

DISSOLVED AIR FLOTATION, ANTISOLVENT CRYSTALLISATION AND
MEMBRANE SEPARATION FOR SEPARATING BUOYANT MATERIALS AND
SALTS FROM WATER

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims priority to, and the benefit of the filing date of, (1) U.S. Patent Application No. 61/878,861, entitled, "Apparatus and Method for Separating Salts from Water, filed on September 17, 2013; (2) U.S. Patent Application No. 61/786,972, entitled "Flotation of Neutrally Buoyant Materials in Water," filed on March 15, 2013; (3) U.S. Patent Application No. 61/784,099, entitled "Selective Separation of Strontium from Produced Water", filed on March 14, 2013; (4) U.S. Patent Application Serial No. 61/768,486, entitled "Wetted Wall Separator Tube and Methods of Separating," filed on February 24, 2013; (5) U.S. Patent Application No. 61/757,891, entitled, "Solvent Precipitation and Concentration of Salts," filed on January 29, 2013; (6) U.S. Patent Application No. 61/735,211, entitled "Process for Converting Brackish/Produced Water to Useful Products and Reusable Water," filed on December 10, 2012, and (7) U.S. Patent Application No. 61/734,491, entitled "Process for Converting Brackish/Produced Water to Useful Products and Reusable Water", filed on December 7, 2012, the disclosures of which are incorporated by reference herein in their entireties.

FIELD OF THE INVENTION

[0002] Aspects of the present invention generally relate to methods of, and apparatus for, separating materials from a liquid, and more specifically relate to methods of, and apparatus for, separating neutrally buoyant materials from a liquid, separating strontium (or other elements) from a liquid, and/or separating salts from a liquid. Such a liquid may be contaminated water (e.g., brackish or produced water, or flowback water from processes such as fracking).

BACKGROUND OF THE INVENTION

[0003] This section is intended to introduce the reader to various aspects of art that may be related to various aspects of the present invention, which are described and/or claimed below. This discussion is believed to be helpful in providing the reader with background information to facilitate a better understanding of various aspects of the present invention. Accordingly, it should be understood that these statements are to be read in this light, and not as admissions of prior art.

[0004] Subsurface geological operations such as mineral mining, oil well drilling, natural gas exploration, and induced hydraulic fracturing generate wastewater contaminated with significant concentrations of impurities. These impurities vary widely in both type and amount depending on the type of geological operation, the nature of the subsurface environment, and the type and amount of soluble minerals present in the native water source. The contaminated water is eventually discharged into surface waters or sub-surface aquifers. In some cases, wastewater generated from drilling and mining operations have resulted in making regional water supplies unusable. Induced hydraulic fracturing (a.k.a. hydro fracturing, or fracking) in particular is a highly water-intensive process, employing water pumped at pressures exceeding 3,000 psi and flow rates exceeding 85 gallons per minute to create fractures in subsurface rock layers. These created fractures intersect with natural fractures, thereby creating a network of flow channels to a well bore. These flow channels allow the release of petroleum and natural gas products for extraction. The flow channels also allow the injected water plus additional native water to flow to the surface along with the fuel products once the fractures are created.

[0005] Flowback water, and produced water, from subsurface geological operations contain a variety of contaminants. Often, produced water is "hard" or brackish and further includes dissolved or dispersed organic and inorganic materials. Flowback water can include chemicals

used in the fracturing operation, such as polymer gels, metals, chemicals and hydrocarbons that are injected along with water to facilitate fracture of the formation during hydro-fracturing.

Produced water can include high concentrations of naturally occurring dissolved and suspended solids such as silt, hydrocarbons, multi- and mono-valent salts, metals, BODs, CODs and other contaminants.

[0006] Produced water also can include chemicals used in the mining operation, such as hydrocarbons that are injected along with water to facilitate fracture formation in hydrofracturing. One common type of contaminant present in produced water from hydrofracturing is a mixture of free and emulsified oil together with gel-like accumulations of hydrocarbons. In most cases, this oily mixture further contains silt, sand, and/or clay particulates gathered by the produced water as it travels to the surface. These oily mixtures are neutrally buoyant -- that is, they neither sink nor float, or they require extended times to sink or float -- in produced water. While in some cases these oily mixtures are visible as agglomerated, black, and tarry-looking residues, in other cases the oily mixtures, or some portion thereof, are finely divided dispersed liquids or liquid/solid droplets or particles present throughout the water phase.

[0007] Conventional oil separation processes relying on density differences are incapable of effectively separating this oily mixture from produced water, since their densities are very close. Conventional filtering methods employ screen or filter media that are quickly clogged by the oily mixture. Gravity separation is not only slow but also requires the use of large tanks and low flow rates in order to provide the long residence times needed to achieve an effective separation. Even with very long residence times, very well dispersed, fine oily mixture droplets are sometimes inseparable from the water phase. Methods such as evaporation of water from the mixture are not only time intensive, but highly energy intensive as well, and impractical for mining

operations where large volumes of produced water are generated in short periods of time.

Evaporation aside, further remediation of produced water is only possible once this oily mixture is removed.

[0008] Therefore, there is a need for a process for effectively removing neutrally buoyant materials from water. For example, in the mining industry, there is a need for a process to effectively remove an oily mixture from produced water in an efficient manner to result in produced water that is substantially free of emulsified petroleum, sand, silt, clay, and gel-like hydrocarbons. There is a need to remove neutrally buoyant materials other than such oily mixtures from water. There is a need for these processes to operate without undue energy expenditure. There is a need for these processes to operate at a rate that is commensurate with water-intensive applications such as hydrofracturing. In certain applications, there is a need for these processes to operate using materials and equipment suitably and conveniently employed on site in a mining operation.

[0009] Other common types of contaminants include dissolved or dispersed organic and inorganic materials. One inorganic material that is commonly observed in flowback water and produced water is strontium. High levels of non-radioactive strontium are known to exist in water drawn from bedrock aquifers that are rich in strontium minerals. Since subsurface geological operations obtain both fuel products and water from bedrock aquifers and nearby areas, the produced water that results is, in some cases, enriched in strontium. In particular, strontium-rich produced water contains strontium in the form of strontium chloride (SrCl_2), a naturally occurring water soluble salt.

[0010] Non-radioactive strontium occurs nearly everywhere in small amounts: air, dust, soil, foods, and drinking water all contain traces of strontium. Ingestion of small amounts of

non-radioactive strontium is not harmful. The U.S. Environmental Protection Agency (EPA) has developed a lifetime health advisory of 4 mg/L for non-radioactive strontium levels in drinking water (Human Health Hazards publication P00292, 10/2011, prepared by the State of Wisconsin Dept. of Health Services). In other words, water that contains more than 4 mg strontium per liter should not be used for drinking water. Produced water, however, can contain up to 100 mg/L of strontium, in some cases as high as 500 mg/L of strontium.

[0011] Previous efforts to separate strontium chloride from produced water have centered on precipitation methodology, employing ion exchange methods that result in the formation of a water-insoluble strontium salt. However, such techniques also result in the precipitation of calcium salts present in the water. Calcium salts, such as calcium chloride (CaCl_2) are often present in significant levels in produced water. In fact, in many cases, the weight ratio of $\text{Ca}^{2+}:\text{Sr}^{2+}$ is between about 10 and 100 and varies greatly depending on the subsurface environment. Since calcium chloride (CaCl_2) and strontium chloride (SrCl_2) have similar solubility in water (and their other salts tend to have very similar solubility as well), it has proven difficult to effectively separate strontium species in water containing both strontium and calcium (i.e., it is difficult to separate strontium from calcium and water, and vice versa).

[0012] Among these previous efforts, for example, U.S. Patent No. 8,158,097 (and related patents and patent applications) describes a method of purifying produced water from hydrofracturing, one step of which includes precipitation of strontium in the form of strontium carbonate. This specialized technique involves adding at least hydrochloric acid, sodium sulfate, and potassium permanganate to the produced water; adjusting the pH to about 3.5 to 4.0; optionally adding a flocculation aid; collecting precipitated barium sulfate; concentrating the effluent; transporting the effluent off-site for continued processing; crystallizing the salt

(ostensibly NaCl) from the effluent; adding sodium hydroxide, sodium carbonate, and a flocculation aid to the effluent; adjusting the pH of the effluent to about 11.5 to 12.0; then precipitating strontium carbonate and/or calcium carbonate. Concentration of effluent, required by this procedure, is a highly time and energy intensive process. Further, transferring the partially processed water to a second location is an expensive and inefficient process considering the large volume of water to be addressed in hydrofracturing operations. Overall, this technique is complicated, expensive, and time consuming. Finally, the disclosure makes no assertion regarding the purity of the strontium salts separated.

[0013] Other approaches that have been used in the past include U.S. Patent 1,831,251 in which strontium chloride is separated from calcium chloride and magnesium chloride by cooling the liquid to a temperature below 31°C, which is just below the saturation point of calcium chloride. However, in this case, a large amount of calcium chloride is also precipitated together with strontium chloride, and the ratio of concentrations in the precipitate is very close to the ratio in solution. In U.S. Patent 3,029,133, strontium sulfate is obtained by evaporating the water until most of the sodium chloride in the water crystallizes out of solution. Strontium chloride is precipitated with carnallite crystals ($\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) by cooling the liquid water and strontium chloride is separated from this precipitate by washing with water, which produces a solution with $\text{Ca}^{++}/\text{Sr}^{++}$ ratio of about 2.7. From this solution, strontium sulfate is precipitated by adding a soluble sulfate to form insoluble strontium sulfate. Hence, in this patent, several treatment steps are involved to reduce the molar ratio of $\text{Ca}^{++}/\text{Sr}^{++}$ to below 20 and preferably below 7.

[0014] As all previous processes are complicated, expensive, time-consuming, and do not adequately selectively separate strontium to the exclusion (or near-exclusion) of other materials (such as calcium), there is a need in the industry for a process to preferentially separate strontium

from water product – e.g., water that contains at least both strontium and calcium - employing simple, rapid, and inexpensive methodology. Because of its energy and time-intensive requirements, it is desirable in particular to avoid the need to concentrate the water product to facilitate the separation. There is a need to achieve the separation employing materials and equipment suitably and conveniently situated near sites where water product is collected. Carrying out a process on-site, for example in a hydrofracturing operation, requires the separation to be accomplished at a rate that is commensurate with the rate of water product collection.

[0015] Another common type of contaminant present is salt (e.g., sodium chloride). In all of these cases, there is a need for low energy-consuming and efficient technologies that can recover reusable water from wastewaters. Since all of these waters contain high concentrations of salts, there is need to be able to remove the soluble salts (such as sodium chloride) from water in an effective, efficient, low-energy, and low-cost manner.

[0016] As described above, much flowback water may contain salts dissolved in the water. As is known to those of ordinary skill in the art, the solubility rules for salts are as follows:

1. Salts containing Group I elements are soluble (Li^+ , Na^+ , K^+ , Cs^+ , Rb^+). Exceptions to this rule are rare. Salts containing the ammonium ion (NH_4^+) are also soluble.
2. Salts containing nitrate ion (NO_3^-) are generally soluble.
3. Salts containing Cl^- , Br^- , I^- are generally soluble. Important exceptions to this rule are halide salts of Ag^+ , Pb^{2+} , and $(\text{Hg}_2)^{2+}$. Thus, AgCl , PbBr_2 , and Hg_2Cl_2 are all insoluble.
4. Most silver salts are insoluble. AgNO_3 and $\text{Ag}(\text{C}_2\text{H}_3\text{O}_2)$ are common soluble salts of silver; virtually anything else is insoluble.

5. Most sulfate salts are soluble. Important exceptions to this rule include BaSO_4 , PbSO_4 , Ag_2SO_4 and SrSO_4 .
6. Most hydroxide salts are only slightly soluble. Hydroxide salts of Group I elements are soluble. Hydroxide salts of Group II elements (Ca, Sr, and Ba) are slightly soluble. Hydroxide salts of transition metals and Al^{3+} are insoluble. Thus, $\text{Fe}(\text{OH})_3$, $\text{Al}(\text{OH})_3$, $\text{Co}(\text{OH})_2$ are not soluble.
7. Most sulfides of transition metals are highly insoluble. Thus, CdS , FeS , ZnS , Ag_2S are all insoluble. Arsenic, antimony, bismuth, and lead sulfides are also insoluble.
8. Carbonates are frequently insoluble. Group II carbonates (Ca, Sr, and Ba) are insoluble. Some other insoluble carbonates include FeCO_3 and PbCO_3 .
9. Chromates are frequently insoluble. Examples: PbCrO_4 , BaCrO_4
10. Phosphates are frequently insoluble. Examples: $\text{Ca}_3(\text{PO}_4)_2$, Ag_3PO_4
11. Fluorides are frequently insoluble. Examples: BaF_2 , MgF_2 , PbF_2 .

[0017] Most alkali chlorides (Group 1 elements) are soluble in water. And, the solubility of most salts increases with temperature, as shown in FIG. 1, for some typical salts. Sodium chloride is an example of a highly soluble salt having a solubility that increases with temperature. As described above, sodium chloride is one of the most prevalent contaminants in water (such as flowback water), and so it would be beneficial to be able to remove sodium chloride in an effective, efficient, low-energy, low-cost manner.

[0018] However, presently there are no simple methods to remove sodium chloride from water that meet these goals. Two methods that have been traditionally used involve either (1) evaporation of water until the salt solution becomes supersaturated and salt begins to precipitate or (2) by freezing water to form pure ice, which allows the salt concentration to increase in the

liquid water portion [this process, coupled with the lowered solubility at freezing temperatures (below 32°F), allows salt to be precipitated from solution]. Unfortunately, both of these methods consume a large amount of energy, which is undesirable. Further, neither of these processes is rapid.

[0019] Additionally, previous patents on recovering water include U.S. Patent No. 8,158,097 B2, which discusses use of chemical precipitation using reagents to produce commercial products such as barium sulfate, strontium carbonate, calcium carbonate, and crystallizing the chemically treated and concentrated flowback brine to produce greater than 99.5% pure salt products, such as sodium and calcium chloride. This patent also discusses the use of evaporation to concentrate the salt from 15 wt% to about 30 wt% and using reagents selected from the group consisting of sodium sulfate, sodium carbonate, sodium hydroxide, hydrochloric acid and mixtures thereof, and recovering sodium chloride solid and calcium chloride with about 98% purity.

[0020] Another patent, U.S. Patent No. 7,083,730 B2, claims recovery of sodium chloride using reverse osmosis to recover water with the reject of the reverse osmosis process being treated in an electrodialysis system to produce a concentrated stream of sodium chloride, from which sodium chloride can be recovered.

[0021] Unfortunately, none of these processes are quick, efficient, low-energy, and low-cost.

[0022] Additionally, once salt has been precipitated, an issue that remains is how to separate the solvent from the salt slurry that is formed once salt is precipitated. U.S. Application No. 61/757,891 does not address an effective, efficient separation apparatus and a method of efficient separation of the water miscible solvent from the salt slurry that results from the solvent-induced salt precipitation. Further, methods currently known for separation of solvents are largely inadequate in the present processes, for myriad reasons (described below).

[0023] Methods previously used to separate solvents from liquids include those using contact of a gas with liquid to promote separation, such as through evaporation. And, there are many devices that have been developed for contacting a gas with a liquid. These include, for example, (1) packed columns, which use media, made from plastic, ceramic, etc., that is either randomly packed or is structured inside a vessel, with gas flowing upward and liquid trickling downward, such that a thin film of liquid that is formed on the outside surface of the media presents a high surface area between the gas and the liquid; (2) spray towers, in which liquid is sprayed in the form of small droplets, and gas flows upward counter to the falling drops; (3) devices where gas is bubbled through a column of liquid, with the gas being bubbled through porous media to form small bubbles, that present a very high surface area between the gas and liquid; (4) membrane contactors, using a porous, hollow fiber membrane, with gas flowing inside the hollow fibers and liquid flowing outside the hollow fiber bundle, with mass transfer occurring through the membrane pores between the gas and liquid phases; (5) venturi systems in which the gas or liquid is drawn in at the throat of the venturi with the other phase flowing through the venturi, thereby allowing turbulent contact between the gas and liquid phases (for example, liquid flows through the venturi while gas is drawn in at the throat due to lower pressure created by the high velocity of the liquid, and the gas forms very small bubbles in the liquid flow, presenting a very high surface area in a very turbulent liquid flow); and (6) other forms of kinetic devices, such as spinning disks, etc., having the objective of shearing the liquid into tiny packets of fluid inside the gas phase.

[0024] However, all the apparatus and methods described above include drawbacks that prevent their use in the presently described situation. These drawbacks include the use of too much energy, the problem with clogging of the systems, an inability to efficiently heat or cool the

liquid phase, and a large size. For example, with respect to energy consumption, if the gas has to be bubbled through a column of water, then the gas has to be pressurized, depending on the height of the water column. This requires considerable energy to pressurize the gas flow. If the liquid has to be sprayed in the form of small droplets in the gas phase, considerable pressure in the liquid phase is needed to create small droplets of liquid, etc. Further, devices such as packed towers easily clog if there are solids present in the liquid or gas phases. Further, in most of the methods mentioned above, simultaneous heat and mass transfer is not achievable. And finally, packed towers are generally large in diameter, having a large footprint, which is undesirable.

SUMMARY OF THE INVENTION

[0025] Certain exemplary aspects of the invention are set forth below. It should be understood that these aspects are presented merely to provide the reader with a brief summary of certain forms the invention might take and that these aspects are not intended to limit the scope of the invention. Indeed, the invention may encompass a variety of aspects that may not be explicitly set forth below.

[0026] Separation of Neutrally Buoyant Materials

[0027] One aspect of the present invention includes methods of separating a neutrally buoyant material or materials from a liquid. As described above, particles or phases which have a lower density than the liquid they are in will move to the surface of the liquid on their own (i.e., float), and particles or phases with densities greater than the liquid will move towards the bottom of the liquid (i.e., settle). The challenge is in removing particles or phases which have a density close to the liquid they are in -- i.e., which are neutrally buoyant or nearly neutrally buoyant -- and which otherwise on their own would take a long time to either settle or float. One method for accomplishing this is described herein. The method includes pressurizing a first liquid with a gas

at a first pressure to form a pressurized liquid, and then contacting the pressurized liquid with a second liquid including a neutrally buoyant material dispersed therein. In this method, the second liquid is maintained at a second pressure that is lower than the first pressure, and the contacting of the pressurized liquid to second liquid includes a gradient pressure change from the first pressure to the second pressure. This gradient pressure change results in the formation of nanobubbles within at least the second liquid. Such nanobubbles may have an average diameter of about 10 nm to 100 nm. The neutrally buoyant material or materials are then separated from the second liquid by association of these bubbles (such as air bubbles) with the neutrally buoyant materials (via attachment or otherwise). For example, such association may occur via hydrogen bonding between an alcohol group and a water molecule. (These and other types of associations are well known to those of ordinary skill in the art.) By virtue of the bubbles' density difference with the second liquid (e.g. water), these neutrally buoyant materials (e.g. particles or phases) are moved to the surface of the second liquid (e.g. water), where they can be skimmed off.

[0028] The formation of nanobubbles is described above as occurring within at least the second liquid. This can be accomplished by contacting the first liquid with the second liquid such that, while a portion of the first and second liquids may be combined, the nanobubbles rise through the second liquid (i.e., a portion of the second liquid that is not combined, or is yet to be combined, with the first liquid). Alternatively, or additionally, the nanobubbles may form and rise within the combined first and second liquids.

[0029] In some embodiments, the first liquid is water. And, in certain embodiments, the first liquid may include a hydrophobically modified water soluble polymer dispersed or dissolved therein. In some such embodiments, the hydrophobically modified water soluble polymer may

include repeat units attributable to monomers including acrylamide, acrylate, methacrylate, or combinations thereof.

[0030] In some embodiments, the second liquid is water. In certain embodiments, the water further includes one or more solids dissolved therein. In some such embodiments, the water is hard water, brackish water, or produced water. In some embodiments the neutrally buoyant material is oil or an oily mixture. In some embodiments, the pressure difference between the first pressure and the second pressure is about 0.1 MPa to 1 MPa. In some embodiments, the second pressure is ambient pressure, or 1 atm (0.101 MPa). The separation includes flotation of the neutrally buoyant material to the surface of the liquid. In certain embodiments, the method is effective for separating at least 90 wt% to 100 wt% of the total weight of neutrally buoyant material from the liquid, or about 93 wt% to 99.9 wt%, or about 95 wt% to 99 wt% by weight of the neutrally buoyant material from the liquid. The method further includes, in some embodiments, removing the separated neutrally buoyant material from the surface of the combined first and second liquid.

[0031] Another aspect of the invention includes methods of forming nanobubbles, the method including dissolving a hydrophobically modified water soluble polymer in water to form a solution, pressurizing the solution with a gas or mixture of gases at elevated pressure to form a pressurized solution, and reducing the pressure applied to the pressurized solution employing a gradient pressure change sufficient to form nanobubbles, the nanobubbles having an average diameter of between about 10nm and 100nm. In this aspect, the hydrophobically modified water soluble polymer may be associated with the nanobubbles.

[0032] Yet another aspect of the invention includes apparatus that achieve separation and removal of a neutrally buoyant material or materials from liquid. Such apparatus may include a

source of pressurized gas; a pressurized tank situated to receive a pressurized solution of a first liquid, the pressurized tank connected to the source of pressurized gas; an element attached to the pressurized tank and disposed to deliver the pressurized solution into a second liquid; a receiving vessel for holding a second liquid having a neutrally buoyant material dispersed therein, wherein the element is disposed within the receiving vessel. The apparatus may further include a skimmer disposed within the receiving vessel and situated to remove a separated layer (including the neutrally buoyant material) from the surface of liquid present within the receiving vessel. The first liquid may be water. The first liquid may include a hydrophobically modified water soluble polymer. The element for delivering the pressurized solution may include one or more headers and/or one or more eductors. The apparatus is useful for achieving separation and removal of neutrally buoyant materials from a liquid, employing the methods described above.

