit may be configured to receive reject water from one or more wastewater streams of at least one or more of the following wastewater streams:

wastewater stream with high concentration of copper;

wastewater stream with high concentration of silica;

wastewater stream with high alkalinity;

wastewater stream with high concentration of sulfate;

local scrubber recyclable system; or

a combination thereof.

30. The system of claim 21, wherein the second treatment unit is configured to treat the collected first reject water, second reject water and/or third reject water from one or more wastewater streams by adding one or more calcium chloride, calcium hydroxide, sodium hydroxide and/or a combination thereof to precipitate fluoride.

31. The system of claim 21, wherein the second treatment unit is configured to treat the collected first reject water, second reject water and/or third reject water from one or more wastewater streams by adding ferric chloride, sodium aluminate, sodium hydroxide and any other suitable agents to coagulate silica.

32. The system of claim 31, wherein the ferric chloride, sodium aluminate, sodium hydroxide and any other suitable agents used is 50 mg/l to 300 mg/l.

33. The system of claim 21, further comprising the third treatment assembly, the third treatment assembly including:

a third treatment assembly input configured to receive the first treated reject water from the second treatment assembly;

a third treatment unit configured to precipitate fluoride and/or silica in the first treated reject water to arrive at a second treated water reject; and

a third treatment assembly output configured to provide the second treated reject water to a sedimentation assembly.

34. The system of claim 33, wherein the third treatment unit is configured to treat the first treated water reject by adding one or more calcium chloride, calcium hydroxide, sodium hydroxide and/or a combination thereof to precipitate fluoride.

35. The system of claim 33, wherein the third treatment unit is configured to treat the first treated water reject by adding ferric chloride, sodium aluminate, sodium hydroxide and any other suitable agents to coagulate silica.

36. The system of claim 35, wherein the ferric chloride, sodium aluminate, sodium hydroxide and any other suitable agents used is 50 mg/l to 300 mg/l.

37. The system of claim 33, further comprising the sedimentation assembly is configured to receive the second treated reject water from the third treatment assembly output to sediment impurities in the second treated reject water to arrive at a first liquid output and calcium fluoride sludge.

38. The system of claim 37, wherein the sedimentation unit is at least one of the following:

horizontal flow tank;

multi-layer tank;

settling tank;

tube settler;

conical bottom tanks; and/or

a combination thereof.

39. The system of claim 21, wherein the reaction unit is configured to treat the first liquid output from the sedimentation assembly by adding one or more flocculants into the first liquid output.

40. The system of claim 39, wherein the one or more flocculants used may be natural polymers, polysaccharides such as starch, gums, alginic acid, cellulose, dextran, and glycogen, polyacrylamide (PAM), polyethylene oxide (PEO), polydiallyl dimethyl ammonium chloride (polyDADMAC), polyacrylic acid and its derivatives, polystyrene sulfonic acid (PSSA) and/or a combination thereof.

41. The system of claim 21, wherein the clarifier assembly unit is configured to further remove solids such as particulates and/or or suspended solids from the second liquid output.

42. The system of claim 41, wherein the clarifier assembly unit may include:

a high rate solid contact clarifier;

lamella clarifier; and/or

a combination thereof.

43. The system of claim 21, further comprising a holding tank assembly, the holding tank assembly including:

a holding tank assembly input configured to receive the calcium fluoride sludge from the sedimentation assembly output and/or the clarifier assembly output;

a holding tank configured to treat the calcium fluoride sludge using flocculants to arrive at a treated calcium fluoride sludge; and

a holding tank assembly output configured to provide the treated calcium fluoride sludge to the filter press assembly.

44. The system of claim 21, further comprising a holding tank assembly, the holding tank assembly including:

a holding tank assembly input configured to receive the calcium fluoride sludge from the second treatment assembly;

a holding tank assembly unit configured to treat the calcium fluoride sludge; and

a holding tank assembly output configured to provide the second treated reject water to a sedimentation assembly.

45. The system of claim 44, where the holding tank unit is further configured to treat the calcium fluoride sludge with one or more flocculant including natural polymers, polysaccharides such as starch, gums, alginic acid, cellulose, dextran, and glycogen, polyacrylamide (PAM), polyethylene oxide (PEO), polydiallyl dimethyl ammonium chloride (polyDADMAC), polyacrylic acid and its derivatives, polystyrene sulfonic acid (PSSA) and/or a combination thereof.

46. A method for managing an aqueous effluent with high concentration of fluoride, the method comprising:

receiving an aqueous effluent with high concentration of fluoride;

treating the aqueous effluent with high concentration of fluoride to increase pH level of the aqueous effluent to arrive at a treated aqueous effluent;

filtering the treated aqueous effluent to arrive at a first permeate and a first reject water;

filtering the first permeate to arrive at a second permeate and a second reject water;

polishing the second permeate to arrive at a first final output and a third reject water;

collecting the first reject water, the second reject water and the third reject water in a collection unit;

treating the collected first reject water, second reject water and/or third reject water by precipitating fluoride and/or silica in the collected first reject water, second reject water and/or third reject water to arrive at a first treated reject water;

sedimenting impurities in the first treated reject water to arrive at a first liquid output and calcium fluoride sludge;

reacting the first liquid output to arrive at a second liquid output;

removing solids in the second liquid output to arrive at an effluent discharge and a calcium fluoride sludge; and

removing liquid from the calcium fluoride sludge to arrive at a second final output.

47. The method of claim 46, wherein the pH level of the aqueous effluent with high concentration of fluoride is increased to pH 6.0 to pH 7.0.

48. The method of claim 47, wherein the pH may be increased using one or more alkaline agents including sodium hydroxide, sodium carbonate, calcium carbonate, magnesium hydroxide, and potassium hydroxide.

49. The method of claim 46, wherein the filtering of the treated aqueous effluent is performed using at least one of the following:

an automatic backwash filter system;

an ultrafiltration system;

a cartridge filtration system;
a multimedia filtration; and/or
a membrane cartridge filtration system.

50. The method of claim 46, wherein the filtering of the first permeate is performed using at least one of the following:
an automatic backwash filter system;
an ultrafiltration system;
a cartridge filtration system;
a multimedia filtration; and/or
a membrane cartridge filtration system.

51. The method of claim 46, further comprising:
filtering the second permeate to arrive at a third permeate and a third reject water.

52. The method of claim 51, wherein the filtering of the second permeate is performed using at least one of the following:
an automatic backwash filter system;
an ultrafiltration system;
a cartridge filtration system;
a multimedia filtration; and/or
a membrane cartridge filtration system.

53. The method of claim 46, wherein the polishing of the second permeate is performed using at least one of the following:
nanofiltration membranes;
brackish water reverse osmosis;
seawater reverse osmosis membranes;
electrodialysis reversal; and/or
forward osmosis.

54. The method of claim 46, wherein the collecting of the first reject water, the second reject water and the third reject water is performed by collecting reject water from one or more wastewater streams of at least one or more of the following wastewater streams:

wastewater stream with high concentration of copper;
wastewater stream with high concentration of silica;
wastewater stream with high alkalinity;
wastewater stream with high concentration of sulfate;
local scrubber recyclable system; or
a combination thereof.

55. The method of claim 46, wherein the treating of the collected first reject water, second reject water and/or third reject water is performed by adding one or more calcium chloride, calcium hydroxide, sodium hydroxide and/or a combination thereof to precipitate fluoride.

56. The method of claim 46, wherein the treating of the collected first reject water, second reject water and/or third reject water is performed by adding ferric chloride, sodium aluminate, sodium hydroxide and any other suitable agents to precipitate silica.

57. The method of claim 56, wherein the ferric chloride, sodium aluminate, sodium hydroxide and any other suitable agents used is 50 mg/l to 300 mg/l.

58. The method of claim 46, further comprising treating the first treated reject water to arrive at a second treated water reject by adding one or more calcium chloride, calcium hydroxide, sodium hydroxide and/or a combination thereof to precipitate fluoride.

59. The method of claim 46, wherein the treating of the first treated water reject to arrive at a second treated water reject is performed by adding ferric chloride, sodium aluminate, sodium hydroxide and any other suitable agents to coagulate silica.

60. The method of claim 59, wherein the ferric chloride, sodium aluminate, sodium hydroxide and any other suitable agents used is 50 mg/l to 300 mg/l.

61. The method of claim 46, wherein the sedimenting of impurities in the second treated reject water is performed using at least one of the following:

horizontal flow tank;

multi-layer tank;

settling tank;

tube settler;

conical bottom tanks; and/or

a combination thereof.

62. The method of claim 46, wherein the reacting of the first liquid output is performed by adding one or more flocculants into the first liquid output.

63. The method of claim 62, wherein the flocculants used may be natural polymers, polysaccharides such as starch, gums, alginic acid, cellulose, dextran, and glycogen, polyacrylamide (PAM), polyethylene oxide (PEO), polydiallyl dimethyl ammonium chloride (polyDADMAC), polyacrylic acid and its derivatives, polystyrene sulfonic acid (PSSA) and/or a combination thereof.

64. The method of claim 46, wherein the removing of solids in the second liquid output is performed using at least one of the following:

high rate solid contact clarifier;

lamella clarifier; and/or

a combination thereof.

65. The method of claim 46, further comprising treating calcium fluoride sludge using flocculants to arrive at a treated calcium fluoride sludge.

66. The method of claim 65, wherein the flocculants used may be natural polymers, polysaccharides such as starch, gums, alginic acid, cellulose, dextran, and glycogen,

polyacrylamide (PAM), polyethylene oxide (PEO), polydiallyl dimethyl ammonium chloride (polyDADMAC), polyacrylic acid and its derivatives, polystyrene sulfonic acid (PSSA) and/or a combination thereof.

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