[0033] The methods of separation and apparatuses employed to separate the neutrally buoyant materials from liquids are useful in a number of applications. Remediation of water from mining operations is one such application. Treatment of seawater is another. Others include separating living biomaterials from a bioreactor tank, or sequestration of carbon dioxide from power plants.

[0034] Selective Separation of an Element

[0035] Another aspect of the present invention provides a composition that facilitates the effective separation of strontium from water. More specifically, disclosed herein is a composition including (a) a water soluble sulfate salt; (b) seed crystals composed substantially of strontium sulfate; and (c) water.

[0036] In certain embodiments, the seed crystals have an average particle size of about 30 to 100 microns. In certain embodiments, the composition is a slurry of the crystals in a water soluble sulfate salt solution. In certain embodiments, the composition includes substantially only the

recited substituents, except that in any of the disclosed embodiments herein, the water soluble sulfate salt may include one or more water soluble sulfate salts; that is, the water soluble sulfate salt includes mixtures of two or more water soluble sulfate salts. When the composition of the invention is added to a water product, wherein the water product is a solution of water having at least both water soluble strontium salts and water soluble calcium salts dissolved therein, the composition results in the preferential precipitation of strontium sulfate from the water product.

[0037] Also disclosed herein is a method of separating strontium from a water product, the method including (a) forming a composition including at least (i) a water soluble sulfate salt, (ii) seed crystals composed substantially of strontium sulfate, and (iii) water; (b) adding the slurry composition to a water product, the water product including at least one soluble strontium salt and one soluble calcium salt; and (c) collecting strontium sulfate.

[0038] In certain embodiments, the seed crystals have an average particle size of about 30 to 100 microns.

[0039] The method is highly selective for precipitation of strontium over calcium wherein the ratio of soluble calcium ions:strontium ions in the water product is between about 0.010 and 1000 on a weight:weight basis. Thus, for example, in some embodiments the method of the invention provides for precipitation of up to about 80 % to 99 % of the strontium dissolved in water, wherein the collected precipitant includes equal to or less than about 0.1 wt% to 1% calcium sulfate among the strontium sulfate. In other embodiments, the methods of the invention provide for precipitation of up to 100 wt% of measurable strontium dissolved in water, wherein the precipitant includes equal to or less than about 1 to 10 wt% calcium sulfate.

[0040] Conventional methods of removing strontium salts from water products result in substantial contamination of the strontium salts with calcium salts. The strontium thus obtained

cannot be used without employing further steps to purify the strontium salts in order to provide utility of the product in industrial applications. In embodiments, the methods described herein result in collection of strontium sulfate that is sufficiently pure, upon drying residual water from the precipitate, to be used directly in such applications. For example, strontium sulfate is industrially useful as a chemical precursor to both strontium carbonate, which is useful in ceramics, and strontium nitrate, which is used in pyrotechnics to impart a red color to fireworks and flares, for example. Strontium metal is also employed in some metal alloys, for example with aluminum or magnesium, for various industrial purposes. Strontium based compounds such as strontium citrate and strontium carbonate, are also used as dietary supplements; strontium ranelate is also available in some countries as a prescription medication useful to treat osteoporosis.

[0041] It will be appreciated by one of skill that the methods of the invention are not limited solely to separation of strontium from water that also contains calcium salts. The methods of the invention are useful to preferentially precipitate any insoluble salt from water that contains a mixture of several salts with very similar solubilities. The methods of the invention therefore include (a) identifying a species of soluble salt to be separated from a starting water product; (b) forming a stable slurry including at least (i) seed crystals composed substantially of a target insoluble salt to be formed from the identified soluble salt species, (ii) a reagent capable of forming the target insoluble salt from the identified soluble salt species, and (iii) water; and (c) adding the slurry to the water product.

[0042] In certain embodiments, the seed crystals have an average particle size of about 30 to 100 microns.

[0043] In some such embodiments, the water product contains two or more soluble salts of similar solubilities, such that separation of individual salt species is not achievable simply by addition of the reagent capable of forming the insoluble salt from the soluble salt species. Stated differently, the methods of the invention are useful for addition to water products where, if the reagent capable of forming the insoluble salt from the soluble salt species is added to the water product without the seed crystals, more than one salt species will form and precipitate, resulting in a mixture of precipitated salt species. In many embodiments, such mixtures of precipitated salt species are inseparable using any practicable method. The methods of the invention result in the selective precipitation of a single targeted salt species present in a water product. In some embodiments, the methods of the invention provide for precipitation of up to about 80% to 99% by weight of the identified soluble salt species dissolved in the water, wherein the precipitant includes the target insoluble salt and equal to or less than about 0.1 to 1% by weight of another salt species. In other embodiments, the methods of the invention provide for precipitation of up to 100% by weight of the identified soluble salt species dissolved in the water product, wherein the precipitant includes equal to or less than about 1% to 10% by weight of another salt species.

[0044] Separation of Salts and Solvents

[0045] The present invention also overcomes the issues with removing contaminants such as salts (e.g., sodium chloride) from water (such as flowback water), as described in the Background. It does so, in one aspect, by using a solvent to precipitate the salt out of solution (i.e., out of the water), and by providing apparatus and methods for same. Other aspects of the present invention may include further processing to (1) remove the precipitated salt from the water and (2) remove the solvent from the water. Another aspect of the present invention is that the method and apparatus accomplish this in an efficient, low-energy, and low-cost manner.

Additionally, the salt removed may ultimately be converted into higher value products (in order to offset any cost, or portion of the cost, of the water treatment).

[0046] Thus, one aspect of the present invention involves precipitating salt out of the water using a solvent. The solvent may be an organic solvent. To that end, ethanol precipitation is a widely used technique to purify or concentrate nucleic acids. In the presence of salt (in particular, monovalent cations such as sodium ions), ethanol efficiently precipitates nucleic acids. Nucleic acids are polar, and a polar solute is very soluble in a highly polar liquid, such as water.

However, unlike salt, nucleic acids do not dissociate in water since the intramolecular forces linking nucleotides together are stronger than the intermolecular forces between the nucleic acids and water. Water forms solvation shells through dipole-dipole interactions with nucleic acids, effectively dissolving the nucleic acids in water. The Coulombic attraction force between the positively charged sodium ions and negatively charged phosphate groups in the nucleic acids is unable to overcome the strength of the dipole-dipole interactions responsible for forming the water solvation shells.

[0047] The Coulombic Force between the positively charged sodium ions and negatively charged phosphate groups depends on the dielectric constant (ϵ) of the solution, and is given by the following equation:

$$F = \frac{q_1 q_2}{4\pi\epsilon_o\epsilon_r r^2} = 8.9875 \times 10^9 \frac{q_1 q_2}{\epsilon_r r^2} \text{ newtons}$$

[0048] Adding a solvent, such as ethanol to a nucleic acid solution in water lowers the dielectric constant, since ethanol has a much lower dielectric constant than water (24 vs 80, respectively). This increases the force of attraction between the sodium ions and phosphate groups in the nucleic acids, thereby allowing the sodium ions to penetrate the water solvation shells, neutralize the phosphate groups and allowing the neutral nucleic acid salts to aggregate and precipitate out

of the solution [as described in Piškur, Jure, and Allan Rupprecht, "Aggregated DNA in ethanol solution," FEBS Letters 375, no. 3 (Nov 1995): 174-8, and Eickbush, Thomas, and Evangelos N. Moudrianakis, "The compaction of DNA helices into either continuous supercoils or folded-fiber rods and toroids," Cell 13, no. 2 (Feb 1978): 295-306, the disclosures of which are incorporated by reference herein in their entireties].

[0049] One aspect of the present invention, then, contemplates that the principles regarding the precipitation of nucleic acids via the introduction of water miscible solvents can also be used to precipitate soluble salts, which, like nucleic acids, have solvation shells formed around the ions. Thus, by lowering the dielectric constant of the solution, the Coulombic attraction between the oppositely charged ions can be increased to cause the neutral salts to precipitate out of solution. This general concept has been discussed by Alfassi, Z B, L Ata. "Separation of the system NaCl-NaBr-NaI by Solventing Out from Aqueous Solution," Separation Sci. and Technol. 18, no. 7 (1983): 593-601, incorporated by reference herein in its entirety, using data on the solubilities of several salts in a mixture of water-miscible organic solvent (MOS), wherein they found that the mass ratio (α) of the water-miscible organic solvent to the total mass of aqueous solution (the mass of water plus the mass of solvent dissolved in the water), i.e.,

$$\alpha = M_{\text{MOS}}/M_{\text{Aqueous Solution}}$$

can be correlated against the fraction of salt precipitated from a saturated brine solution, f , (i.e., the ratio of mass of salt precipitated to the mass of salt in the brine) as follows:

$$f = K * \alpha$$

where K is a precipitation constant. FIG. 2 shows a plot of f versus α for sodium chloride in water using ethylamine as an organic solvent. Ethylamine was selected in the illustrated

embodiment of FIG. 2 because it has a number of characteristics that are useful for a solvent in accordance with the principles of the present invention: It has a low heat of vaporization, is completely miscible with water in all proportions, has a low dielectric constant, and can be easily separated from water since its boiling point is quite different than water. The actual amount of salt precipitated is "f" times the mass of salt in a saturated brine solution.

[0050] Thus, one aspect of the present invention provides method of separating water soluble salts from an aqueous solution. The method may include (1) adding a solvent to a solution of salt in liquid to form an aqueous mixture, wherein the mass ratio of the solvent to the total volume of aqueous mixture is about 0.05 to 0.3; (2) separating a salt slurry from the aqueous mixture; and (3) evaporating the water miscible solvent from the salt slurry to form a concentrated salt slurry.

[0051] That method of separating water soluble salts from an aqueous solution may more specifically include – in certain embodiments -- (1) adding a water miscible solvent to a solution of salt in water to form an aqueous mixture, wherein the mass ratio of the water miscible solvent to the total volume of aqueous mixture is about 0.05 to 0.3, and wherein the water miscible solvent is characterized by (a) infinite solubility in water at 25°C; (b) a boiling point of greater than 25°C at 0.101 MPa; (c) a heat of vaporization of about 0.5 cal/g or less; and (d) no capability to form an azeotrope with water; (2) separating a salt slurry from the aqueous mixture; and (3) evaporating the water miscible solvent from the salt slurry to form a concentrated salt slurry.

[0052] As described above, once salt is precipitated out of solution, another aspect of the present invention involves removing the precipitated salt from the water. For example, in one

embodiment, the precipitated salt may be removed from the water via use of apparatus such as hydrocyclones.

[0053] A further aspect of the present invention involves removing the solvent from the water following precipitation of salt. The solvent may be removed via multiple methods. In one embodiment, the solvent may be evaporated from the water using apparatus that allows for rapid evaporation of solvent (this apparatus may also assist in removing any remaining precipitated salt). In order to minimize the energy for removal of organic solvent after separation, the use of low-boiling temperature organic solvents is contemplated.

[0054] Another aspect of the present invention provides a system for separating a solvent from an aqueous mixture. The system may include (1) a separator including: (a) a housing having at least one wall defining an interior space, an open top end, and an open bottom end, wherein the at least one wall has an inner surface and an outer surface; and (b) a contour disposed on or defined by at least a portion of the inner surface of the at least one wall; and (2) wherein a flow path for an aqueous mixture is provided by at least a portion of the contour and the inner surface of the at least one wall.

[0055] One example of a separator is a wetted wall column (such as a wetted wall static separator). While wetted wall columns have been known in the prior art, they were developed for quantitatively determining the mass transfer coefficient in laboratories, and have never been used for industrial applications, mainly due to two reasons. First, the surface area is very limited, and so they would not be considered an efficient apparatus to use at the high flow rates of water in processes such as fracking. In wetted wall columns, the contact surface area between the gas and liquid phases is basically $\pi \cdot D \cdot L$ where $\pi = 3.142$, D is the inner diameter of the tube and L is the length of the tube. Thus, even if one uses multiple tubes, the total surface area would be

limited, or the number of tubes needed to operate in an industrial use, such as at fracking flow rates, would be prohibitive. The second reason such columns have not been used in industrial applications is because the flow of liquid down the inner surface of the tube is initially laminar and then gets turbulent beyond a certain length, as the liquid flows downwards due to gravity. Because the initial part of the flow is laminar, it will have poor mass transfer characteristics. And so, this initial entrance region with laminar flow has limited applicability in industrial applications wherein high mass transfer rates are desired.

[0056] Due to these limitations, wetted wall columns have been confined to laboratories and are basically used to teach the principles of mass transfer to chemical engineering students or to quantify the mass transfer coefficient for a given gas-liquid system. However, the particular separator (e.g., wetted wall column) of the present invention is structured in a novel manner that allows for its effective use in removing solvent on the scale needed.

[0057] The wetted wall separator tube may include, in one embodiment, a hollow cylindrical pipe having a top opening, a bottom opening, an inner wall, and an outer wall, and further including a helical threaded feature disposed on at least a portion of the inner wall. In other words, in this embodiment, the helical threaded feature is the contour described above.

[0058] A further aspect of the present invention provides an evaporator apparatus including one or more wetted wall separator tubes comprising a hollow cylindrical pipe having a top opening, a bottom opening, an inner wall, and an outer wall, and including a helical threaded feature disposed on at least a portion of the inner wall. The evaporator further contemplates, in some embodiments, the use of a wetted wall separation tube in the shape of a hollow cylinder or a pipe, or it can be a hollow frustoconical shape, or a hollow cylinder or a pipe having a frustoconical portion.

[0059] In certain embodiments, the tube includes an inner wall and an outer wall, wherein a contour defined by at least a portion of the inner wall. In certain embodiments, the contour may include a helical threaded feature defined by at least a portion of the inner wall, or disposed on or in at least a portion of the inner wall. In some embodiments, the helical threads are of substantially the same dimensions throughout the portion of the inner wall where they are located; in other embodiments, helical threads of different dimensions occupy different continuous or discontinuous areas of the tube. The helical shape is easy to manufacture using a mandrel, and it also provides a gravity force for solids to slide down, instead of having obstructions that would allow the solids to build up.

[0060] In some embodiments, a series of fins defines at least a portion of the outer wall. In some embodiments, the tubes also include one or more weirs proximal to, or spanning the opening of one end of the tube. In some embodiments, the tubes also include a smooth inner wall portion proximal to one end of the tube.

[0061] In certain embodiments, one or more wetted wall separation tubes may be employed to carry out the evaporating described above. The method of evaporating the water miscible solvent from the aqueous mixture may include disposing the tube in a vertical position, flowing a salt slurry into the top opening, and allowing the slurry to proceed down the tube as aided solely by gravity. In some embodiments, a vacuum is applied to the top of the tube, or a flow of air or another gas is applied through the bottom of the tube, or both. Movement of gas upward through the tube maximizes the evaporation rate of the water-miscible solvent. In some embodiments, the tube is heated in order to mitigate the loss of heat of evaporation. In some embodiments, a significant amount of the precipitated salt follow the path of the helical thread and proceeds in a circular pattern downward through the tube, while the water/water miscible solvent blend flows

substantially vertically, such that the helices present multiple "weirs" or walls over which the water flows. This in turn causes turbulence in the vertical flow. The turbulent flow aids in the evaporation of the water miscible solvent. In some embodiments, the turbulent flow is substantially separate from the substantially laminar flow that proceeds within the helical threads. The water at the bottom of the tube is significantly free, or substantially free, of the water miscible organic solvent.

[0062] It is useful in the wetted wall separator tubes of the various aspects of the present invention that the length of the tubes, and the number thereof employed in the evaporation process, are easily selected and optimized in order to achieve the separation of the selected water miscible solvent from the slurry formed in the separation.

[0063] In some embodiments, the method further includes isolating the solid salt after evaporating the solvent from the slurry. In some embodiments, the flow within the helical threads is substantially laminar, and so the precipitated salt particles or crystals do not tend to re-mix with the water as the water miscible solvent is evaporated. Thus, the particles may be dispensed from the bottom of the tube in precipitated form. In such embodiments, the precipitated salt from the slurry added to the top of the tube is substantially recovered at the bottom of the tube. The isolating may be carried out using conventional means, such as filtration. The water that is also recovered in the isolation has significantly reduced, or even substantially reduced salt content compared to the solution of salt in water that was employed to form the aqueous mixture.

[0064] In some embodiments, the tubes may be surrounded by a source of heat to aid in the evaporation. In some embodiments, the water miscible organic solvent is collected by providing a condenser or other means of trapping the evaporated solvent that exits the top of the wetted

wall separator tubes due to the flow of gas upward through the tubes. The evaporated solvent is significantly free, or substantially free, of evaporated water, which enables the isolation of sufficiently pure solvent. The ability to collect the water miscible solvent enables the solvent to be incorporated in a closed system of solvent recycling within the overall precipitation and evaporation process.

[0065] The concept disclosed herein, namely, that of the separation of evaporated solvent from a liquid-solid slurry while maintaining the separation of the solid from the liquid, is applicable to other systems as well. For example, in wastewater remediation, anaerobic digesters are employed to digest waste products, and produce a substantial amount of ammonia gas which remains dissolved in the water. The separator tubes of the invention are useful to provide separation of the ammonia from the water, while maintaining separate flows of the solid waste from the liquid. At the end of the tube, the solid is easily isolated from the liquid and the ammonia is stripped away from the liquid.

[0066] It will be appreciated that depending on the type of gas-liquid-solid separation to be carried out, the ratio of liquid to solid in the slurry, and the flow rate selected for the slurry through the tube, the inner diameter of the tube, the helix angle of the helical thread, and the dimensions of the helical features will necessarily be different in order to effect the most efficient separation.

[0067] Thus, the present invention, in certain aspects, provides a wetted wall column from separation of solvent from a salt slurry. As was described above, wetted wall columns have been known. However, they were developed for quantitatively determining the mass transfer coefficient in laboratories, and have never been used industrially for any application.

[0068] The separator (such as a wetted wall column including a contour feature) described herein overcomes the limitations of, for example, wetted wall columns of the prior art, which could not be used on an industrial scale for such separations. This is due at least to the following non-limiting list of novel features and aspects of the separator, system, and method of the present invention:

[0069] First, in the present separator, the tubes have a projection or projections inside the tube (e.g., contour, such as a helical threaded feature) that allow the liquid flow to get turbulent right away (as opposed to laminar flow) and additionally creates a very large surface area between the turbulent liquid flow and the gas phase (which enhances the volume and rate of evaporation of solvent – and thus separation of same – from liquid). Second, the contact surface area between the gas and liquid phases is not just $\pi \cdot D \cdot L$, as in the case of laminar flow, but significantly higher as the liquid flow is broken down by the projection or projections (i.e., contour or contours) into many small flows and creates mixing of the liquid as it flows downwards by gravity. Third, by having the contour or contours inside the tube, and corrugated fins outside (as will be described in greater detail below), a large surface area is created for heat transfer into the liquid phase. Thus, the separators (e.g., wetted wall columns) of the present invention achieve not only a very high mass transfer coefficient, but a high heat transfer coefficient for effective heat transfer into the liquid phase. Fourth, a very large number of tubes can be fit inside a very small diameter shell; thus, various embodiments of the present invention contemplate and allow for a compact system. And fifth, if there are solids present in the liquid flow, the tubes will not get clogged, as in the case of plastic media packed towers. Rather, as described above, the contour or contours can be designed to allow for any solids present to proceed to an exit point of the separator.

[0070] In another embodiment, the solvent may be removed using alternate apparatus, such as a packed tower or spray tower. Alternatively, a multi-effect distillation column may be used to remove the solvent from the water.

[0071] These described methods and apparatus for solvent removal involve vaporization of the solvent. However, non-vaporization apparatus and methods may be used to remove the solvent from the water. For example, membranes may be used to remove the solvent. Such a method may include one membrane or multiple membranes. Further, such a method may include one or more of ultrafiltration membranes, nanofiltration membranes, and reverse osmosis in varying configurations.

[0072] The membranes described above may also be used to separate a precipitated salt or salts from the water, as opposed to, or in addition to, removing solvent from the water.

[0073] Thus, various aspects of the invention regarding membrane separation may include (1) using the membrane or membranes as described herein in conjunction with the solvent to concentrate salts and precipitate them in the membrane itself; (2) using the membrane systems described herein to reject solvent so that it is recaptured for reuse; and/or (3) using the solvent in solution to prevent fouling of the membrane via saturation gradient control.

[0074] There are other aspects of the present invention related to this concept of preventing fouling of a membrane or membranes. These additional aspects may use processes such as forward osmosis to prevent fouling.

[0075] These and other advantages of the application will be apparent to those of skill in the art with reference to the drawings and the detailed description below.

BRIEF DESCRIPTION OF THE DRAWINGS

[0076] The accompanying drawings, which are incorporated in and constitute a part of this specification, illustrate embodiments of the invention and, together with the general description of the invention given above and the detailed description of the embodiments given below, serve to explain the principles of the present invention.

[0077] FIG. 1 is a graph showing a plot of aqueous solubility of some typical salts as a function of temperature.

[0078] FIG. 2 is a graph showing a plot of a fraction of salt precipitated from water using various amounts of ethylamine as the solvent.

[0079] FIG. 3 is a schematic showing a nanobubble formed in the presence of a hydrophobically modified water soluble polymer, in accordance with the principles of the present invention.

[0080] FIG. 4 is a schematic and table demonstrating the principle of the Young-Laplace equation.

[0081] FIG. 5 is a chart demonstrating that smaller nanobubbles exhibit a larger area for contact with neutrally buoyant materials.

[0082] FIG. 6 is a schematic of an apparatus employed to carry out the invention.

[0083] FIG. 7 and FIG. 7A are a schematic of an embodiment of a nozzle wherein the water and air are introduced tangentially and the nanobubbles and water exit from the narrow section of the nozzle, and a cross-section of same.

[0084] FIG. 8 is a schematic representation of a hydrophobically modified polymer and its attachment to nanobubbles, for the use thereof.

[0085] FIG. 9 is a schematic representation of a hydrophobically modified polymer and its attachment to nanobubbles, for the use thereof.

[0086] FIG. 10 is a schematic view of a seed crystal of strontium sulfate and its use.

[0087] FIG. 11 is a schematic view of an apparatus in accordance with the principles of the present invention.

[0088] FIG. 12A is a schematic showing an embodiment of a method and apparatus for precipitation of salt in accordance with the principles of the present invention.

[0089] FIG. 12B is a schematic showing an embodiment of a method and apparatus for precipitation of salt in accordance with the principles of the present invention, including an underflow degassing process and system for removal of solvent, among other materials.

[0090] FIG. 12C is a schematic showing an embodiment of a method and apparatus for the precipitation of salt in accordance with the principles of the present invention, including an overflow degassing process and system for removal of solvent, among other materials.

[0091] FIGS. 13A and 13B are cross-sectional views of an embodiment of apparatus used in separating solvent from a liquid (e.g., water) in the underflow and overflow degassing processes and systems depicted in FIGS. 12B and 12C.

[0092] FIG. 14 is a schematic of another embodiment of a precipitation process and system showing the use of a multi-effect distillation column system for separation of solvent.

[0093] FIG. 15 is a schematic showing an embodiment of the precipitation process and system coupled with a membrane ultrafiltration process.

[0094] FIG. 16 is a schematic showing an embodiment of the precipitation process and system in conjunction with a membrane process and system.

[0095] FIG. 17 is a diagram showing how blockage of membrane pores may be prevented.

[0096] FIG. 18 is a schematic comparing flush cycles and membrane recovery in conventional (prior art) membranes versus membranes used in accordance with the principles of the present invention.

[0097] FIG. 19 depicts fouling in conventional (prior art) membranes.

[0098] FIG. 20 depicts the prevention of fouling in membranes in accordance with the principles of the present invention.

[0099] FIG. 21 is a schematic showing an asymmetrical membrane with salt deposition within the membrane due to salt supersaturation conditions occurring within the membrane material.

[00100] FIG. 22 is a schematic showing an asymmetrical membrane with salt crystallization occurring outside the membrane as the solvent concentration in the water increases due to selective water permeation through the membrane.

[00101] FIG. 23 is a schematic showing a system and apparatus including membranes in accordance with the principles of the present invention.

[00102] FIG. 24 shows a schematic representation of an experimental setup.

[00103] FIG. 25 is a plot of mass transfer number as a function of Reynolds Number for a water/ammonia solution in a control experiment.

[00104] FIG. 26 is a process flow diagram of one embodiment of a precipitation process and system in accordance with the principles of the present invention.

[00105] FIG. 27 is a schematic of a membrane test apparatus.

[00106] FIG. 28 is a graph showing superficial velocity of the flow within a membrane cell as a function of volumetric flow rate and spacer heights.

[00107] FIG. 29 is an exploded view of a membrane cell.

DETAILED DESCRIPTION OF THE INVENTION

[00108] One or more specific embodiments of the present invention will be described below. In an effort to provide a concise description of these embodiments, all features of an actual implementation may not be described in the specification. It should be appreciated that in the development of any such actual implementation, as in any engineering or design project, numerous implementation-specific decisions must be made to achieve the developers' specific goals, such as compliance with system-related and business-related constraints, which may vary from one implementation to another. Moreover, it should be appreciated that such a development effort might be complex and time consuming, but would nevertheless be a routine undertaking of design, fabrication, and manufacture for those of ordinary skill having the benefit of this disclosure.

[00109] Separation of Neutrally Buoyant Materials

[00110] As described above, one aspect of the present invention includes methods of separating a neutrally buoyant material or materials from a liquid. As described above, particles or phases which have a lower density than the liquid they are in will move to the surface of the liquid on their own (i.e., float), and particles or phases with densities greater than the liquid will move towards the bottom of the liquid (i.e., settle). The challenge is in removing particles or phases which have a density close to the liquid they are in -- i.e., which are neutrally buoyant or nearly neutrally buoyant -- and which otherwise on their own would take a long time to either settle or float. One method for accomplishing this is described herein. The method includes pressurizing a first liquid with a gas at a first pressure to form a pressurized liquid, and then contacting the pressurized liquid with a second liquid including a neutrally buoyant material dispersed therein. In this method, the second liquid is maintained at a second pressure that is lower than the first

pressure, and the contacting of the pressurized liquid to second liquid includes a gradient pressure change from the first pressure to the second pressure. This gradient pressure change results in the formation of nanobubbles within at least the second liquid. Such nanobubbles may have an average diameter of about 10 nm to 100 nm. The neutrally buoyant material or materials are then separated from the second liquid by association of these bubbles (such as air bubbles) with the neutrally buoyant materials (via attachment or otherwise). For example, such association may occur via hydrogen bonding between an alcohol group and a water molecule.. By virtue of the bubbles' density difference with the second liquid (e.g. water), these neutrally buoyant materials (e.g. particles or phases) are moved to the surface of the second liquid (e.g. water), where they can be skimmed off.

[00111] The formation of nanobubbles is described above as occurring within at least the second liquid. This can be accomplished by contacting the first liquid with the second liquid such that, while a portion of the first and second liquids may be combined, the nanobubbles rise through the second liquid (i.e., a portion of the second liquid that is not combined, or is yet to be combined, with the first liquid). Alternatively, or additionally, the nanobubbles may form and rise within the combined first and second liquids.

[00112] In some embodiments, the first liquid is water. And, in certain embodiments, the first liquid may include a hydrophobically modified water soluble polymer dispersed or dissolved therein. In some such embodiments, the hydrophobically modified water soluble polymer may include repeat units attributable to monomers including acrylamide, acrylate, methacrylate, or combinations thereof.

[00113] In some embodiments, the second liquid is water. In certain embodiments, the water further includes one or more solids dissolved therein. In some such embodiments, the water is

hard water, brackish water, or produced water. In some embodiments the neutrally buoyant material is oil or an oily mixture. In some embodiments, the pressure difference between the first pressure and the second pressure is about 0.1 MPa to 1 MPa. In some embodiments, the second pressure is ambient pressure, or 1 atm (0.101 MPa). The separation includes flotation of the neutrally buoyant material to the surface of the liquid. In certain embodiments, the method is effective for separating at least 90 wt% to 100 wt% of the total weight of neutrally buoyant material from the liquid, or about 93 wt% to 99.9 wt%, or about 95 wt% to 99 wt% by weight of the neutrally buoyant material from the liquid. The method further includes, in some embodiments, removing the separated neutrally buoyant material from the surface of the combined first and second liquid.

[00114] Another aspect of the invention includes methods of forming nanobubbles, the method including pressurizing the solution with a gas or mixture of gases at elevated pressure to form a pressurized solution, and reducing the pressure applied to the pressurized solution employing a gradient pressure change sufficient to form nanobubbles, the nanobubbles having an average diameter of between about 10nm and 100nm.

[00115] Another aspect of the invention includes methods of forming nanobubbles, the method including dissolving a hydrophobically modified water soluble polymer in water to form a solution, pressurizing the solution with a gas or mixture of gases at elevated pressure to form a pressurized solution, and reducing the pressure applied to the pressurized solution employing a gradient pressure change sufficient to form nanobubbles, the nanobubbles having an average diameter of between about 10nm and 100nm. In this aspect, the hydrophobically modified water soluble polymer may be associated with the nanobubbles.

[00116] Yet another aspect of the invention includes apparatus that separate and remove a neutrally buoyant material or materials from liquid. Such apparatus may include (1) a source of pressurized gas; (2) a pressurized tank situated to receive a pressurized solution of a first liquid, with the pressurized tank being connected to the source of pressurized gas; (3) an element attached to the pressurized tank and disposed to deliver the pressurized solution into a second liquid; and (4) a receiving vessel for holding a second liquid having a neutrally buoyant material dispersed therein. The element is disposed within the receiving vessel. The apparatus may further include a skimmer disposed within the receiving vessel and situated to remove a separated layer (including the neutrally buoyant material) from the surface of liquid present within the receiving vessel. The first liquid may include a hydrophobically modified water soluble polymer. The element for delivering the pressurized solution may include one or more headers and/or one or more eductors. The apparatus is useful for achieving separation and removal of neutrally buoyant materials from a liquid, employing the methods described above.

[00117] 1. *Definitions*

[00118] The following definitions relate to the discussion of separation of neutrally buoyant materials.

[00119] As used herein, the term "water" means pure water, water with some mineral content, water with some organic content, hard water, or brackish water; or combinations of these. As used herein, the term "hard water" means water having at least about 30 mg/L, in some cases as much as about 25,000 mg/L, of CaCO_3 dissolved therein. In some cases the hard water has other ionic compounds dissolved or dispersed therein, and/or other materials dissolved or dispersed therein. As used herein, the term "brackish water" means water having at least about 400 mg/L, in some cases as much as about 80,000 mg/L, of sodium, present as NaCl, dissolved therein. In

some cases the brackish water has other ionic compounds dissolved or dispersed therein, and/or other materials dissolved or dispersed therein.

[00120] As used herein, the term "produced water" means leachates, flow back, or surface water obtained as the result of, or contaminated with the byproducts of, a subsurface geological operation. In some embodiments the produced water is hard water or brackish water. In some embodiments the subsurface geological operation is hydrofracturing.

[00121] Herein, methods and apparatus will be described for the separation of materials, such as neutrally buoyant materials, from water. At times, this water may be referred to as "hard" water, or "brackish" water, or "produced" water, or another type of water (which may even include waters not subjected to subsurface geological operations, such as seawater). However, those of ordinary skill in the art will recognize that the methods and apparatus described do not have to be seen as only used with the particular type of water mentioned (whether "wastewater," "produced," "hard," "brackish," "flowback," "contaminated," etc.), but with any water from any source containing a material or materials that one wishes to remove.

[00122] As used herein, the term "neutrally buoyant material" means a solid or liquid material in a liquid (and may be a solid or liquid phase material that is phase separated in a liquid), and wherein spontaneous flotation or sinking of the material either does not occur at temperatures near 25°C, or occurs over a period of more than about 20 minutes. In some embodiments, the neutrally buoyant material has an average density that is between about 95% and 105% of the density of the surrounding liquid. The neutrally buoyant material may be, in various embodiments, dispersed, emulsified, gelled, or agglomerated within the liquid; or combinations thereof. In various embodiments, the neutrally buoyant material may be a single compound, a range of related compounds, or a heterogeneous mixture of compounds. The neutrally buoyant

material may include a single phase or multiple phases, such as a mixture of a solid and a gel, or a solid and an emulsified liquid particulate, and the like. In some embodiments, the neutrally buoyant material may be an oily mixture. It will be understood by those skilled in the art that the use of "neutrally buoyant" herein refers to materials that are neutrally buoyant, and to materials that are nearly neutrally buoyant. Further, it will be understood by those skilled in the art that a reference to a neutrally buoyant "material" in a liquid may encompass a single such material, or multiple materials.

[00123] As used herein, the term "oily mixture" means a mixture that includes one or more chemicals used in a mining operation, one or more surfactants, one or more petroleum products such as oil, emulsified petroleum products, gel-like accumulations of hydrocarbons and/or petroleum products, one or more particulates including silt, sand, or clay, or a combination of two or more thereof.

[00124] As used herein, the term "gas" means a substance that is present as a gas at temperatures at or above a temperature of 0°C to 20°C, at or above a pressure of 0.2 MPa to 1 MPa, or both. "Gas" may include both single chemical compounds or elements, or mixtures of two or more compounds or elements. Air is an example of a gas, wherein air includes a mixture of oxygen, nitrogen, carbon dioxide, and many trace compounds and elements; varying levels of water vapor are often included in air.

[00125] As used herein, the term "first liquid" means the liquid in which gas is dissolved. The gas may be dissolved by applying a first pressure of the gas to the liquid in order to dissolve some amount of gas therein. The liquid may be a single compound, such as water, or a mixture of different compounds, such as an aqueous solution of an alcohol, or a solution of a hydrophobically modified water soluble polymer in water. As used herein, the "second liquid"

means a liquid that includes a neutrally buoyant material. The second liquid may be maintained at a second pressure that is less than the first pressure.

[00126] As used herein, the term "nanobubbles" means bubbles of a gas within a liquid, wherein the bubbles having an average diameter of about 10nm to 100nm and have a density that is 90% or less of the density of the liquid.

[00127] As used herein, the term "hydrophobically modified water soluble polymer" or "HMP" means a polymer having a majority by weight of content that is dispersible or dissolvable in water, and about 0.01 wt% to about 5 wt%, based on the dry weight of the polymer, of hydrophobic moieties covalently bonded to and pendant from, incorporated within, or present at the termini of the polymer backbone. When discussing mixtures of HMP in water, the terms "soluble" or "solution" indicate either a solution or dispersion of polymer in water, as those terms of art are employed.

[00128] As used herein, the term "hydrophobic moieties" means moieties that exhibit a tendency to aggregate in water (such as pure water, hard water, and/or brackish water) and exclude water molecules. In some cases, hydrophobic moieties are nonpolar, such as linear alkane moieties. In various embodiments, hydrophobic moieties include hydrocarbon, siloxane, or fluorocarbon content or a combination thereof.

[00129] As used herein, the term "elevated pressure" means any pressure in excess of atmospheric pressure. As used herein, the term "ambient pressure" means inherent pressure upon equilibration with atmospheric pressure, that is, 0.101 MPa or 1 atm.

[00130] As used herein, the term "about" modifying, for example, the quantity of an ingredient in a composition, concentration, volume, process temperature, process time, yield, flow rate, pressure, and like values, and ranges thereof, employed in describing the embodiments of the

disclosure, refers to variation in the numerical quantity that can occur, for example, through typical measuring and handling procedures used for making compounds, compositions, concentrates or use formulations; through inadvertent error in these procedures; through differences in the manufacture, source, or purity of starting materials or ingredients used to carry out the methods, and like proximate considerations. The term "about" also encompasses amounts that differ due to aging of a formulation with a particular initial concentration or mixture, and amounts that differ due to mixing or processing a formulation with a particular initial concentration or mixture. Where modified by the term "about" the claims appended hereto include equivalents to these quantities.

[00131] As used herein, the term "optional" or "optionally" means that the subsequently described event or circumstance may occur, but need not occur, and that the description includes instances where the event or circumstance occurs and instances in which it does not.

[00132] 2. *Formation of nanobubbles*

[00133] As described above, one aspect of the present invention includes methods for separating neutrally buoyant materials from a liquid via the use of bubbles (such as air bubbles). Methods for generating small bubbles in water typically include the use of one or more of nozzles, membranes, porous tubes, venturis, and the like, wherein a mixture of air and water is mixed in a moving system. These methods rely on kinetic and/or pressure energy to divide the air flow into the water phase. However, unless a significant amount of energy is expended in a small flow of air, it is difficult to form nanobubbles. This is principally due to the fact that the air/water interface has a high surface tension, and therefore it takes considerable energy to produce a high air/water surface area, usually requiring ultrasonic or high acoustic energy dissipation. For example, in a typical nanobubble generation system, the water and the air have to be mixed and

released at considerable flow pressures in order to form small bubbles. At lesser pressures, the air bubbles formed are much bigger in size, and hence do not have the high gas-liquid surface contact area that is desirable. And, at the higher pressures required to decrease bubble size to form nanobubbles, much energy is required, which is undesirable.

[00134] For example, U.S. Patent Application Publication No. 2007/0108640, is an example of the consumption of high energy to form small bubbles. In the '640 application, Takahashi et al. claim a device which first dissolves air under pressure and then draws, using suction through a mixer unit, the dissolved air-enriched-water and a stream of air, using a nozzle. The dissolved air-enriched-water becomes supersaturated and requires less pressurization overall and thus the air forms microbubbles. In U.S. Patent Application Publication No. 2007/0119987, Vion demonstrates a three-staged compression system with a pre-release stage with modest decompression, a nozzle release stage and a transition chamber which brings the pressure to saturation, before a final outlet tube which confines cavitation and limits the reattachment of the bubble to the tube walls, thus preventing coalescence of the bubbles into a larger bubble. This also requires an undesirable amount of energy.

[00135] In certain embodiments of the invention, nanobubbles are generated by pressurizing a liquid with a gas to dissolve some portion of the gas in the liquid, then reducing the pressure to form bubbles as the dissolved gas or gaseous mixture comes out of solution. By reducing the pressure in a gradient or stepwise fashion, bubbles are formed having decreased average diameter compared to bubbles that form when pressure is changed in a single step. Thus, by carefully controlling the gradient pressure change, bubbles can be formed having an average diameter of 100 nm or less, for example between 10 nm and 100 nm. And, the methods and

apparatus described herein achieve these nanobubbles without the high expenditure of energy seen in the prior art.

[00136] Further, in some embodiments the pressurized liquid is water, the gas is air, and the water includes hydrophobically modified water soluble polymers dissolved therein. The presence of the hydrophobically modified water soluble polymers increases the solubility of air in water, and enhances the formation/stability of nanobubbles, as will be described in greater detail below.

[00137] The nanobubbles are useful in separating neutrally buoyant materials from liquids, by causing efficient flotation of the neutrally buoyant materials. The nanobubbles, which for a given volume of gas provide a higher gas-liquid interfacial area compared to conventional bubbles, provide for a high efficiency of flotation due to enhanced degree of contact between the neutrally buoyant materials and the buoyant gas bubbles.

[00138] In certain embodiments, the gaseous mixture employed to form the nanobubbles is air. Ambient or atmospheric air is comprised principally of a characteristic mixture of nitrogen and oxygen, along with various trace compounds and elements such as argon, neon, carbon dioxide, methane, and the like. Table 1 shows the amount of dry ambient air that may be dissolved in plain water at 25°C. Ambient pressure, that is, 0.10 MPa (1 atm), results in deionized-distilled water having about 0.023g of air dissolved per kilogram of plain water. And, about 5.9 times more air can be dissolved at 0.61 MPa (6 atm), compared to the amount that is dissolved at 0.10 MPa.

[00139] **Table 1. Amount of ambient air dissolved in deionized-distilled water over a range of pressures.**

Pressure (atm)	1	2	3	4	5	6
Pressure (MPa)	0.10	0.20	0.30	0.41	0.51	0.61

Amount of Air Dissolved (g/kg H ₂ O, 25°C)	0.023	0.045	0.068	0.091	0.114	0.136
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[00140] While Table 1 describes air as being the gas dissolved in the first liquid, the gas does not have to be air. Useful gases and gaseous mixtures employed to form nanobubbles using various methods include, but are not limited to, carbon dioxide (CO₂), nitrogen (N₂), helium (He), argon (Ar), air enriched with N₂, CO₂, oxygen (O₂), He, and/or Ar, and the like. It will be appreciated that various gases and gaseous mixtures have different densities at a particular temperature, and these density differences lead to varying inherent rates of flotation when nanobubbles are formed in water (or other liquid), as will be recognized by those of ordinary skill in the art.

Additionally, in some embodiments, the chemical makeup of the gas or gaseous mixture is useful for facilitating, or maximizing yield of, a desired chemical reaction or set of reactions; or, in other embodiments, the chemical makeup of the gas or gaseous mixture is useful for preventing, or minimizing yield of, one or more undesirable chemical reactions. For example, in some embodiments it may be useful to prevent oxidation of chemical species present in the water; in such embodiments, it is desirable to exclude oxygen from the gaseous mixture and provide, for example, nitrogen or carbon dioxide in place of air or another mixture containing O₂.

[00141] It has been determined by the present inventors that, in the presence of hydrophobically modified polymers (or HMP), greater amounts of air can be dissolved in water at the same pressures, as compared to the amount of air that can be dissolved without the HMP. This in turn leads to a greater yield of nanobubbles per unit volume of water when the pressure is reduced. Additionally, the present inventors have determined that the presence of HMP leads to stabilized nanobubbles. By stabilized, it is meant that the nanobubbles appear to resist consolidation and popping (especially as compared to nanobubbles that are formed without the presence of HMP,

although nanobubbles that are formed without the presence of HMP may still be useful in separating neutrally-buoyant materials and are used in certain embodiments of the present invention). While the observation of increased stability is consistent with observations of conventional bubbles in the presence of HMP, the stabilization effect is unexpected in conjunction with nanobubbles due to the large increase in air/water interfacial area. (This result is unexpected since nanobubbles have a much higher gas pressure inside the bubble than a microbubble, and hence nanobubbles are not usually stable. This will be explained in greater detail below, with reference to the Young-Laplace equation).

[00142] Further, a greater yield of nanobubbles due to the increased solubility of air in water in the presence of the HMP, is a novel feature of the method of the invention. In other words, greater amounts of air can be dissolved in water (than the amounts that can be dissolved when no HMP is present. Without being bound to any theory, it is believed this is because, by using polymers, the nanobubble walls become stronger, because the wall of each nanobubbles is formed with a bi-layer structure, as shown in FIG. 3. This structure allows a higher pressure within the nanobubble and hence larger amounts of gas can be dissolved within each nanobubble. This phenomenon also leads to greater stability of the nanobubbles within the water.

[00143] Also the size of the nanobubbles decreases because smaller bubbles can have (can withstand) a higher gas pressure inside the bubble. Typically, bubbles are formed without HMP, and thus without a bi-layer structure. As a result, the bubbles are much larger, since they can only withstand a lower air pressure inside and hence smaller bubbles would burst and combine to form larger air bubbles. However, with stronger bubble walls due to the bi-layer structure achieved via the present invention, smaller bubbles are formed, since they can withstand higher

air pressures. The increase in gas pressure with bubble size is given by the Young-Laplace equation, shown in FIG. 4.

[00144] Not only do the methods and other aspects of the present invention allow for smaller bubbles to form (and be stable), but these bubbles also exhibit a greater ability to associate with and remove neutrally-buoyant materials. Smaller nanobubbles exhibit a much larger area of contact with the near neutrally buoyant emulsified oil droplets and gels, as shown in FIG. 5. Additionally, the inventors have observed that the stabilized nanobubbles are more effective at flotation of neutrally buoyant materials in liquids than nanobubbles formed without HMP, due to the ability of the HMP to associate with the neutrally buoyant material to be separated. And, HMP leads to nanobubbles having a greater stability than nanobubbles not associated with HMP.

[00145] Nanobubbles are by nature slightly hydrophobic due to their surface curvature, so they would not attach as well to hydrophobic molecules, such as droplets of oil. Gels used in fracking are hydrophilic, and they will not be removed as well also, since the nanobubbles are not highly hydrophilic either. The HMP, however, helps to increase the hydrophobicity of the nanobubbles, as well as increase their capacity to reach these near neutrally buoyant emulsified oil droplets and gels. Further, nanobubbles with large molecular chains sticking out have a much larger surface area of sweep within the water than just nanobubbles rising through water.

[00146] In various embodiments, useful HMP may include any water soluble polymer, wherein the polymer has a minor amount of covalently attached hydrophobic moieties. In various embodiments, the polymer may be synthetic, naturally occurring, or a synthetically modified naturally occurring polymer. In various embodiments, the polymer is linear, branched, hyperbranched, or dendritic. In embodiments, the hydrophobic moieties are bonded to the HMP in amounts of about 0.01 wt% to 5 wt% based on the dry weight of the HMP, or about 0.05 wt%

to 2 wt% based on the dry weight of the HMP, or about 0.1 wt% to 1 wt% based on the dry weight of the HMP. In some embodiments, the hydrophobic moiety is present within the polymer backbone, whether randomly dispersed or present in the form of blocks. In other embodiments, the hydrophobic moiety is an endgroup, and is present substantially only at the termini of a polymer; thus, in such embodiments where a linear polymer is employed, a maximum of two hydrophobic moieties are present per polymer chain. In other such embodiments, branched, hyperbranched, or dendritic polymers are capable of having more than two such terminal hydrophobic moieties.

[00147] In some embodiments, the hydrophobic moieties are pendant to the polymer backbone. Pendant moieties are either grafted to the polymer backbone, or present as the result of copolymerization. Such grafting or copolymerization is, in various embodiments, random or blocky. In some such embodiments, pendant hydrophobic moieties are incorporated into the polymer via copolymerization at about 0.01 mole% to 1 mole% of the repeat units of the polymer. Pendant hydrophobic moieties are easily incorporated, for example, by copolymerization of water soluble and hydrophobic vinyl monomers. In embodiments, acrylic acid, methacrylic acid, acrylate salts, or methacrylate salts (collectively, acrylates); and acrylamide and methacrylamide (collectively, acrylamides) are water soluble monomers. These monomers are suitably copolymerized with acrylate esters, methacrylate esters, or N-functional acrylamide, N,N-difunctional acrylamide, N-functional methacrylamide, or N,N-difunctional methacrylamide monomers having hydrophobic moieties present as the ester or N-functional group(s). In such embodiments, examples of useful hydrophobic moieties include linear, cyclic, or branched alkyl, aryl, or alkaryl moieties having between 6 and 24 carbons; perfluorinated or partially fluorinated versions of these moieties, and fluorinated alkyl groups having one or more

heteroatoms, including perfluoroalkylsulfonamidoalkyl moieties; dialkylsiloxane, diarylsiloxane, or alkylarylsiloxane moieties having between 3 and 10 siloxane repeat units; and the like. In some embodiments, dodecyl, perfluorooctyl, or dimethyltrisiloxane moieties are useful and effective hydrophobic groups. In some embodiments, an HMP is synthesized from acrylamide and 1 mole% or less of dodecylacrylamide, N, N-dihexylacrylamide, or dodecylmethacrylate, or dodecylacrylate.

[00148] Techniques employed to achieve copolymerization of acrylate or acrylamide based HMPs are well documented in the literature, and thus are well known to those of ordinary skill in the relevant art. Typically, emulsion polymerization in a bulk water phase is accomplished using free radical initiators activated by heat or UV irradiation at a specific range of wavelengths; redox polymerization is also conveniently accomplished in some embodiments. Representative examples of suitable emulsion polymerization methodology are described in Schulz, D. and Glass, J., eds., *Polymers as Rheology Modifiers*, ©1991 American Chemical Society, p. 191; and Glass, J., ed., *Polymers in Aqueous Media*, © 1989 American Chemical Society, pp. 399-410 (incorporated by reference herein in their entireties). One of skill will readily understand how to vary these methods to form high polymers using acrylate or acrylamide monomers in emulsion polymerization schemes.

[00149] Acrylamide or methacrylamide based HMP are, in some embodiments, partially hydrolyzed to form some of the corresponding carboxylate salt after synthesis; copolymerization of acrylate salts with acrylamide or methacrylamide results in the same end product. In embodiments where the anticipated end use of the HMP is in water having significant amounts of electrolytes (including NaCl), acrylamide based copolymers are particularly useful, because

acrylamides are less sensitive to the presence of electrolytes in water than are acrylate salts. In such embodiments, it is also desirable to avoid hydrolysis of the acrylamide moieties.

[00150] Some representative examples of other useful HMP include hydrophobically modified cellulose, hydrophobically modified hydroxyethylcellulose, hydrophobically modified chitosan, ethoxylated urethane polymers having hydrophobic endgroups, hydrophobically modified starch polymers such as starches from plants including potatoes, corn, and the like. Also useful as alternatives to hydrophobically modified polymers are naturally occurring polysaccharide thickeners such as xanthan gum, locust bean gum, guar gum, and the like. Where hydrophobically modified, examples of useful hydrophobic moieties for modification of polymers include linear, cyclic, or branched alkyl, aryl, or alkaryl moieties having between 6 and 24 carbons; perfluorinated or partially fluorinated versions of these moieties, and fluorinated alkyl groups having one or more heteroatoms, including perfluoroalkylsulfonamidoalkyl moieties; dialkylsiloxane, diarylsiloxane, or alkylarylsiloxane moieties having between 3 and 10 siloxane repeat units; and the like.

[00151] Effective amounts of HMP employed in water will vary depending on the type of HMP and, to some extent, the gas or gaseous mixture employed. Optimization of HMP amount will be readily deduced by one of skill by observing the amount of the desired gas or gaseous mixture that is entrained in the water at a selected pressure. In some embodiments, the optimization centers around entraining the maximum amount of gas into the water. In other embodiments, the optimization is a balance of entraining more gas without using large amounts of polymer that can act as a contaminant when employed in an application. In some embodiments, the amount of HMP employed is about 0.001 wt% to 3 wt%, or about 0.01 wt% to 1 wt% in water. In some embodiments where the gaseous mixture is air and the HMP is a copolymer of acrylamide and a

hydrophobically functionalized acrylate ester or N-functional acrylamide, 0.01 wt% to 0.5 wt% HMP in water, or 0.02 wt% to 0.1 wt% HMP in water is employed to facilitate.

[00152] Regarding examples of methods to be used for the optimization of the amount of HMP useful for a particular application: The amount of HMP may be based on the amount of neutrally buoyant contaminant (e.g., gel or emulsified oil) that is present in the second liquid (and which is measureable). In this embodiment, then, the amount of dissolved gas that is converted into nanobubbles is based on the amount of emulsified oil/gel. Since the solubility of air in water increases with pressure, the water flow needed to dissolve the required amount of air that is needed to be formed into nanobubbles can be determined. For example, the saturation concentration of air in water at 1 atm and 25 deg C is 0.000219 lbs of air/gallon of water. If the pressure used to dissolve more air at the higher pressure is 100 psig or 114.7 psia, then the theoretical air released when the pressure of water saturated with air at 114.7 psia is decreased to 14.7 psia or 1 atm will be equal to $0.000219 \text{ lbs of air/gallon of water} \times ((114.7/14.7) - 1) = 0.0015 \text{ lbs of air/gallon water}$. If the amount of air needed to be converted to nanobubbles is 0.0105 lbs of air/min, then the flow of water needed is $0.0105/0.0015 = 7 \text{ gallons per minute}$. Further, one does not want to use pressure above the maximum pressure that can be achieved by typical air compressors, which is about 100 psig.

[00153] The means of dissolving or dispersing the HMP in water are widely described in the literature well known in the art; for commercially obtained HMP, directions specific to the polymer are often provided to enable one of skill to dissolve or disperse the polymer satisfactorily. For example, for some HMP, it is necessary to use chilled water to obtain a fully dispersed polymer when starting from a dried product. In some embodiments, HMP are ideally used directly from the emulsion employed to facilitate the polymerization; this avoids what can

be a time consuming dissolution process and instead amounts to a simple dilution. In some embodiments, mixing, tumbling, shaking, or sonication is useful to facilitate dispersion. Again, the methods for dispersion may be dependent on the selected HMP, and are well known to those skilled in the art.

[00154] The solution of HMP in the first liquid is, in some embodiments, a solution of HMP in water. In other embodiments, the first liquid is a mixture of water and a second liquid. In still other embodiments, the first liquid is a liquid or mixture of liquids that does not include water.

[00155] The amount of gas pressure applied to the first liquid is not particularly limited and is selected by one of skill based on the targeted application, equipment employed, and the like. The greater the pressure, the greater the amount of gas dissolved in the first liquid; and the greater the number of nanobubbles that can be achieved upon release of the pressure. In many embodiments, the amount of pressure employed is limited by equipment capabilities or safety considerations. For example, for safety considerations, the maximum pressure may be limited to below 100 psia which is a typical maximum pressure for certain air compressors.

[00156] The amount of time required to achieve a saturated or nearly saturated solution of the selected gas or gaseous mixture is, in practicality, a function of the ratio of surface area to volume for the first liquid during exposure to the pressurized gas. For example, in some embodiments, the first liquid is placed in a tank or vessel, the vessel is sealed, and pressurized gas is applied to the vessel. In such embodiments, pressure is typically applied for a period of time reach the maximum amount of dissolved gas at the selected pressure, as is easily determined by one of skill using conventional techniques. In some such embodiments, the first liquid is stirred or agitated to increase the rate of dissolution. In still other embodiments, the first liquid is delivered through a fine spray nozzle into a chamber in which compressed gas is stored. In such

embodiments, the maximum dissolution of gas is typically entrained during the spraying. One of skill will appreciate that in any such embodiment, the ratio of surface area to volume ratio of the first liquid during exposure to the pressurized gas will determine the amount of time required to reach a saturated solution of the gas in the first liquid; and that the amount of time required is easily determined for a given apparatus, makeup of the first liquid, etc.

[00157] Such techniques to dissolve a gas in the first liquid are also useful for dissolving gases in various types of liquids and mixtures employed as the first liquid. The liquid is, in various embodiments, water, an organic liquid having between 1 and 8 carbons, or an aqueous solution of water and a water soluble organic liquid. Examples of suitable water soluble organic liquids include alcohols, such as methanol, ethanol, or propanol; amines such as ethylamine, diethanolamine, triethanolamine, and the like; ketones, such as acetone or methyl ethyl ketone; aldehydes, such as formaldehyde, acetaldehyde, and the like; and other organic compounds; or mixtures thereof. In many embodiments, the first liquid is water or water with an HMP dissolved or dispersed therein.

[00158] 3. *Release of nanobubbles for flotation*

[00159] Once the selected amount of gas or gaseous mixture is entrained in the first liquid, the pressurized first liquid, or pressurized solution, is deployed in one or more applications where nanobubbles are released. Upon gradient depressurization of the pressurized solution, nanobubbles will form. In many embodiments, depressurization is desirably carried out during delivery of the first liquid to a second liquid, where the nanobubbles will form and achieve association with, and thereby flotation of, neutrally buoyant materials (e.g. debris, oily dispersed materials, and the like). In such applications, it will be appreciated that the pressurized solution is effectively a nanobubble "concentrate" wherein the amount of bubbles formed upon release of

pressure is suitable for flotation of neutrally buoyant materials in a much larger volume of liquid (i.e., the second liquid). Thus, one aspect of a method of the invention is the contemporaneous gradient or stepwise release of pressure, and dilution in a vessel containing a second liquid and neutrally buoyant material. However, the methods of the invention are not limited to contemporaneous release of pressure and dilution; thus, in some embodiments, gradient release of pressure and dilution are suitably carried out in separate steps (in those other embodiments then, nanobubbles are first formed and then introduced into a second liquid, rather than being formed during contact within the second liquid).

[00160] The gradient release of pressure of the pressurized solution results in the formation of nanobubbles. The nanobubbles are formed in conjunction with contact of the pressurized solution with a second liquid that is maintained at a lower pressure than the pressurized solution, wherein the gradient pressure change results in the first liquid contacting the second liquid and reaching a final pressure that is the pressure of the second liquid. In embodiments, the gradient release of pressure is accomplished using conventional equipment designs that provide control of pressure release. For example, in embodiments, the gradient release of pressure is accomplished by delivering the first liquid into a larger vessel filled with the second liquid, wherein the delivery is via Venturi eductor, that is, a converging-diverging nozzle that converts the pressure energy to velocity energy, wherein the low pressure zone formed by the velocity energy of the first liquid serves to pull in an amount of the second liquid, and the combined liquids are ejected from the eductor into the vessel containing the second liquid. In other embodiments, the first liquid is introduced into a series of chambers, wherein each chamber has a slightly lower pressure therein, and the first liquid is eventually released into the vessel containing the second liquid.

[00161] As described above, the nanobubbles may be of a particular size, or within a range of size. The size of the nanobubbles depends on at least two factors: (1) gradient release of pressure, which ensures that smaller bubbles form ; and (2) increased nanobubble stability, which depends on the bubble wall being able to withstand the higher air pressure inside the nanobubble. If the liquid pressure is released abruptly, then larger bubbles would form, since the bubbles would grow to accommodate the air that is coming out of solution due to pressure. And, if there are no HMPs or surfactants, smaller bubbles form, which then burst and coalesce into larger bubbles.

[00162] In embodiments, the second liquid is maintained at ambient pressure, that is, 0.101 MPa or 1 atm. In other embodiments, the second liquid is maintained at a pressure that is higher or lower than ambient pressure. The second liquid must be maintained at a pressure that is lower than the pressure applied to the pressurized solution, wherein the pressure differential is sufficient to result in the formation of nanobubbles when a gradient pressure release is carried out and the first liquid is contacted with the second liquid. In embodiments, the pressure differential between the pressurized solution and the second liquid is at least 0.1 MPa, such as between 0.1 MPa and 1 MPa, or between 0.3 MPa and 0.8 MPa.

[00163] In certain embodiments, the dilution of the pressurized solution is selected based on the nature of second liquid, the type and amount of the neutrally buoyant material to be addressed, and the amount of pressure applied to the first liquid to form the pressurized solution. Where the first liquid is water containing an HMP and the second liquid is produced water that is hard water or brackish water containing an oily mixture as the neutrally buoyant material, the dilution factor for HMP/water mixtures described above, pressurized at about 0.6 MPa, the dilution factor ranges from about 30:1 to 5:1 vol:vol [water]: [pressurized HMP/water], or about 30:1 to 10:1

vol:vol [water]: [pressurized HMP/water], or about 25:1 to 10:1 vol:vol [water]: [pressurized HMP/water].

[00164] Each of these processes, i.e. pressurizing the first liquid, dilution of the first liquid with the second liquid, and pressure release of the pressurized solution are, in various embodiments, accomplished in continuous feed or in single batch mode.

[00165] 4. *Apparatus and method useful for separation of neutrally buoyant materials*

[00166] FIG. 6 shows one embodiment of an apparatus 800 of the invention. The apparatus enables the formation of nanobubbles and use thereof to separate a neutrally buoyant material from a liquid. In some embodiments, the liquid is water. In some such embodiments, the water is produced water. In some embodiments the neutrally buoyant material is an oily mixture.

[00167] In the embodiment of the apparatus 800 shown in FIG. 6, a holding tank 802 contains a solution or dispersion of HMP in water 804. The HMP/water solution 804 is pumped via pump 806 via path 808 to spray head 810, and is sprayed by spray head 810 into pressurized tank 812. Pressurized tank 812 is maintained at elevated pressure by pressurized gas source 814.

Pressurized gas source 814 contains a gas or a mixture of gases that is selected by the user, wherein the gas or mixture of gases is present at elevated pressure. One example of an apparatus that comprise the pressurized gas source 814 is an air compressor. In some embodiments, the pressurized gas source 814 is in equilibrium with the pressure in the pressurized tank 812. In other embodiments, the pressurized gas source 814 is maintained at a higher pressure than pressurized tank 812, and the pressure is stepped down by a pressure regulator, valve, or other suitable apparatus (not shown) disposed between pressurized gas source 814 and pressurized tank 812. In embodiments, the elevated pressure range for pressurized tank 812 is about 0.102 MPa (1.01 atm) to 2.03 MPa (20 atm), or about 0.203 MPa (2 atm) to 1.52 MPa (15 atm), or

about 0.507 MPa (5 atm) to 1.01 MPa (10 atm). A pressure range for the pressurized tank 812 to operate may be 14.7 to 200 psia. At the higher operating pressures, significant amounts of air can be dissolved into the water. The pressurized tank 812 also serves as a holding tank for a solution or dispersion of HMP in water 804 that is saturated with gas from pressurized gas source 814.

[00168] The pressurized HMP/water solution 804 flows from the pressurized tank 812 into a header 816 having eductors 818. As is known to those of ordinary skill in the art, an educator is a type of pump that uses the Venturi effect of a converging-diverging nozzle to convert the pressure energy of a motive fluid to velocity energy which creates a low pressure zone that draws in and entrains a suction fluid. An example of a nozzle that can be used to make the nanobubbles is shown in FIG. 7 and FIG. 7A. After passing through the throat of the injector, the mixed fluid expands and the velocity is reduced which results in recompressing the mixed fluids by converting velocity energy back into pressure energy. Referring back to FIG. 6, the header 816 and eductors 818 are disposed within a vessel 820, and may be (in certain embodiments) further situated at or near the bottom 822 thereof. A pump 824 pumps a liquid 826 into the vessel 820 via an inlet 828 situated near the bottom 822 of vessel 820. The liquid may be water containing a neutrally buoyant material that one wishes to separate and remove from the water. During operation of the apparatus 800, header 816 and eductors 818 are fully immersed in the liquid. Vessel 820 may also have a baffle 830 partitioning vessel 820 into first and second compartments 832, 834 such that the liquid entering vessel 820 enters vessel 820 via first compartment 832 and must flow over baffle 830 to reach second compartment 834. Header 816 passes through baffle 830 and is in fluid connection with eductors 818 and pressurized tank 812.

[00169] FIG. 7 and FIG. 7A show one implementation of the above principle of achieving a reduced pressure gradient is to introduce gas and liquid simultaneously and tangentially into a

conical cylinder, as shown in FIG. 7 and FIG. 7A, which generates a high speed rotational flow. The nozzle 850 includes a conical section length 852 and a base width 854 and a nozzle exit width 856. The centrifugal force forces the liquid in the outer circle of the flow rotation, gas and liquid flows in the concentric space between the outside liquid flow and the inner gas core. The friction between the swirling layers creates the nanobubbles of the gas in the liquid, as the gas-liquid mixture flows out of the nozzle.

[00170] Experiments were conducted with a conical test section, shown in FIG. 7 and FIG. 7A. The flow of water and air were measured by rotameters. The volumetric fluxes of the water and gas are determined as follows:

[00171] $[JL] = Q_L/A$ and $[JG] = Q_G/A$ where Q_L and Q_G are liquid and gas flowrates in m^3/s , and A is the cross-sectional area of the cone in the entrance region of the nozzle, i.e., $A = \pi D_o^2/4$, where D_o is the diameter of the entrance cone. The liquid volumetric flux, $[JL]$ is kept below 0.2 m/s and the gas volumetric flux $[JG]$ is kept below 0.03 m/s. In this regime of gas-liquid flow, the gas forms nanobubbles due to the gradual loss of pressure, as the rotational flow moves from the entrance region to the outlet part of the nozzle.

[00172] Referring back to FIG. 6, vessel 820 may be maintained at ambient pressure. As liquid 826 is pumped by pump 824 into inlet 828 near the bottom 822 of vessel 820, the HMP/water solution 804, under pressure and containing dissolved gas from pressurized gas source 814, is released by eductors 818 into vessel 820 at or near the bottom 822 thereof. As the pressure within pressurized tank 812 and header 816 is released, nanobubbles form. As the HMP/water solution 804 is forced out of each eductor 818 by the pressure from pressurized tank 812, it draws in a portion of liquid 826 from the vessel 820 and creates a well-mixed stream that flows

out from the top of each eductor 818. The mixing contributes to a well-dispersed stream of HMP nanobubbles that flow from eductors 818 and float generally toward skimmer 836.

[00173] As the nanobubbles progress from eductors 818 toward skimmer 836, they interact with neutrally buoyant material present in the liquid 826 pumped into vessel 820, and cause flotation of the neutrally buoyant material (as described above), thereby separating the neutrally buoyant material from the liquid. The decrease of pressure of the HMP/water solution 804 to almost atmospheric pressure, coupled with good mixing achieved by the eductor 818, creates a swarm or cloud of nanobubbles within vessel 820. The nanobubbles, having higher surface area than larger bubbles, act to separate even very finely divided and dispersed neutrally buoyant materials from the liquid in vessel 820. The nanobubbles in the presence of HMP further exhibit enhanced ability to separate such neutrally buoyant material from liquids, as described above.

[00174] Also disposed within vessel 820 is skimmer 836, as mentioned above. Skimmer 836 is situated in a floating and variable level configuration, in contact with the surface of the liquid within the vessel 820 and is connected to collection vessel 838. Skimmer 836 contacts the surface of the liquid in vessel 820 and suctions a surface layer 840 therefrom. The suctioned surface layer 840 is deposited into collection vessel 838. Suction is provided by a vacuum pump or other suction means 842, which is attached to collection vessel 838. Skimmer 836 removes surface layers from both first and second compartments 832, 834 of vessel 820. Liquid from compartment 834 may be removed from the vessel 820 by pump 844 through outlet 846. Pump 844 is, in some embodiments of the invention, connected to one or more additional apparatuses (not shown). In some such embodiments, the one or more apparatuses are designed and situated for further purification or processing of the liquid. In other embodiments, liquid is removed from compartment 834 by pump 844 through outlet 846 to a tank or other holding apparatus (not

shown). Additionally, some treated water is pumped by pump 848 into the spray head 810, located in the pressurized tank 822, and air dissolves in the water at the higher pressure.

[00175] In some embodiments of apparatus 800 or alternative embodiments thereof as described herein, the liquid pumped into vessel 820 by pump 824 is produced water. In some such embodiments, the neutrally buoyant material is an oily mixture. In some embodiments, the liquid removed by pump 844 is brackish water. In some embodiments, the liquid removed by pump 844 is hard water.

[00176] Thus, FIG. 6 shows the implementation of an air nanobubble embodiment using hydrophobically modified polymers to enhance the attachment of the nanobubbles to the emulsified oil droplets and to the floating oil layer (or other neutrally buoyant material), to enhance the density difference between the oil/gel/clay/sand/silt sludge and the water, containing a high concentration of dissolved salts.

[00177] FIG. 6 shows one embodiment of an apparatus of the invention. Alternative embodiments are envisioned, as will be readily understood by one of skill. For example, in some embodiments, the HMP/water solution or dispersion in holding tank 802 is connected directly to pressurized gas source 814, and there is no spray head 810 or separate pressurized tank 812. Instead, in such embodiments, holding tank 802 is also a pressurized tank, and the pressurized gas is allowed to saturate the HMP/water solution or dispersion 804 as it resides in the tank 802. In some such embodiments, pressurized gas source 814 is connected to holding tank 802 at the bottom thereof, and the gas within pressurized gas source 814 is bubbled through the HMP/water solution or dispersion in holding tank 802. In other such embodiments, holding tank 802 may have a means of agitation, such as an impeller or other stirring mechanism, and the contents of the tank are stirred to increase the rate of gas saturation of the HMP/water solution or dispersion.

[00178] In the illustrated embodiment of FIG. 6, there are two compartments 832, 834 in vessel 820. In other embodiments of the apparatuses of the invention, three, four, five, or more compartments are advantageously employed, wherein each compartment is a further division of vessel 820 separated by a baffle 830 and wherein each compartment has at least one eductor 818 or other means present to dispense nanobubbles, and a skimming apparatus such as skimmer 836. Addition of more compartments in this manner causes additional separation steps, which in turn results in a greater yield of separated neutrally buoyant materials from the liquid provided to vessel 820.

[00179] Further, in the illustrated embodiment of FIG. 6, there are three eductors 818 in each compartment 832, 834. It will be appreciated that in various embodiments of the apparatuses of the invention, the eductors 818 are present in varying numbers and locations as dictated by the size and dimensions of the vessel 820, shape of header 816, volume of liquid having neutrally buoyant material, and type and amount of neutrally buoyant material encountered in the application. However, at least one eductor 818 is required. Where only one eductor 818 is present, the eductor 818 may be disposed within compartment 832.

[00180] In some embodiments, instead of eductors 818 as shown in apparatus 800, an alternative means of introducing pressurized HMP/water solution into vessel 820 is employed. For example, spray heads, needle injectors, and the like are employed in some embodiments.

[00181] Before the water is sprayed as described above and shown in FIG. 6, a hydrophobically modified polymer may be added in small amounts to the water using pump 806 and this polymer liquid is stored in vessel 802. This hydrophobically modified polymer, which is soluble in water, goes into solution, and when the water is bubbled through the eductors in vessel 820,

nanobubbles of air are created due to decreased pressure, and the hydrophobically modified polymer spontaneously partitions at the air-water interface.

[00182] This hydrophobically modified polymer is basically a hydrophilic backbone with side chains that are hydrophobic. Examples of hydrophobically modified polymers include acrylamide copolymers, partially hydrolyzed polyacrylamide (HPAM) or biopolymers such as xanthan or guar gum. Typically, these polymers are water soluble polymers that contain a small number (less than 1 mole %) of hydrophobic groups attached directly to the polymer backbone. FIG. 8 shows a schematic of a hydrophobically modified polymer (dotted line) 860 with hydrophobic groups 862 (shown as dark line segments), attached directly to the polymer backbone. Referring to FIG. 8 and FIG. 9, when these hydrophobically modified polymers are present in water which has air bubbles, these polymers partition at the air/water interface of each bubble spontaneously, with some hydrophobic groups exposed to the water, as shown in FIG. 8 and FIG. 9. These hydrophobic groups are instrumental in increasing the hydrophobicity of the nanobubbles and allowing these nanobubbles of air to attach to oil droplets 864 emulsified in the water and to the oil layer (as the oil is likewise hydrophobic), as also shown in FIG. 8 and FIG. 9. By allowing this large number of nanobubbles into the oil, the density difference between the oil and water is increased substantially allowing the oil to separate from the water faster than otherwise.

[00183] Additional equipment added to the apparatus to facilitate continuous or batch operation thereof include various gauges, valves, balances, flow regulators, pressure regulators, pumps, controlling and automation equipment including hardware, firmware, and software employed to monitor and control the apparatus, baffles, stratified flow features, weirs, level sensors, temperature sensors, and the like. For example, in some embodiments an apparatus similar to

that shown in FIG. 6 will include a source of hydrophobically modified polymer in a substantially dry state or a highly concentrated state in water, a source of pure water, and means to mix the HMP and water in a selected ratio prior to introduction to holding tank 802. In some embodiments where the liquid from the outlet 846 is water, a similar mixing setup will include a fluid connection between outlet 846 and the mixing apparatus wherein a portion of the liquid exiting vessel 820 is partitioned from the outlet and directed into holding tank 802 to be blended with the HMP. Such a setup negates the need for an additional source of pure water.

[00184] 5. *Results of separating neutrally buoyant materials*

[00185] Association of and/or interaction of the neutrally buoyant materials with the nanobubbles decreases the overall density of the neutrally buoyant materials attached to nanobubbles (i.e., the combined material/nanobubble density) and allows the neutrally buoyant materials to separate from the liquid by floating toward the surface of the liquid at a higher rate than without the nanobubbles. Combining the use of nanobubbles with HMP allows the neutrally buoyant materials to rapidly rise through the liquid to the surface where they can be easily skimmed off using conventional skimming operations. Due to the large number of nanobubbles and large gas/liquid interfacial area imparted by the use of nanobubbles, it is a feature of the method of the invention that the resulting increased interaction of bubble interfacial area with finely dispersed, unagglomerated phase separated neutrally buoyant materials are contacted with the nanobubbles in sufficient amounts to effectively and efficiently separate even these materials from the liquid. Thus, for example, finely divided emulsified or gelled oily materials dispersed in produced water from a mining operation are effectively separated from produced water by use of the methods of the invention.

[00186] Without wishing to be limited by theory, it is believed that the presence of HMP in the water used to form the nanobubbles enhances the interaction of the nanobubbles with the phase separated neutrally buoyant materials to result in a greater yield of total removed phase separated neutrally buoyant materials than the observed degree of separation observed when nanobubbles are formed from deionized-distilled water or solutions of water without HMP. Additionally, judicious selection of HMP structure and chemistry provides an enhanced means to remove neutrally buoyant materials from hard water or brackish water. For example, as described above, where the liquid containing neutrally buoyant materials is water having electrolytes dissolved therein, such as brackish water, it is desirable to select a nonionic HMP such as a polyacrylamide based HMP to avoid the collapse of the HMP from solution when contacted with the electrolyte-bearing water having neutrally buoyant materials dispersed therein.

[00187] Where HMP facilitated nanobubbles are employed, the yield of separated neutrally buoyant materials is greater than the yield realized by using conventional bubbles or even nanobubbles formed in the absence of HMP. Yield of separated neutrally buoyant materials is calculated as the weight percent of the total weight of neutrally buoyant materials from the liquid that is present at the surface of the liquid in a sufficiently stable separated layer for removal by conventional apparatuses such as skimmers. In various embodiments, between 75% by weight and 100% by weight of the total amount by weight of neutrally buoyant materials are separated from liquid using the HMP facilitated nanobubble flotation methods described above. In some embodiments where the liquid is produced water and the neutrally buoyant material is an oily mixture, between about 80 wt% and 100 wt% of the oily mixture present in the produced water is separated, or between about 90 wt% and 99.9 wt% of the oily mixture present in the produced water is separated, or between about 95 wt% and 99 wt% of the oily mixture present in the

produced water is separated, or between about 97 wt% and 99 wt% of the oily mixture present in the produced water is separated, or between about 97 wt% and 99.9 wt% of the oily mixture present in the produced water is separated.

[00188]6. *Application to produced water from hydrofracturing*

[00189] In some embodiments, nanobubble facilitated separation is employed as a first step in the remediation of produced water from mining operations. In some such embodiments, the produced water contains a significant amount of dissolved ferrous ions, for example about 2 mg/mL to 3000 mg/mL of ferrous ions. Ferrous ions are undesirable in water due to staining (when ferric salts form during subsequent treatment or use) and fouling of water remediation apparatuses such as ion exchange resins and filtration membranes. Ferrous ions are soluble in water and are not phase separated.

[00190] In such embodiments, an additional benefit of the methods and apparatuses of the invention is realized by employing air, air enriched with oxygen, or another gas mixture including oxygen, to pressurize the HMP/water solution. By employing an oxygen-containing gas to pressurize the HMP/water solution and subsequently releasing the pressurized solution into the produced water as described above, the oxygen reacts with the ferrous ions in the water to form ferric salts, which are insoluble in water. Because of the large amount of gas-water interface area provided by the nanobubbles, oxidation is efficient and in embodiments even up to 3000 mg/mL of ferrous ions are converted to insoluble ferric salts during the separation of oily mixtures from the water. Further, the nanobubbles also cause flotation of the ferric salts as they form, effectively separating them from the produced water. This is a benefit in the overall remediation of water, and is a further benefit in embodiments where further water remediation equipment is located downstream from the oily mixture separation apparatus, since removal of

the ferric salts avoids fouling of filtration membranes and ion exchange resins and deposition of ferric salts on other pipes and equipment.

[00191] In embodiments, between about 75 wt% and 100 wt% of the ferrous ions present in the produced water are removed by employing the apparatuses and methods described above, wherein the gas employed to form the nanobubbles contains at least about 20% oxygen. In other embodiments, between about 85 wt% and 99 wt% of the ferrous ions present in the produced water are removed, or about 90 wt% to 98 wt% of the ferrous ions present in produced water are removed. Enriching the oxygen content of air, for example, or increasing the amount of nanobubbles dispensed in a given volume of produced water – for example by adding more eductors 818 to apparatus 800 of FIG. 6 or by adding additional compartments to the vessel 820 as discussed above - are methods that will increase the amount of oxidation and separation of ferrous ions from water as will be readily appreciated by one of skill.

[00192] Selective Separation of an Element

[00193] Another aspect of the present invention provides a composition that facilitates the effective separation of an element, such as strontium, from water. More specifically, disclosed herein is a composition including (a) a water soluble sulfate salt; (b) seed crystals composed substantially only of strontium sulfate; and (c) water.

[00194] In certain embodiments, the seed crystals have an average particle size of about 30 to 100 microns. In certain embodiments, the composition is a slurry of the crystals in a water soluble sulfate salt solution. In certain embodiments, the composition includes substantially only the recited substituents, except that in any of the disclosed embodiments herein, the water soluble sulfate salt may include one or more water soluble sulfate salts; that is, the water soluble sulfate salt includes mixtures of two or more water soluble sulfate salts.

[00195] When the composition of the invention is added to a water product, wherein the water product is a solution of water having at least both water soluble strontium salts and water soluble calcium salts dissolved therein, the composition results in the preferential precipitation of strontium sulfate from the water product. Though not being bound by any theory, and with reference to FIG. 10, it is believed that this process works as follows:

[00196] Normally, when a chemical crystallizes out of solution, it does so because the concentration of the chemical in the solution exceeds the solubility limit for that chemical. However, when the seed crystals of a particular chemical are used in accordance with the principles of the present invention, the process of crystallization occurs before the solubility limit of the particular chemical is reached. This is due to the following reasons.

[00197] First, the portion of the liquid proximal to the seed crystal becomes a near-saturated solution of the chemical comprising the seed crystal. Thus, when additional molecules of this chemical diffuse into this portion of the bulk liquid proximal to the seed crystal, the chemical concentration within that portion of the liquid crosses the solubility limit and crystallization of the chemical occurs. More specifically, FIG. 10 shows two rate phenomena that are occurring simultaneously during this process. The first rate phenomenon is the dissolution of strontium sulfate in a thin film region 904 of water surrounding a seed crystal 900 within the bulk water 902 containing dissolved strontium sulfate. This produces a radial diffusion of dissolved strontium sulfate moving outwards from the surface of the seed crystal 900. The second rate phenomenon is the crystallization 906 of strontium sulfate from the solution surrounding the seed crystal 900, as shown in FIG. 10.

[00198] The second reason that crystallization occurs before the solubility limit is reached is due to the energy effect of strontium sulfate, i.e., the heat of dissolution of strontium sulfate in water

and the heat of crystallization of strontium sulfate from solution. Crystallization process is controlled by two factors: (1) mass transfer of the salt towards the crystal surface, described in the paragraph above with respect to FIG. 10; and (2) the energetics of the process, which is based on the energy balance.

[00199] The process that opposes crystallization is the fact that dissolution of a crystal is favored entropically, while crystallization decreases entropy. The overall process is hence dependent on both the mass transfer rates, which controls the rate of crystal growth, energetics of the process and the entropy change, which opposes the process, with the net effect being described by the change in free energy, which combines the energetics and entropy change into one thermodynamic variable.

[00200] With respect to the reasons listed above, it is known that the free energy change of seed-crystal assisted crystallization = $\Delta H - T\Delta S$, where ΔH is the energy change in this crystallization/dissolution process and ΔS is the entropy change, which favors dissolution of the seed crystal. ΔH = Heat of solution – Heat of adsorption, and ΔS = Entropy of strontium sulfate in solution – Entropy of crystallized strontium sulfate. ΔS will be greater than zero, since strontium sulfate in solution has more disorder than strontium sulfate crystallized. Thus, for any spontaneous process, the free energy change has to be negative and as large as possible, hence $T\Delta S > \Delta H$.

[00201] To ensure that ΔH is as large as possible, strontium sulfate seed crystals are used to assist the crystallization of strontium sulfate preferentially, since this would make the heat of adsorption zero, since strontium sulfate is adsorbing on strontium sulfate seed crystals. On the other hand, precipitation of calcium sulfate using strontium sulfate crystals is not as favorable as precipitation of strontium sulfate, since there is a finite heat of adsorption of calcium sulfate on

strontium sulfate. This makes the free energy change of calcium sulfate precipitation less negative than the precipitation of strontium sulfate. The result is that strontium sulfate will preferentially precipitate out of solution.

[00202] Also disclosed herein is a method of separating strontium from a water product, the method including (a) forming a composition including at least (i) a water soluble sulfate salt, (ii) seed crystals composed substantially of strontium sulfate, and (iii) water; (b) adding the slurry composition to a water product, the water product including at least one soluble strontium salt and one soluble calcium salt; and (c) collecting strontium sulfate.

[00203] In certain embodiments, the seed crystals have an average particle size of about 30 to 100 microns.

[00204] The method is highly selective for precipitation of strontium over calcium wherein the ratio of soluble calcium ions:strontium ions in the water product is between about 0.010 and 1000 on a weight:weight basis. Thus, for example, in some embodiments the method of the invention provides for precipitation of up to about 80 % to 99 % of the strontium dissolved in water, wherein the collected precipitant includes equal to or less than about 0.1 wt% to 1% calcium sulfate among the strontium sulfate. In other embodiments, the methods of the invention provide for precipitation of up to 100 wt% of measurable strontium dissolved in water, wherein the precipitant includes equal to or less than about 1 to 10 wt% calcium sulfate.

[00205] Conventional methods of removing strontium salts from water products result in substantial contamination of the strontium salts with calcium salts. The strontium thus obtained cannot be used without employing further steps to purify the strontium salts in order to provide utility of the product in industrial applications. In embodiments, the methods described herein result in collection of strontium sulfate that is sufficiently pure, upon drying residual water from

the precipitate, to be used directly in such applications. For example, strontium sulfate is industrially useful as a chemical precursor to both strontium carbonate, which is useful in ceramics, and strontium nitrate, which is used in pyrotechnics to impart a red color to fireworks and flares, for example. Strontium metal is also employed in some metal alloys, for example with aluminum or magnesium, for various industrial purposes. Strontium based compounds such as strontium citrate and strontium carbonate, are also used as dietary supplements; strontium ranelate is also available in some countries as a prescription medication useful to treat osteoporosis.

[00206] It will be appreciated by one of ordinary skill in the art that the methods of the invention are not limited solely to separation of strontium from water that also contains calcium salts. The methods of the invention are useful to preferentially precipitate any insoluble salt from water that contains a mixture of several salts with very similar solubilities. The methods of the invention therefore include (a) identifying a species of soluble salt to be separated from a starting water product; (b) forming a stable slurry including at least (i) seed crystals composed substantially of a target insoluble salt to be formed from the identified soluble salt species, (ii) a reagent capable of forming the target insoluble salt from the identified soluble salt species, and (iii) water; and (c) adding the slurry to the water product.

[00207] In certain embodiments, the seed crystals have an average particle size of about 30 to 100 microns.

[00208] In some such embodiments, the water product contains two or more soluble salts of similar solubilities, such that separation of individual salt species is not achievable simply by addition of the reagent capable of forming the insoluble salt from the soluble salt species. Stated differently, the methods of the invention are useful for addition to water products where, if the

reagent capable of forming the insoluble salt from the soluble salt species is added to the water product without the seed crystals, more than one salt species will form and precipitate, resulting in a mixture of precipitated salt species. In many embodiments, such mixtures of precipitated salt species are inseparable using any practicable method. The methods of the invention result in the selective precipitation of a single targeted salt species present in a water product. In some embodiments, the methods of the invention provide for precipitation of up to about 80 % to 99 % by weight of the identified soluble salt species dissolved in the water, wherein the precipitant includes the target insoluble salt and equal to or less than about 0.1 to 1 % by weight of another salt species. In other embodiments, the methods of the invention provide for precipitation of up to 100% by weight of the identified soluble salt species dissolved in the water product, wherein the precipitant includes equal to or less than about 1 % to 10 % by weight of another salt species.

[00209] Additional advantages and novel features of the invention will be set forth in part in the description that follows, and in part will become apparent to those skilled in the art upon examination of the following, or may be learned through routine experimentation upon practice of the invention.

[00210] 1. *Definitions*

[00211] The definitions listed below relate to the discussion of the separation of an element, such as strontium, from water.

[00212] As used herein, the term "water" means pure water, water with some mineral content, water with some organic content, hard water, or brackish water; or combinations of these as determined by context. As used herein, the term "hard water" means water having at least about 30 mg/L, in some cases as much as about 25,000 mg/L, of CaCO_3 dissolved therein. In some cases the hard water has other ionic compounds dissolved or dispersed therein, and/or other

materials dissolved or dispersed therein. Hard water can have as much as 300,000 parts per million by weight of total dissolved solids (TDS). As used herein, the term "brackish water" means water having at least about 400 mg/L, in some cases as much as about 80,000 mg/L, of sodium, present as NaCl, dissolved therein. In some cases the brackish water has other ionic compounds dissolved or dispersed therein, and/or other materials dissolved or dispersed therein.

[00213] As used herein, the term "produced water" means leachates, flow back, or surface water obtained as the result of, or contaminated with the byproducts of, a subsurface geological operation. In some embodiments the produced water is hard water or brackish water. In some embodiments the subsurface geological operation is hydrofracturing.

[00214] As used herein, the term "water product" means water having at least two salt species dissolved therein, wherein the salt species have similar solubilities and reactivities. In embodiments, two salt species having similar solubilities and reactivities are a water soluble calcium salt and a water soluble strontium salt. In embodiments the water product contains additional materials, whether or not dissolved therein, without limitation. The water product is, in some embodiments, hard water, brackish water, salt water, or produced water.

[00215] As used herein, the term "treated water product" means a water product that has been treated using the methods of the invention, wherein the treated water product has reduced content of one of the at least two salt species have similar solubilities and reactivities, compared to the water product. In embodiments, the water product has a reduced strontium content compared to the water product, or substantially no strontium content.

[00216] Herein, methods and apparatus will be described for the separation of materials, such as strontium, from water. At times, this water may be referred to as "hard" water, or "brackish" water, or "produced" water, or another type of water (which may even include waters not

subjected to subsurface geological operations, such as seawater). However, those of ordinary skill in the art will recognize that the methods and apparatus described do not have to be seen as only used with the particular type of water mentioned (whether "wastewater," "produced," "hard," "brackish," "flowback," "contaminated," etc.), but with any water from any source containing a material or materials that one wishes to remove.

[00217] As used herein, the term "stable slurry" means a combination of insoluble crystals and one or more reagents in water, wherein the crystals do not have a substantial tendency to agglomerate or grow in size or number, and the reagents and any additional materials present in the slurry do not cause a chemical reaction that results in net formation or dissolution of species within the slurry. Stability is present at least within a selected temperature range and for a selected amount of time. While in some embodiments some or all of the crystals in a stable slurry settle due to gravity when not agitated for some period of time, simple agitation is sufficient to redisperse the crystals without undue effort or shear.

[00218] As used herein, the term "about" modifying, for example, the quantity of an ingredient in a composition, concentration, volume, process temperature, process time, yield, flow rate, pressure, and like values, and ranges thereof, employed in describing the embodiments of the disclosure, refers to variation in the numerical quantity that can occur, for example, through typical measuring and handling procedures used for making compounds, compositions, concentrates or use formulations; through inadvertent error in these procedures; through differences in the manufacture, source, or purity of starting materials or ingredients used to carry out the methods, and like proximate considerations. The term "about" also encompasses amounts that differ due to aging of a formulation with a particular initial concentration or mixture, and amounts that differ due to mixing or processing a formulation with a particular initial

concentration or mixture. Where modified by the term "about" the claims appended hereto include equivalents to these quantities.

[00219] As used herein, the term "optional" or "optionally" means that the subsequently described event or circumstance may but need not occur, and that the description includes instances where the event or circumstance occurs and instances in which it does not.

[00220] As used herein, the term "substantially" means nearly completely, and includes completely. For example, a solution that is "substantially free" of a specified compound or material may be free of that compound or material, or may have a trace amount of that compound or material present, such as through unintended contamination.

[00221] 2. *Compositions*

[00222] In certain embodiments, the compositions of the invention include water, one or more water soluble sulfate salts, and crystals composed substantially of strontium sulfate. In some embodiments of the invention, the composition contains substantially only one or more water soluble sulfate salts, strontium sulfate crystals, and water. The composition may be in the form of a slurry. Other components may be present; for example, one or more soluble salts that are not sulfates, such as sodium chloride, may be present in the compositions (e.g., slurries) of the invention. In various embodiments, one or more of surfactants, thermal stabilizers, water soluble or water dispersible polymers, water soluble cosolvents, pH buffers, or adjuvants may be added to the composition (e.g., slurry). In some embodiments, water soluble or dispersible viscosifying agents such as clays or gums are added to maintain the consistency of the composition and prevent precipitation during use. In some embodiments, calcium salts are excluded from the compositions. In some embodiments, the pH of the compositions is maintained between about 6 and 7.5, for example between about 6.5 and 7.

[00223] The water soluble sulfate salts include any compounds that are soluble in water, except protonated sulfate adducts including sulfuric acid and metal hydrogen sulfates, since these compounds bind to the strontium sulfate crystals and prevent further crystal growth.. Suitable metal sulfates include, but are not limited to, sodium sulfate, potassium sulfate, lithium sulfate, ammonium sulfate, and magnesium sulfate. In embodiments, the water soluble sulfate is sodium sulfate. In embodiments, more than one soluble metal sulfate is included in the compositions of the invention.

[00224] While it is not necessary for the water used to form the composition (e.g., slurry) to be pure, it is desirable in some embodiments to exclude calcium salts, and it is desirable in some embodiments to maintain pH within the range of 6 and 7.5 as discussed above. Generally, purified water such as softened tap water is acceptable to form slurries of certain embodiments. However, substantially pure water is also useful. In some embodiments, the compositions contain substantially only one or more water soluble sulfate salts, strontium sulfate crystals, and water. In some embodiments the compositions contain substantially only one or more water soluble sulfate salts, strontium sulfate crystals, a side product salt as described below, and water. In some embodiments the compositions contain substantially only sodium sulfate, strontium sulfate crystals, and water. In some such embodiments, the compositions further contain sodium chloride.

[00225] Strontium sulfate is nearly insoluble in pure water, having a reported solubility of 0.135g/100 mL at 25°C and 0.014 g/100 mL at 30°C. Crystals of strontium sulfate in water may be used to form a stable slurry in certain embodiments of the invention. Slurries of strontium sulfate crystals in a water solution containing one or more water soluble sulfate salts are stable slurries. The crystals that are useful for the purpose of separating strontium from other dissolved

metal ions in water are composed substantially only of strontium sulfate; that is, only unintentional traces of other materials are present in certain embodiments. Higher purity strontium sulfate crystals correspond to higher purity of precipitated strontium sulfate from the water solutions when the slurries are employed in the methods of the invention. The crystals used in various embodiments of the invention may have an average particle size of about 30 μm to 100 μm , for example about 40 μm to 90 μm , or about 50 μm to 80 μm , and may be round, elongated, irregular, or any other shape, wherein the average particle size reflects the average largest crystal dimension.

[00226] The methods employed to form the seed crystals and disperse them in the slurry composition are not particularly limited. Suitable methods of forming the crystals employ conventional techniques well known to those of ordinary skill in the art, including precipitation of strontium sulfate from water, and dividing of celestite or another source of substantially pure strontium sulfate.

[00227] Suitable precipitation techniques used to form the seed crystals include any technique whereby a chemical reaction causes strontium sulfate to form in a solution of a water soluble strontium salt. In such embodiments, a water soluble strontium salt is mixed with a water soluble sulfate salt to result in precipitation of strontium sulfate. For example, a solution of substantially pure strontium chloride is formed in water, and then sodium sulfate, or another water soluble sulfate salt such as ammonium sulfate, lithium sulfate, or potassium sulfate, is added to the solution. This may be accomplished by mixing the two dry salts in the water, or by forming separate water-based solutions of strontium chloride and sulfate salt, followed by mixing the two solutions together. It will be appreciated that suitable precipitation techniques result in the in situ

formation of strontium sulfate, which is insoluble in water and precipitates to form the seed crystals.

[00228] It will be appreciated by one of skill that the starting concentration of the soluble strontium salt, the mode of addition of the sulfate salt (dry addition vs. mixing two solutions) and rate of addition of sulfate salt to the strontium salt, may be selected in order to form strontium sulfate crystals having an average particle size in the range of about 30 μ m to 100 μ m. In certain embodiments, turbulence in the slurry is maintained during crystal formation, in order to provide for seed crystals forming in the desired size range. The means of providing turbulence is not particularly limited. In one embodiment, for example, mixing sulfuric acid or sodium sulfate solution and produced water containing dissolved strontium chloride in a venturi provides turbulent mixing of the two reactive streams, allowing small seed crystals of strontium sulfate from forming. Alternatively, this could also be accomplished by mixing the two streams in a tank that is well stirred using a mechanical mixer. To ensure that the crystals formed are in the 30-100 micron range, the turbulence of the mixing process has to be kept high, which prevents crystal growth and assists in formation of new crystals. The crystal sizes in the slurry can be measured using standard instrumentation as is known to those of ordinary skill in the art, and thus, one of ordinary skill in the art will be able to optimize the production of nanobubbles in order to form them in the 30-100 micron range, for example.

[00229] In some embodiments, about 10 to 50 mole % of the total amount of the water soluble sulfate salt needed for a stoichiometric conversion to 100% strontium sulfate is added to the solution of strontium chloride solution, or about 10 to 20 mole% of the stoichiometric amount is added to the strontium chloride solution. In embodiments, a higher concentration of strontium sulfate formed requires a higher amount of turbulence during the addition, in order to maintain a

seed crystal size of about 30 μm to 100 μm . Similarly, a higher temperature employed during the addition causes a faster rate of reaction and precipitation to occur, further requiring a higher amount of turbulence during the addition in order to maintain a seed crystal size of about 30 μm to 100 μm . Turbulence during the addition is suitably supplied using conventional means, including for example Venturi type mixing apparatuses, impellers, sonicators, static mixers, and the like.

[00230] In some embodiments, pH adjustment is carried out by addition of an acid, or a base, or by employing a buffer to maintain a constant pH. Depending on the other chemical components in the mixture, if there are insufficient buffering agents such as bicarbonates and carbonates present, pH will not remain constant. In some embodiments, the formation of strontium sulfate is carried out at ambient temperatures; in other embodiments, one or both slurry components are heated or cooled during formation. It will be appreciated that the addition of heat will increase the rate of reaction, and therefore the rate of precipitation, to form strontium sulfate and the amount of turbulence required to maintain growth of crystals in the range of 30 μm to 100 μm will increase with increasing temperature during the addition. Cooling one or both components of slurry formation will have the effect of lowering the rate of precipitation and therefore the amount of turbulence required to maintain growth of crystals in the range of 30 μm to 100 μm .

[00231] In some embodiments, precipitation techniques also cause a side product to form. For example, in the case of the reaction of strontium chloride and sodium sulfate, the side product is sodium chloride. Since sodium chloride is water soluble, in some embodiments the strontium sulfate crystals are retained as a slurry of crystals in a sodium chloride solution. In other embodiments, the crystals are filtered and washed with substantially pure water to remove substantially all the sodium chloride. In some embodiments, a molar excess of the water soluble

sulfate salt is added to the soluble strontium salt, to result in a mixture of at least the strontium sulfate crystals and water soluble sulfate salt. In some such embodiments, the slurry composition is a slurry of seed crystals in water, plus water soluble sulfate salt that is useful as a composition of the invention. In such embodiments, any side products of the reaction, such as sodium chloride, are also present in the composition.

[00232] Once the reaction of the strontium chloride and water soluble sulfate salt is complete, the slurry compositions are stable; that is, the seed crystals do not tend to further agglomerate or grow, and no further reaction takes place until the slurry is mixed with a water product.

[00233] Suitable means to divide a source of pure strontium sulfate, in order to form the seed crystals employed in the slurry compositions of the invention, include grinding and milling.

Suitable grinding and milling of strontium sulfate, or celestite (celestine), is accomplished using conventional techniques. Grinding and/or milling is employed to break up coarse strontium sulfate particles, "rocks", or chunks – for example, having sizes of over 100 μm , such as 1 mm particles or crystals, up to rocks, crystals, or particulate agglomerates having an average diameter of 0.1 meter or even up to 0.5 meter. Grinding and milling operations can be carried out wet or dry. More than one grinding or milling step is suitably employed, for example, a first step to break up large rocks to form smaller rocks or coarse powders; and a second step to break up these products further into particles having an average particle size of 30 μm to 100 μm . Suitable equipment employed to grind or mill such materials include ball mills, media mills, powder grinders, jet mills, vertical mills, and high pressure grinders.

[00234] Where strontium sulfate such as celestite is employed as the source of seed crystals in the slurry compositions of the invention, the suitably divided particles are slurried in water and an amount of water soluble sulfate salt is added to the slurry to yield a slurry composition of the

invention. It will be appreciated that by using strontium sulfate as the source of seed crystals, it is possible to form a slurry composition including substantially only the seed crystals and the water soluble sulfate salt in water, without any further steps such as filtration of crystals.

[00235] In some embodiments, the slurry of seed crystals thus formed, whether alone in water or in the presence of sodium chloride, water soluble sulfate salt, or both, is used as is. In other embodiments, additional water soluble sulfate salt is added to the slurry in order to provide a suitable slurry composition of the invention. The ratio of water soluble sulfate salt to seed crystals in the compositions of the invention is not particularly limited.

[00236] 3. *Method of Substantially Separating a Single Salt Species from Water*

[00237] The methods of the invention are useful to preferentially precipitate a single salt species from water that contains a mixture of at least two salt species with very similar solubilities, and wherein various counterionic species also have similar solubilities. In a non-limiting example, calcium and strontium salts have similar solubilities in water, such that various counterionic species of these metals have similar solubilities in water. Thus, strontium chloride and calcium chloride are highly water soluble, and strontium sulfate and calcium sulfate are nearly water insoluble. Such similarities in soluble species give rise to difficulties in separation. Other examples include calcium and barium.

[00238] Conventional water purification methodology involves addition of a reagent capable of forming an insoluble salt from a targeted soluble salt species to the water product, wherein the resulting ion exchange results in the coprecipitation of salt species with very similar solubilities, such as calcium, magnesium, and strontium salts. Sedimentation or filtration of these coprecipitants does yield a treated water product; however, as described above, the coprecipitates

are an industrially useless mixture that is impracticable to separate. The salt mixture is thus discarded as a waste product.

[00239] The methods of the invention provide a means to form treated water product and industrially useful precipitated salts that are, in embodiments, substantially free of coprecipitated species. Thus, the methods of the invention include (a) identifying a species of soluble salt to be separated from a starting water product; (b) forming a stable slurry including at least (i) seed crystals composed substantially of a target insoluble salt to be formed from the identified soluble salt species, (ii) a reagent capable of forming the target insoluble salt from the identified soluble salt species, and (iii) water; and (c) adding the slurry to the water product.

[00240] In certain embodiments, the seed crystals have an average particle size of about 30 to 100 microns.

[00241] In some such embodiments, the water product contains two or more soluble salts of similar solubilities, such that separation of an individual salt species is not achievable simply by addition of the reagent capable of forming the insoluble salt from the soluble salt species. In certain embodiments, the reagent is the sulfate solution, which makes the metal sulfates into an insoluble form. We are mainly talking about metals that have very similar properties, and hence having crystals of one metal sulfate will favor selective precipitation of that metal sulfate over the other competing metal sulfates.) Stated differently, the methods of the invention are useful for addition to water products where, if the reagent capable of forming the insoluble salt from the soluble salt species is added to the water product without the seed crystals, more than one salt species will form and precipitate, resulting in a mixture of precipitated salt species. In many embodiments, such mixtures of precipitated salt species are inseparable using any practicable method.

[00242] The methods of the invention result in the selective precipitation of a single targeted salt species present in a water product. In some embodiments, the methods of the invention provide for precipitation of up to about 80 % to 99 % by weight of the identified soluble salt species dissolved in the water, wherein the precipitated target insoluble salt includes equal to or less than about 0.1 % to 1 % by weight of another salt species. In other embodiments, the methods of the invention provide for precipitation of up to 100% by weight of the identified soluble salt species dissolved in the water product, wherein the precipitant includes equal to or less than about 1 % to 10 % by weight of another salt species.

[00243] 4. *Method of Separating an Element, such as Strontium, from Water*

[00244] One particular embodiment of the invention includes a method of treating a water product to separate strontium ions from other dissolved ions in water products, in particular wherein the dissolved ions include at least calcium ions. In some embodiments, the dissolved ions further include magnesium ions or barium ions or a mixture thereof. In some embodiments, the water includes other dissolved or dispersed solids and/or ionic compounds. In some such embodiments, the water product contains dispersed or dissolved liquids or gels. In some embodiments, the water product includes hydrocarbon compounds, surfactants, petroleum products, dispersed sand or silt, or mixtures thereof. In embodiments, the water product is hard water or brackish water. In embodiments, the water product is produced water. In some such embodiments, produced water is the product of hydrofracturing.

[00245] In embodiments, the water product is pretreated prior to the carrying out the methods of the invention. In some such embodiments, a suitable pre-treatment includes the removal of insoluble but dispersed solids, liquids, and gels from the water product, for example the removal of hydrocarbons dispersed in the water product. Such removal is, in embodiments, carried out

according to methods known by those of skill in the art of water purification. Suitable removal techniques include sedimentation, flotation, and filtration. Other pretreatments that are carried out in some embodiments include aeration, evaporation, acidification, and the like, according to the knowledge of the skilled artisan. However, it will be recognized that an advantage of the current invention is that no pretreatment of water product is necessary prior to carrying out the methods disclosed herein. The methods of the invention are effective to selectively separate strontium from other metal ions in water product without any pretreatment whatsoever. Further, it is an advantage of the current invention that where the water product is produced water, a simple pretreatment to remove insoluble but dispersed solids, liquids, and gels from the produced water is sufficient to provide a water product from which substantially pure strontium sulfate is easily collected.

[00246] In certain embodiments, the water product that is the starting material from which strontium will be obtained may contain a total of 130 to 300,000 mg/L of total dissolved solids. In some such embodiments, the water product is produced water, wherein produced water is a product of hydrofracturing or another mining operation. In embodiments, the soluble strontium salt that is the source of strontium ions in the water product is strontium chloride, or SrCl_2 . In embodiments, the soluble metal salts that are the source of other metal ions in the water product include calcium chloride, or CaCl_2 . In certain embodiments, the water product may contain about 10 to 50,000 mg/L of calcium ions. In certain embodiments, the water product may contain between about 1 to 1000 mg/L of strontium ions. In certain embodiments, the ratio of soluble calcium salts to soluble strontium salts in the water product may be about 0.01 to 1000, or about 0.1 to 500, or about 1 to 100, or about 5 to 50. In certain embodiments, the water product further includes water soluble magnesium salts, water soluble barium salts, or both.

[00247] The method of separating strontium from water in this embodiment of the invention includes (a) forming a slurry composition including water, one or more water soluble sulfate salts, and crystals composed substantially of strontium sulfate; (b) adding the slurry composition to a water product, the water product including at least one soluble strontium salt and one soluble calcium salt; and (c) collecting strontium sulfate.

[00248] In some embodiments, the methods of the invention are carried out between about 10°C to 150°C. In embodiments where the temperature employed is near or in excess of 100°C, an enclosed vessel system is employed; in some such embodiments, additional pressure is added to the enclosed vessel. In embodiments, the rate of separation, and therefore collection, of strontium is observed to increase with increasing temperature.

[00249] In some embodiments the ratio of soluble calcium : strontium ions in the water product prior to carrying out the methods of the invention is between about 0.01 and 1000 on a weight : weight basis. In some such embodiments, the methods of the invention provide for precipitation of up to about 80% to 99% by weight of the strontium present in the water product, wherein the collected strontium sulfate precipitant includes equal to or less than about 0.1% to 1% calcium sulfate by weight. In other embodiments, the methods of the invention provide for precipitation of up to 100% by weight of the strontium in the water product wherein the precipitant includes equal to or less than about 1% to 10% calcium sulfate by weight. In embodiments, strontium sulfate is collected at the end of the process, and treated water is the second product that is collected. The treated water is the water product after treating using the methods of the invention, wherein between about 80 % and 100% by weight of measurable strontium in the water product is removed, or between about 90 % and 99 % by weight of measurable strontium in the water product is removed to result in the treated water.

[00250] In some embodiments, it is advantageous to determine the amount of strontium present in the water product prior to carrying out the addition of the slurry composition to the water product. In these embodiments, once this amount of strontium is determined, the amount of slurry composition added to the water product corresponds to about one molar equivalent of water soluble sulfate salt in the slurry composition per mole of strontium present in the water product. While it is not necessary to determine the amount of strontium in a water product prior to carrying out the method of the invention, this determination can lead to a greater yield of isolated strontium sulfate and can further minimize the amount of excess water soluble sulfate salt added to the treated water product. Methods that are useful to determine strontium levels in the water product include, but are not limited to, spectrophotometric methods such as atomic absorption spectrophotometry.

[00251] Once the amount of strontium in the water product has been determined, an amount of the slurry concentration is added to the water product. In embodiments where the water product is treated in batch mode, the slurry composition is added in a single batch to the total volume of water product. In other embodiments, the slurry composition is added in aliquots to a batch of water product. In some such embodiments, precipitated strontium sulfate is collected after each aliquot is added, then a subsequent precipitation and collection step is carried out, for example, in a separate vessel. In embodiments where the water product is treated in continuous mode, the slurry composition is added continuously at a rate that is based on the volume of water product moving into and out of a treatment vessel where the strontium is to be separated. In one embodiment, the two streams are mixed in a venturi to provide sufficient turbulence to allow proper mixing of the slurry with the produced water flow.

[00252] In another embodiment of the invention, a mixture of ground or milled strontium sulfate having a particle size of about 30 μm to 100 μm is mixed as a dry powder with a dry water soluble metal salt, and the dry mixture is added to the water product. In some such embodiments, a means of dispersing the dry components in the water product is useful. Suitable means for dispersing include but are not limited to impeller mixing, static mixing, sonication, shaking, tumbling, combinations thereof, and the like. In various embodiments, a batchwise or continuous mode of addition of the dry mixture to the water product is used.

[00253] In certain embodiments, the slurry may be added in a total amount corresponding to about 50 mole% to 150 mole% of soluble sulfate salt to soluble strontium salt in the water product; or about 70 mole% to 130 mole% of soluble sulfate salt to soluble strontium salt in the water product; or about 90 mole% to 100 mole% of soluble sulfate salt to soluble strontium salt in the water product; or about 90 mole% to 120 mole% of soluble sulfate salt to soluble strontium salt in the water product. In a particular embodiment, the slurry composition contains a suitable ratio of strontium sulfate seed crystals to water soluble sulfate salt to provide utility in the methods of the invention with respect to a particular water product. That is, a selected volume of the slurry contains an approximately a stoichiometric amount of water soluble sulfate salt to water soluble strontium salt in the water product, when the selected volume of slurry composition is added to a selected volume of the water product. Further, in this particular embodiment, the selected volume of slurry composition contains a suitable amount of seed crystals of strontium sulfate to provide for the selective precipitation of strontium sulfate.

[00254] In such an embodiment, the "suitable amount" of seed crystals may be determined as follows: The aqueous solubility of strontium sulfate is known to be 1.4×10^{-4} gms of strontium sulfate per gram of water, at 30°C. This corresponds to a concentration of 140 ppm of strontium

sulfate in water. The concentration of strontium chloride in Marcellus Shale water, for example, is 2,500 ppm (the Marcellus Shale is an area of marine sedimentary rock found largely in the eastern to northeastern part of the United States, and contains natural gas reserves -- with Marcellus Shale, water being water, such as flowback water from fracking, in the Marcellus Shale). Since $\text{SrCl}_2 + \text{Na}_2\text{SO}_4 \rightarrow \text{SrSO}_4 + 2\text{NaCl}$, that means 158.52 gm of SrCl_2 will form 183.62 gms of SrSO_4 (strontium sulfate). Thus, 2,500 ppm of SrCl_2 in Marcellus Shale Water will form 2,896 ppm of strontium sulfate in the water.

[00255] Clearly the strontium sulfate solution will be supersaturated and the ratio of supersaturated and saturated solution concentration will be $= \alpha = 2896/140 = 20.7$. Above, we had calculated that 2,500 ppm of SrCl_2 will form 2,896 ppm of strontium sulfate in water. 140 ppm is the solubility of strontium sulfate in water at 30°C (as shown, previously, above). Since the solution is highly supersaturated, the number of seed crystals required will be small.

[00256] The preferential formation of strontium sulfate over calcium sulfate is caused by nucleation of strontium sulfate by the seed crystals, resulting in isolation of substantially pure strontium sulfate from the water. The rate of nucleation is given by the following equation (Preckshot, G.W. and G.G. Brown, Ind. Eng. Chem., 44:1314(1952))

$$B^o = 10^{25} \exp \left[-\frac{16\pi V_M^2 N_a \sigma_a^2}{3(RT)^3 v^2 s^2} \right]$$

where B^o = nucleation rate (number / $\text{cm}^2 \cdot \text{s}$)

N_a = Avogadro Number = 6.0222×10^{23} molecules / gmole

R = Gas Constant = 8.3143×10^7 ergs / gmole.deg K

C = Frequency Factor

V_M = Molar volume of crystal

σ_a = average interfacial tension between solid and liquid

$s = \alpha - 1$ where α is Supersaturated Solution Conc. / Saturated Soln. conc.

v = number of ions per molecule of solute

[00257] The factor C does not appear in the equation above, but is a statistical measure of the rate of formation of crystals that reach a critical size. It is proportional to the concentration of the individual particles and to the rate of collision of these particles with a crystal of the size required to form a stable nucleus. It is of the order of 1025 nuclei/cm³.s. Its accurate value is not important since the kinetics of crystallization is dominated by the $\ln \propto$ term in the exponent.

[00258] The value of σ in the above equation, which is the interfacial tension between the crystal and solution is about 80-100 ergs/cm² for typical salts (See, CRC Handbook of Chemistry and Physics).

[00259] V_M for Strontium Sulfate = Mol. Wt/Crystal Density = 183.68/3.96 = 46.38 cm³/gmole.

[00260] The exponent in the above equation is =
$$-\frac{16\pi(46.38)^2 \times 6.0222 \times 10^{23} \times 2.5^3}{3(300 \times 8.3134 \times 10^7)^3 (3)^2 (19.7)^2} = -38.94$$

[00261] The value of $B^0 = 1,230$ nuclei/cm³.s. This gives the number of seed crystals that have to be added to the vessel as can be calculated by one of ordinary skill in the art, given the above equations.

[00262] We have found that the amount of seed crystals added to the water affects the rate of precipitation of strontium sulfate from the water, but does not affect the yield. (As will be recognized, the yield is the net amount of strontium sulfate precipitated; the amount of seed crystals added affects the rate of precipitation, not the total amount precipitated, which depends on the amounts of the chemicals that have been added, i.e., stoichiometry.) Thus, in applications involving very high continuous rates of water product throughput, an increased ratio of crystals provided in the slurry composition of the invention relative to the amount of water product is usefully employed in order to increase the rate of strontium sulfate precipitation from the water product. The use of a higher ratio of seed crystals to water product affects, in turn, the ratio of seed crystals to water soluble sulfate salt employed in the slurry compositions, since the amount

of water soluble sulfate salt depends on the amount of strontium in the water product and the activity thereof depends only on the rate of mixing.

[00263] In embodiments, strontium sulfate is collected at the end of the process, and treated water product is also collected. The treated water product includes, in embodiments, about 0% to 10% by weight of strontium initially measured in the water product, or between about 0.1% and 5% by weight of strontium initially measured in the water product. The treated water product further contains, in embodiments, between about 90% and 100% by weight of the measurable calcium ions that were present in the water product initially, or about 95% and 99% by weight of the measurable calcium ions that were present in the water product initially. In other words, the methods of the invention remove little to no calcium while removing a large proportion or all of the strontium from the water product. In embodiments, the treated water product is substantially free of strontium. In some embodiments the treated water contains one or more side products as defined above, that is, a salt that is added to the slurry composition by virtue of employing in-situ precipitation methodology as described above. In some embodiments, the treated water product further contains one or more additional additives employed in the slurry compositions of the invention and therefore added to the water product employing the methods of the invention. In some embodiments, the treated water also contains the chloride salt that is the product formed as the water soluble sulfate salt reacts with strontium chloride to form strontium sulfate. Thus, in embodiments, magnesium, ammonium, sodium, lithium, or potassium chloride is present in the treated water as a result of the reaction of strontium chloride with the water soluble sulfate salt to form strontium sulfate.

[00264] In embodiments, the process to remove strontium from the water product is repeated with other ions once the separation of strontium is complete. For example, once the strontium is

substantially removed from the water product, the treated water product is subsequently treated again to selectively remove calcium ions and thereby separate calcium from e.g. magnesium salts also present in the treated water product. In such embodiments, a method similar to any of the above embodiments of the method to remove strontium is repeated, only using seed crystals of calcium sulfate in a slurry with a water soluble sulfate salt such as sodium sulfate. In still other embodiments, the method of the invention is carried out to separate calcium from the water product, followed by separation of strontium. In still other embodiments, the method of the invention is carried out to separate magnesium from the water product, followed by separation of strontium, calcium, or another salt of similar solubility, in any order as will be selected by one of skill. In some embodiments, it is desirable to determine the amounts of various salts in the water product, and select the order of removal such that the ion present in the highest concentration is removed first, or the ion of lowest concentration is removed first, or some other order based on efficiency and equipment considerations.

[00265] 5. *Apparatus Useful for Selectively Separating Strontium from Water*

[00266] Apparatus that are useful for carrying out the methods of the invention will now be described. It will be appreciated by those of skill that the various apparatus described are provided by way of illustration only and that various modifications and changes may be made without following the examples of embodiments and applications illustrated and described herein, wherein such modifications and changes are within the scope of the apparatus of the invention. It will also be appreciated that while the apparatus described are intended for the indicated precipitation of strontium, the apparatus or individual features thereof are useful for carrying out the broader methods of the invention; that is, the addition of stable slurries to water products, and isolation of a resulting target insoluble salt and a treated water product.

[00267] FIG. 11 shows one embodiment of an apparatus 908 of the invention. Apparatus 908 includes a source 910 of water product, a tank 912 to hold the slurry composition 914, a precipitator vessel 916, a collecting apparatus 918, and a system (pump) 920 for removing treated water product.

[00268] The source 910 of water product is not particularly limited. The source 910 is, in various exemplary embodiments, a wellbore; a pipe or tube connected to a wellbore or to some other flowing source of a water product; a holding tank containing the water product, wherein the holding tank has, in some embodiments, a separate pump system (not shown) to provide flow of the water product to the apparatus 908; or a pretreatment system that produces the water product as the product of the pretreatment process. In some embodiments, source 910 is connected to regulator 922. In some such embodiments, regulator 922 is a pump that pulls water product into the apparatus 908. In some embodiments, regulator 922 regulates water flow, for example by creating back pressure or by shunting excess volume to a holding tank (not shown). In still other embodiments, regulator 922 is some other means of controlling overall volume and rate of flow of water product. Source 910 of water product is further connected to tank 912 in a manner such that a combined flow 924 of the water product 926 and a slurry composition 914 of the invention is formed. Tank 912 is equipped to hold and dispense a slurry composition 914 of the invention such that a combined flow 924 of water product 926 and slurry composition 914 is formed and directed towards and into mixing apparatus 928. Tank 912 has, in some embodiments, a flow regulator (not shown) to regulate or meter the rate of flow of slurry composition 914 into the water product 926 to form combined flow 924.

[00269] Mixing apparatus 928 receives and mixes the combined flow 924 and delivers it to precipitator vessel 916. Mixing apparatus 928 may be an in-line mixer capable of mixing the

combined flow 924 to provide a substantially constant distribution of the seed crystals therein. In various embodiments, the mixing apparatus 928 is a static mixer, an impeller mixer, a vortex mixer, or another means for mixing as will be understood by those of skill in the art.

[00270] In some embodiments, apparatus 908 does not include tank 912 for holding the slurry composition 914. In such embodiments, various alternative means of supplying both a water soluble sulfate salt and seed crystals of strontium sulfate are used with equal advantage to supplying slurry composition 914 to the source 910 of water product 926. For example, dry powder metering systems for addition of seed crystals, water soluble sulfate salt, or a single apparatus for providing a blend of both components are employed in some embodiments to deliver the dry material components directly to the water product 926 as it flows into the mixing apparatus 928, whereupon the components are mixed directly into the water product. Where added separately, the order of addition of the components is not limited; however, in some embodiments, it is advantageous to add the seed crystals prior to addition of the water soluble sulfate salt since the salt initiates the reaction to precipitate the strontium sulfate and it is desirable to provide the seed crystals at the outset of the reaction. In particular embodiments, the seed crystals have to be added before the addition of the soluble sulfate, so that the strontium sulfate precipitates preferentially on these seed crystals instead of the calcium sulfate, especially since the calcium in concentration is much higher than the strontium ion.

[00271] In another alternative embodiment, there are two tanks (not shown) attached in a manner that is suitable to provide materials to the source 910 of water product 926, wherein one tank holds a solution of water soluble sulfate salt, and the second holds a slurry of strontium sulfate seed crystals. The tanks are used to feed their respective materials to the source 910 of water product 926 prior to form the combined flow 924 that enters mixing apparatus 928. The two

tanks add the strontium sulfate slurry and the solution of water soluble sulfate salt contemporaneously or in series to the water product 926 to form combined flow 924. The order of addition of the individual tank components is not limited; however, in some embodiments, it is advantageous to add the seed crystal slurry prior to addition of the solution of water soluble sulfate salt since the salt initiates the reaction to precipitate the strontium sulfate and it is desirable to provide the seed crystals at the outset of the reaction.

[00272] After the combined flow 924 is mixed using mixing apparatus 928, the substantially homogeneously dispersed combined flow 924 is dispensed into the precipitator vessel 916. The vessel 916 is designed to provide the requisite residence time to allow for completion of the reaction to form strontium sulfate from strontium chloride present in the combined flow 924, and to allow for sedimentation of the strontium sulfate precipitate that forms as a result of the seeded precipitation reaction. The precipitation and sedimentation is adjusted by the rate of addition of components of the combined flow 924, relative amounts of the components of the combined flow 924, and flow rate of the combined flow 924. The seeded crystal precipitation, and sedimentation of the precipitants formed, is aided by in-line media 930. In-line media 930 includes tubes, plates, baffles, or the like, for example inclined plates or tubes that serve to increase surface area inside precipitator vessel 916; or, in other embodiments, prevent turbulence during addition of incoming combined flow 924 from mixing apparatus 928; or in yet other embodiments accomplish both increase of interior surface area and prevention of turbulence in the interior of vessel 916. Residence time of the combined flow 924 within the vessel 916 is carefully determined based on rate of precipitation and sedimentation.

[00273] As the strontium sulfate precipitates from the combined flow 924, treated water product is removed via top port 932 and a concentrated slurry of strontium sulfate in treated water is

removed via bottom port 934. The concentrated slurry of strontium sulfate exiting vessel 916 via bottom port 934 is transported via regulator 936 to the collecting apparatus 918. In some embodiments, regulator 936 is a pump that assists the concentrated slurry of strontium sulfate to flow into collecting apparatus 918. In some embodiments, regulator 936 regulates flow of the concentrated strontium sulfate slurry, wherein excess volume is directed to, for example, a holding tank or other apparatus (not shown). In some embodiments, regulator 936 further includes an in-line mixer or other apparatus for maintaining a substantially uniform slurry flow directed toward collecting apparatus 918.

[00274] Collecting apparatus 918 is generally a filtration means capable of separating strontium sulfate solids from the concentrated slurry of strontium sulfate, resulting in wet solid strontium sulfate and treated water. While apparatus 908 is not particularly limited in the type of collection apparatus 918 employed, in the embodiment of apparatus 908 shown in FIG. 11, the collection apparatus 918 is a cylinder former.

[00275] The concentrated strontium sulfate slurry in treated water is deposited into a vat 938 that is part of collection apparatus 918. Collection apparatus 918 as shown is the same or similar to cylinder formers developed for papermaking applications, as will be appreciated by those of skill. Collection apparatus 918 includes a horizontally situated cylinder 940 with a wire, fabric, or plastic cloth or scrim surface that rotates in the vat 938 containing the concentrated strontium sulfate slurry from vessel 916, as dispensed from bottom port 934 and transported via regulator 936. Treated water associated with the slurry is drained through the cylinder and a layer of strontium sulfate precipitate is deposited on the wire or cloth. The drainage rate, in some designs, is determined by the slurry concentration and treated water level inside the cylinder such that a pressure differential is formed. As the cylinder turns and treated water is drained, the precipitate

layer that is deposited on the cylinder is peeled or scraped off of the wire or cloth, such as with a scraper blade (not shown) and continuously transferred, such as via a belt 942 or other apparatus, to receptacle 944. In some embodiments, during transport of the deposited layer of strontium sulfate to the receptacle 944, the strontium sulfate is washed, such as by applying a spray of clean water (not shown) across the belt 942 that transports the strontium sulfate to receptacle 944. In some embodiments, during transport of the deposited layer of strontium sulfate to the receptacle 944, the strontium sulfate is dried, such as by applying a hot air knife (not shown) across the belt 942 that transports the strontium sulfate to receptacle 944 or by heating belt 942 directly, or by some other conventional means of drying strontium sulfate crystals. Receptacle 944 thus contains a collection, such as an agglomerated "rock" or "chunk" of wet strontium sulfate 946.

[00276] In some embodiments, the strontium sulfate 946 is used for an industrially useful application as is discussed above. In some embodiments, a portion of the strontium sulfate 946 is partitioned from the collected amount and redeployed as a source of seed crystals to be used in the slurry 914 or a dry feed of seed crystals used to form the combined flow 924. In such embodiments, it may be necessary to grind or mill the collected and partitioned strontium sulfate using a conventional grinding or milling apparatus such as those described above. In still other embodiments, the collection apparatus 918 is configured to allow strontium particles having particle sizes of about 30 μm to 100 μm to flow through the filtration means (cloth, wire, etc.) to be captured elsewhere, such as by traditional nonwoven or membrane filtration or the like, and these small particles are washed and used as seed crystals in the slurry composition 914.

[00277] In still other embodiments, a portion of the concentrated slurry collected from exit port 934 is partitioned from the main channel transporting the flow to the collection apparatus 918

and this partitioned portion of slurry is filtered and washed to collect seed crystals of strontium sulfate to be used in slurry composition 914.

[00278] An alternative type of cylinder former (not shown) useful in conjunction with apparatus 908, causes the concentrated strontium sulfate slurry to be deposited directly along the rotating cylinder. The area of the cylinder contacting the slurry, called the “forming area,” is restricted compared to that of vat designs. This type of cylinder former design has no associated vat, as slurry is applied directly to the cylinder that is the same as or similar to cylinder 940. Such cylinder former designs are called “dry vat” type formers. Suction formers are dry vat type formers that further utilize vacuum dewatering inside of the cylinder. The greater rate of treated water removal afforded by vacuum dewatering facilitates increased line speed relative to “gravity” type drainage. Pressure formers are another dry vat type variation that employ a pressurized slurry instead of vacuum suction as a means to control the pressure differential. Any of these embodiments of cylinder formers are useful as the cylinder former 918 in apparatus 908 of the invention, as well as variations thereof as will be appreciated by those of skill.

[00279] The treated water product removed via top port 932 is carried via tubes, pipes, or the like 948 to be combined with the treated water product drained or suctioned from the interior of cylinder 940, and the combined treated water product is collected via regulator 920 and conveyed to outside location 950. Outside location 950 is, in various embodiments, an additional treatment apparatus, a holding tank, or some other location where the treated water product is used, subjected to further treatment, or dispensed.

[00280] The apparatus 908 has, in various embodiments, additional control and infrastructure features that provide for greater rates of strontium sulfate recovery, greater efficiency, greater yield, and the like as will be appreciated by one of skill. Valves, gauges, pipes, tubes, coolant

jackets or other means of temperature adjustment, means of measurement in-line, electronic controls or measurements, feedback controls digitally connected in cooperation with in-line measurements, and the like are optionally added at any location in apparatus 908. For example, an in-line atomic absorption spectrometer may be added in-line for water product source 910, prior to addition of slurry 914, in order to determine strontium level in the water product source 910. The data may be continuously fed to a metering regulator attached to tank 912 to control the rate of addition of slurry 914, such that an optimized amount of slurry 914 is added to form combined flow 924. Many other such features are easily envisioned by one of skill. In some embodiments, vessel 912 is enclosed in order to allow pressure to be applied or to develop inside vessel 912 and, in some such embodiments, elsewhere within the apparatus 908. In some such embodiments, vessel 912 includes a source of heat in order to raise the temperature of the water product to as high as 150°C. In some embodiments, the source 910 of water product is a heated source.

[00281] In some embodiments, the apparatus 908 shown in FIG. 11 is expanded to include several precipitation vessels 916, wherein aliquots of slurry are added in each vessel, a partially treated water product is removed via top port 932 and a concentrated slurry of strontium sulfate in partially treated water is removed via bottom port 934; then the partially treated water product removed via top port 932 is carried via tubes, pipes, or the like 948 to be combined with a partially treated water product drained or suctioned from the interior of cylinder 940, and the combined partially treated water product is collected via regulator 920 and conveyed to outside location 950 wherein the outside location 950 is another precipitation vessel 916. In the second precipitation vessel, a subsequent aliquot of slurry from the same source tank 912 or a different source is added to the partially treated water and the precipitation and collection of treated water

product is repeated. In this manner, two or more such precipitation steps are carried out to result in a treated water product. In some embodiments where two or more such precipitation steps are carried out, strontium sulfate is collected separately in each step; in other embodiments, the precipitates of each step are combined, either after collection and filtration or by transferring the precipitates to the same collection apparatus and combining prior to filtration.

[00282] In some embodiments of apparatus 908, the slurry source tank 912 is not used, and instead a separate source of water soluble sulfate salt and strontium sulfate crystals are used. Then these two slurry components are mixed in-line, such as by mixing apparatus 928 or a separate similar to in-line mixing apparatus 928, just before or contemporaneously with addition of the slurry to the water product. In such embodiments, the ratio of seed crystals to water soluble sulfate salt is easily adjusted based on measured amounts of strontium and/or other salt species present in the water product as the source of the water product changes. When the apparatus 908 shown in FIG. 11 is expanded to include several precipitation vessels 916, and aliquots of slurry are added in each vessel, the ratios of water soluble sulfate salt to seed crystals may be easily adjusted for each tank such that an ideal ratio of slurry components is provided for each step in order to maximize yield and purity of the precipitate, for example based on the actual collected yield of strontium sulfate collected in the previous step. Finally, providing the slurry components separately allows for flexibility in order of addition: in some embodiments, seed crystals are added to the water product, followed by addition of the water soluble sulfate salt. In other embodiments, the water soluble sulfate salt is added to the water product, followed by addition of the seed crystals. Such flexibility in order of addition allows for optimization of the process based on the source and composition of water product to be treated.

[00283] In some embodiments, a similar apparatus to apparatus 908 shown in FIG. 11 is employed to carry out a separation of insoluble salt other than strontium salts from a water product. For example, in some embodiments, hard water contains negligible or acceptable amounts of strontium salts and thus strontium separation is unnecessary; however, hard water typically contains large concentrations of calcium and thus calcium removal is desirable. The methods of the invention, as described above, are also useful for separation of calcium sulfate from water products containing salts of similar solubility and reactivity to calcium chloride. The methods of the invention are therefore useful for selective separation of calcium sulfate from such water products to result in collection of a substantially pure calcium sulfate product. That is, a slurry composition of calcium sulfate seed crystals and a water soluble sulfate salt is employed to selectively separate calcium sulfate from the water product, using materials and methods as described above. In other similar embodiments, it is desirable to selectively separate both calcium and strontium from a water product; in such embodiments, apparatuses such as apparatus 908 shown in FIG. 11 are useful wherein strontium is separated in one or more steps and calcium is also separated in one or more additional steps by sending the treated water product from one separation to a separate apparatus 908 for a subsequent separation. The order of separation is selected by the practitioner for efficiency and may be based, for example, on the composition of the water product. Each such step employs a source of seed crystals that preferentially precipitates the desired product as described above. In some such embodiments, the same water soluble sulfate salt is employed to preferentially precipitate different salt species; in other embodiments, the water soluble sulfate salt is different in each addition of slurry to the water product or partially treated water product.

[00284] Similarly to the methods described above, two, three, or more salts with similar solubilities and reactivities are selectively separated from a single water product. The compositions, methods, and apparatuses employed in carrying out two or more such separations are not particularly limited. It is an advantage of the compositions, methods, and apparatuses of the invention that the practitioner has flexibility in providing for such separations to meet the requirements of the type of water product expected as well as the volume of flow of the water product, the desired amount of selective capture of substantially pure precipitated sulfate salts, and the like.

[00285] Separation of Salts and Solvents

[00286] As described above, the present invention overcomes the issues with removing contaminants such as salts (e.g., sodium chloride) from water (such as flowback water), as described in the Background. It does so, in one aspect, by using a solvent to precipitate the salt out of solution (i.e., out of the water), and by providing apparatus and methods for same. Other aspects of the present invention may include further processing to (1) remove the precipitated salt from the water and (2) remove the solvent from the water. Another aspect of the present invention is that the method and apparatus accomplish this in an efficient, low-energy, and low-cost manner. Additionally, the salt removed may ultimately be converted into higher value products (in order to offset any cost, or portion of the cost, of the water treatment).

[00287] One aspect of the present invention provides method of separating water soluble salts from an aqueous solution. The method may include (1) adding a solvent to a solution of salt in liquid to form an aqueous mixture, wherein the mass ratio of the solvent to the total volume of aqueous mixture is about 0.05 to 0.3; (2) separating a salt slurry from the aqueous mixture; and (3) evaporating the water miscible solvent from the salt slurry to form a concentrated salt slurry.

[00288] That method of separating water soluble salts from an aqueous solution may more specifically include – in certain embodiments -- (1) adding a water miscible solvent to a solution of salt in water to form an aqueous mixture, wherein the mass ratio of the water miscible solvent to the total volume of aqueous mixture is about 0.05 to 0.3, and wherein the water miscible solvent is characterized by (a) infinite solubility in water at 25°C; (b) a boiling point of greater than 25°C at 0.101 MPa; (c) a heat of vaporization of about 0.5 cal/g or less; and (d) no capability to form an azeotrope with water; (2) separating a salt slurry from the aqueous mixture; and (3) evaporating the water miscible solvent from the salt slurry to form a concentrated salt slurry.

[00289] Thus, one aspect of the present invention involves precipitating salt out of the water using a solvent. The solvent may be an organic solvent. To that end, ethanol precipitation is a widely used technique to purify or concentrate nucleic acids. In the presence of salt (in particular, monovalent cations such as sodium ions), ethanol efficiently precipitates nucleic acids. Nucleic acids are polar, and a polar solute is very soluble in a highly polar liquid, such as water.

However, unlike salt, nucleic acids do not dissociate in water since the intramolecular forces linking nucleotides together are stronger than the intermolecular forces between the nucleic acids and water. Water forms solvation shells through dipole-dipole interactions with nucleic acids, effectively dissolving the nucleic acids in water. The Coulombic attraction force between the positively charged sodium ions and negatively charged phosphate groups in the nucleic acids is unable to overcome the strength of the dipole-dipole interactions responsible for forming the water solvation shells.

[00290] The Coulombic Force between the positively charged sodium ions and negatively charged phosphate groups depends on the dielectric constant (ϵ) of the solution, and is given by the following equation:

$$F = \frac{q_1 q_2}{4\pi\epsilon_0\epsilon_r r^2} = 8.9875 \times 10^9 \frac{q_1 q_2}{\epsilon_r r^2} \text{ newtons}$$

[00291] Adding a solvent, such as ethanol to a nucleic acid solution in water lowers the dielectric constant, since ethanol has a much lower dielectric constant than water (24 vs 80, respectively). This increases the force of attraction between the sodium ions and phosphate groups in the nucleic acids, thereby allowing the sodium ions to penetrate the water solvation shells, neutralize the phosphate groups and allowing the neutral nucleic acid salts to aggregate and precipitate out of the solution [as described in Piškur, Jure, and Allan Rupprecht, "Aggregated DNA in ethanol solution," FEBS Letters 375, no. 3 (Nov 1995): 174-8, and Eickbush, Thomas, and Evangelos N. Moudrianakis, "The compaction of DNA helices into either continuous supercoils or folded-fiber rods and toroids," Cell 13, no. 2 (Feb 1978): 295-306, the disclosures of which are incorporated by reference herein in their entireties].

[00292] One aspect of the present invention contemplates that the principles regarding the precipitation of nucleic acids via the introduction of water miscible solvents can also be used to precipitate soluble salts, which, like nucleic acids, have solvation shells formed around the ions. Thus, by lowering the dielectric constant of the solution, the Coulombic attraction between the oppositely charged ions can be increased to cause the neutral salts to precipitate out of solution. This general concept has been discussed by Alfassi, Z B, L Ata. "Separation of the system NaCl-NaBr-NaI by Solventing Out from Aqueous Solution," Separation Sci. and Technol. 18, no. 7 (1983): 593-601, incorporated by reference herein in its entirety, using data on the solubilities of several salts in a mixture of water-miscible organic solvent (MOS), wherein they found that the

mass ratio (α) of the water-miscible organic solvent (MOS) to the total mass of aqueous solution (the mass of water plus the mass of solvent dissolved in the water), i.e.,

$$\alpha = M_{\text{MOS}}/M_{\text{Aqueous Solution}}$$

can be correlated against the fraction of salt precipitated from a saturated brine solution, f , as follows:

$$f = K * \alpha$$

where K is a precipitation constant. As discussed above, FIG. 2 shows a plot of f versus α for sodium chloride in water using ethylamine as an organic solvent. The actual amount of salt precipitated is f times the mass of salt in a saturated brine solution.

[00293] Additionally, if an organic solvent is added to an unsaturated brine solution, then salt precipitation may not begin right away, and there is a minimum amount of solvent needed to begin salt precipitation. This value of α is denoted as α_{min} , and so the equation " $f = K * \alpha$ " can be rewritten as follows for unsaturated salt solution:

$$f = \alpha_{\text{min}} + K\alpha$$

[00294] The value of α_{min} depends on the concentration of salt in the water. Table 2 (below) shows the value of " f " as a function of α for sodium chloride precipitated from a saturated brine with addition of ethylamine.

Table 2. Value of " f " as a function of the α for NaCl precipitated from a saturated brine with addition of ethylamine.

alpha	f
0.05	0.09469697
0.1	0.143939394
0.2	0.189393939
0.3	0.231060606
0.4	0.303030303
0.5	0.378787879
0.6	0.416666667
0.75	0.515151515

[00295] While ethylamine is discussed above as being the organic solvent, its use is merely an example, and there are other possible organic solvents (which will cause precipitation of the salt) that can be used instead of ethylamine. These possible solvents include those shown in Table 3 (with the information therein obtained from CRC Handbook of Chemistry and Physics; Organic Solvents by Riddick and Bunger; and Handbook of Solvents by Schefflan and Jacobs).

Table 3. Partial List of Organic Solvents that can be used to precipitate salt from water.

Organic Solvent	Solubility in Water (kg/L)	Heat of Vaporization (cal/g)	Specific Heat (cal/g.deg C)
Methylamine	1.08	198.1	0.385
Dimethylamine	3.54	140.4	0.366
Trimethylamine	5.5	92.7	0.371
Ethylamine	Completely	145.7	0.50
Acetaldehyde	Completely	147.5	0.336
Methylformate	0.23	112.4	0.478
Isopropylamine	Completely	109.9	0.668
Propylene Oxide	0.405	118.3	0.495
Dimethoxymethane	0.244	90.7	0.507
t-Butylamine	Completely	92.8	0.628
Propionaldehyde	0.306		0.522
N-propylamine	Completely	120.2	0.656
Allylamine	Completely		
Diethylamine	0.449	97.5	0.577
Acetone	Completely	119.7	0.249
s-Butylamine	Completely	104.9	
Ethanolamine	Completely	185.5	
Acetic acid	Completely	97.1	
Acetonitrile	Completely		
1,3-Butanediol	Completely		
1,4 Butanediol	Completely		
Butyric acid	Completely		
Diethanolamine	Completely		
2-Butoxyethanol	Completely		
Diethylenetriamine	Completely		
Dimethylformamide	Completely		
Dimethoxyethane	Completely		
1,4-Dioxane	Completely		
Ethanol	Completely	200	

Organic Solvent	Solubility in Water (kg/L)	Heat of Vaporization (cal/g)	Specific Heat (cal/g.deg C)
Ethylene glycol	Completely		
Formic acid	Completely	115.5	
Furfuryl alcohol	Completely		
Glycerol	Completely		
Methanol	Completely	263.0	
Methyl diethanolamine	Completely		
1-Propanol	Completely		
1,3-Propanediol	Completely		
1,5-Pentanediol	Completely		
2-Propanol	Completely		
Propanoic acid	Completely		
Propylene glycol	Completely		
Pyridine	Completely		
Tetrahydrofuran	Completely		
Triethylene glycol	Completely		

[00296] One or more of the solvents listed above (or other suitable solvent or solvents), or a combination of solvents, may be used to precipitate salts in accordance with the principles of the present invention. It is within the knowledge of one of ordinary skill in the art to choose which solvent or solvents to use, and such choice may be based on parameters such as the particular liquid or environment (e.g., produced water from fracking, etc.), the salt or salts to be precipitated, etc.

[00297] 1. *Definitions*

[00298] As used herein, the term "salt" means an ionic compound that undergoes dissociation in water at 25°C. The salt can have organic functionality, but in many embodiments is inorganic. The salt is a single salt species or a mixture of salts.

[00299] As used herein, the term "water miscible solvent" means an organic or inorganic solvent or mixture of two or more solvents. The solvent or mixture thereof is characterized by infinite solubility in water at 25°C, a boiling point of greater than 25°C at 0.101 MPa, a heat of

vaporization of about 0.5 cal/g or less, and no capability to form an azeotrope with water at any temperature.

[00300] As used herein, the term "significant" or "significantly" means at least half. For example, a solution that contains a "significant amount" of a component contains 50% or more of that component by weight, or by volume, or by some other measure as appropriate and in context. A solution wherein a significant portion of a component has been removed has had at least 50% of the original amount of that component removed by weight, or by volume, or by some other measure as appropriate and in context.

[00301] As used herein, the term "substantial" or "substantially" means nearly completely, and includes completely. For example, a solution that is "substantially free" of a specified compound or material may be free of that compound or material, or may have a trace amount of that compound or material present, such as through unintended contamination or incomplete purification. A composition that has "substantially only" a provided list of components may consist of only those components, or have a trace amount of some other component present, or have one or more additional components that do not materially affect the properties of the composition. For example, a "substantially planar" surface may have minor defects, or embossed features that do not materially affect the overall planarity of the film. In terms of compositions, "substantially" means greater than about 90%, for example about 95% to 100%, or about 97% to 99.9%, for example by weight, or by volume, or by some other measure as appropriate and in context.

[00302] As used herein, the term "about" modifying, for example, the quantity of an ingredient in a composition, concentration, volume, process temperature, process time, yield, flow rate, pressure, and like values, and ranges thereof, employed in describing the embodiments of the

disclosure, refers to variation in the numerical quantity that can occur, for example, through typical measuring and handling procedures used for making compounds, compositions, concentrates or use formulations; through inadvertent error in these procedures; through differences in the manufacture, source, or purity of starting materials or ingredients used to carry out the methods, and like proximate considerations. The term "about" also encompasses amounts that differ due to aging of a formulation with a particular initial concentration or mixture, and amounts that differ due to mixing or processing a formulation with a particular initial concentration or mixture. Where modified by the term "about" the claims appended hereto include equivalents to these quantities.

[00303] As used herein, the term "optional" or "optionally" means that the subsequently described event or circumstance may but need not occur, and that the description includes 15 instances where the event or circumstance occurs and instances in which it does not.

[00304][0073] Herein, methods and apparatus will be described for the separation of materials, such as salts or solvents, from water. At times, this water may be referred to as "hard" water, or "brackish" water, or "produced" water, or another type of water (which may even include waters not subjected to subsurface geological operations, such as seawater). However, those of ordinary skill in the art will recognize that the methods and apparatus described do not have to be seen as only used with the particular type of water mentioned (whether "wastewater," "produced," "hard," "brackish," "flowback," "contaminated," etc.), but with any water from any source containing a material or materials that one wishes to remove.

[00305] 2. *Process and Apparatus for Separating Salts*

[00306] One embodiment of the process (including apparatus) used to precipitate salts via the addition of an organic solvent to solution is shown in FIG. 12A. In general, in this process saline

water is mixed with a selected organic solvent, as per the discussion above. In one embodiment, this organic solvent has the following properties: (1) miscible with water; (2) boiling point higher than ambient temperature of 25°C; (3) low heat of vaporization; and (4) does not form an azeotrope with water. Additionally, the organic solvent may be non-toxic, odorless, and low cost. For example, ethylamine has a low heat of vaporization, as per Table 3, is completely miscible with water in all proportions, has a low dielectric constant and can be easily separated from water (since its boiling point is quite different than water). Those of ordinary skill in the art will recognize that other solvents (or combinations of solvents) may also be useful. For example, the use of membranes to separate solvent from water will be discussed in greater detail below. When using a membrane or membranes for solvent separation, the boiling point differences between the solvent and water are not as important (as when one separates solvent using a vaporization process). Thus, if one were to use a membrane for solvent separation, one could select a larger amine molecule, such as butylamine or even a larger amine molecule, as long as it was miscible with water and had a low dielectric constant. Again, the choice of solvent or solvents is within the knowledge of one of ordinary skill in the art.

[00307] In general, once a salt solution (such as water contaminated with one or more salts) and an organic solvent are combined, the use of the solvent will then begin to cause precipitation of salt. As salt begins to precipitate, it may be separated from the solution using at least one hydrocyclone or, as in the illustrated embodiment, multiple hydrocyclones (as will be described in greater detail below). In one embodiment, the ratio (α) of organic solvent added to the salt solution is in the range of 0.05 to 0.3. In a particular embodiment of the present invention, the entire solvent may not be added in one stage. Initially, the amount of solvent added results in salt precipitation, and the salt is separated from the solution using a hydrocyclone. The overflow

from this hydrocyclone may then be mixed with more organic solvent to achieve a concentration to make the salt precipitate, which is again separated using a second hydrocyclone. This process of incrementally adding solvent to maintain a solvent concentration for precipitation may be used to precipitate almost 70-95% of the salt from the brine.

[00308] Referring to FIG. 12A, a system 10 is shown that includes apparatus suitable for carrying out the methods of the various aspects of the invention. A liquid 12 (such as water), having one or more inorganic salts dissolved therein, such as sodium chloride, magnesium chloride, or calcium chloride, enters from source 14 via pump 16. Path 18 connects the source 14 to at least one hydrocyclone 20. Path 18 includes an in-line mixing apparatus 22. Also connected to path 18, between pump 16 and in-line mixing apparatus 22, is water miscible organic solvent source 24 including solvent 26. Thus, an initial amount of water miscible organic solvent 26, delivered from solvent source 24, is added to water 12 from source 14 in path 18, and the two components are mixed with in-line mixing apparatus 22, resulting in precipitation of some amount of the salt present in the water 12. Path 18 dispenses the mixture into hydrocyclone 20.

[00309] Hydrocyclones, in general, are devices that separate particles in a liquid suspension based on the ratio of their centripetal force to fluid resistance. Hydrocyclones generally (and as in the illustrated embodiment) have a cylindrical section 28 at the top where the slurry or suspension is fed tangentially, and a conical base 30. The angle, and hence length of the conical section, plays a role in determining operating characteristics. The hydrocyclone has two exits: a smaller exit 32 on the bottom (underflow) and a larger exit 34 at the top (overflow). The underflow is generally the denser or coarser fraction, while the overflow is the lighter or finer fraction.

[00310] Within hydrocyclone 20, a concentrated salt slurry is separated from the aqueous mixture and dispensed at exit point 32 as an underflow. The concentrated salt slurry includes at least

water, precipitated salt, and water miscible solvent. The concentrated slurry has a greater amount of precipitated salt than the overflow. The underflow exiting from exit point 32 of hydrocyclone 20 is channeled via pathway 36 to the system shown in FIG. 12B (which will be described in greater detail below). The overflow from hydrocyclone 20 is directed via path 38 to a second hydrocyclone 20'. Path 38 may include an in-line mixing apparatus 40. Also connected to path 38 may be a second water miscible organic solvent source 24'. In some embodiments, source 24 may be used by being also in fluid communication with second hydrocyclone. Thus, an additional amount of water miscible organic solvent 26, delivered from solvent source 24', is added to the overflow in path 38, and the components are mixed with in-line mixing apparatus 40, resulting in precipitation of an additional amount of the salt present in the water, and the salt is separated from the mixture in hydrocyclone apparatus 20'. A concentrated salt slurry is separated from the mixture in hydrocyclone apparatus 20' and is dispensed at exit point 32' as an underflow, which is combined with the underflow from exit point 32 of hydrocyclone 20 and flows via pathway 36 to the system shown in FIG. 12B. Overflow from hydrocyclone 20' may proceed via path 38' to a third hydrocyclone 20". Path 38' includes in-line mixing apparatus 40'. Also connected to path 38' is water miscible organic solvent source 24". In some embodiments, source 24 or source 24' may be used by being also in fluid communication with second hydrocyclone. Thus, in the illustrated embodiment, an additional amount of water miscible organic solvent 26, delivered from solvent source 24", is added to the overflow in path 38', and the components are mixed with in-line mixing apparatus 40', resulting in precipitation of an additional amount of the salt present in the water, and the salt is separated from the mixture in hydrocyclone apparatus 20". A concentrated salt slurry is separated from the mixture in hydrocyclone apparatus 20" and is dispensed at exit point 32" as an underflow, which is

combined with the underflow from exit points 32 and 32' of hydrocyclones 20 and 20', respectively, and flows via pathway 36 to the system shown in FIG. 12B.

[00311] In this manner, an unlimited number of hydrocyclones 20n are arranged in series, wherein overflows from each of the 20n hydrocyclones proceed along each path 38n to the next hydrocyclone in the series, and in each of the paths 38n, water miscible organic solvent 26 from a source 24n delivers an aliquot of water miscible organic solvent 26 to the path 38n, resulting in precipitation of an additional amount of the salt present in the water. Mixing of the combined flows in each path 38n is accomplished by an in-line mixing apparatus 40n. Salt precipitated by the addition of water miscible organic solvent 26 from each source 24n is separated from the mixture in the corresponding hydrocyclone 20n apparatus. A concentrated salt slurry is dispensed at each exit point 32n as an underflow. The underflow from all exit points 32n of the hydrocyclones 20n is combined; the combined underflow proceeds via pathway 36 to the underflow separation system shown in FIG. 12B. The final separation from the last of the hydrocyclones 20n in the series results in the exiting of a solution of water and water miscible solvent via path 42. In some embodiments, the solution in path 42 is significantly free of salt. In other embodiments, the solution in path 42 is substantially free of salt.

[00312] Because the water miscible solvent does not form an azeotrope with water, the water miscible solvent is easily separated from the overflow exiting system 10 via path 42 by the use of conventional methods such as membrane separation or distillation.

[00313] In an embodiment including the use of conventional methods such as membrane separation, a certain amount of salt may need to be removed by the series of hydrocyclones so as to prevent fouling of the membranes. (In other words, in such an embodiment, the goal is to achieve a salt concentration which would allow a membrane process to then become technically

feasible. For a membrane process to become technically feasible, the osmotic pressure difference across the membrane, in one embodiment, may be less than 1,000 psi. The osmotic pressure difference across the membrane can be calculated as follows:

$$\Delta P_{Osmotic Press} = \left[\frac{(TDS_{Feed} + TDS_{Reject})}{2} - TDS_{Permeate} \right] * 0.01$$

where $\Delta P_{Osmotic Press}$ = Osmotic Pressure Difference in psi

$TDS_{Feed}, TDS_{Reject}, TDS_{Permeate}$ = Total Dissolved Solids (TDS) in feed, reject, and permeate flows in mg / L

[00314] In other embodiments, as will be described later, the particular membrane or membranes, and their particular arrangement and/or use may also serve to prevent membrane fouling.

[00315] In other embodiments, anywhere from 50% to 99.9% of the salt may be precipitated out of the overflow water via the present process. The water miscible solvent may thus be available for recycling and can be returned, for example, to a source 24n to be reused in system 10. In some embodiments, the overflow exiting system 10 via path 42 is sent to the system shown in FIG. 12B, or a separate but similar system to that shown in FIG. 12B, such as that shown in FIG. 12C.

[00316] It will be understood that the apparatus of the invention employs at least one hydrocyclone, and optionally employs more than one hydrocyclone such as two hydrocyclones, or the three or more hydrocyclones shown in FIG. 12A, or 20n hydrocyclones. How many hydrocyclones are required to carry out effective separation will depend on many factors, including the specific water solution being addressed and the desired total percent separation of salt desired. In some embodiments, between 2 and 20 hydrocyclones are employed. The type of salt, the amount of salt, the presence of more than one species of salt, and the presence of additional dissolved materials within the water phase of the aqueous solution, for example are

relevant considerations contributing to the optimized design of the system 10. Variations thereof will be easily envisioned by one of skill.

[00317] By employing system 10 and the described separation methodology, a significant amount of salt is separated from the starting solution of inorganic salt in water, when the final water-water miscible solvent mixture that leaves system 10 as overflow is compared to the original solution of inorganic salt in water. For example, in some embodiments, about 50% to 99.9% of the salt is separated from the starting solution of inorganic salt in water, wherein the inorganic salt is separated in the form of the salt slurry. In embodiments, substantially all the salt is separated from the starting solution of inorganic salt in water.

[00318] Both the overflow from the final hydrocyclone in the series of hydrocyclones 20n... and the combined underflows from each hydrocyclone 20n will contain the organic solvent. The underflows are the separated salt slurry from the aqueous mixture formed by adding the water-miscible solvent to the solution of the inorganic salt in water. The underflows are combined into a single stream that proceeds via path 36 to an underflow separation system. One embodiment of an underflow separation system is shown in FIG. 12B. Herein this separation system may also be referred to as a degassing system. "Degassing" is a term used herein to refer to the process to remove solvent, such as that illustrated in FIG. 12B and FIG. 12C.

[00319] 3. *Separating Solvent: Vaporization Processes for Solvent Separation*

[00320] As described above, once salt is precipitated out of solution, another aspect of the present invention involves removing the solvent from the water. In order to minimize the energy for removal of solvent after separation, low-boiling temperature organic solvents may be used. The energy required to evaporate saturated brine to recover salt is 1505.5 Cal/gm of salt recovered. For ethylamine, however, the amount of energy required to heat brine and ethylamine to the

boiling point using an α value of 0.75, (i.e., 75 g of ethylamine for 100 g of saturated brine with 26.4 g of sodium chloride in solution), is 803.5 cal/g of salt precipitated. Hence, the energy ratio of the energy required to vaporize ethylamine per unit weight of salt precipitated to the energy required to vaporize water from brine per unit weight of salt precipitated is 0.53 ($803.5/1505.5 = 0.53$). Hence, the energy consumption to obtain salt using the method of the present invention using ethylamine is about half the energy that would have been expended in evaporating water from brine (one of the prior art methods).

[00321] Table 4 (below) gives the ratio of the energy needed to evaporate ethylamine to the energy required to evaporate the water. Note that this calculation is approximate since it neglects the sensible heat effects of heating the brine to its boiling point and the sensible heat required to heat the solvent mixture to the boiling point of the solvent. It is estimated that these sensible heat effects will be small compared to the heats of vaporization of the water and solvent.

Table 4. Ratio of Energy required to evaporate the Solvent, Ethylamine and the Energy required to evaporate water from the brine solution.

alpha	Energy Ratio
0.05	0.19
0.1	0.25
0.2	0.39
0.3	0.48
0.4	0.48
0.5	0.48
0.6	0.53
0.75	0.53

[00322] As noted above, alpha (α) is the ratio of the mass of solvent (in this case, ethylamine) added to the total mass of solution. The energy ratio is minimized when the amount of solvent added is the least, as shown in the table. In other words, the less organic solvent used, i.e., lower

the value of alpha, the amount of energy used to evaporate this solvent will also be less, as shown in Table 4.

[00323] Another aspect of the present invention provides a system for separating a solvent (such as the solvent used to precipitate a salt or salts) from an aqueous mixture. The system may include (1) a separator including: (a) a housing having at least one wall defining an interior space, an open top end, and an open bottom end, wherein the at least one wall has an inner surface and an outer surface; and (b) a contour disposed on, or in, or defined by, at least a portion of the inner surface of the at least one wall; and (2) wherein a flow path for an aqueous mixture may be provided by at least a portion of the contour and the inner surface of the at least one wall.

[00324] One example of a separator is a wetted wall column. As is known to those of ordinary skill in the art, a wetted wall column is a vertical column that operates with the inner wall or walls thereof being wetted by the liquid being processed, and these columns are used in theoretical studies of mass transfer rates and in analytical distillations. Thus, while wetted wall columns have been known in the prior art, they were developed for quantitatively determining the mass transfer coefficient in laboratories (i.e., the theoretical studies referenced above), and have never been used for industrial applications, mainly due to two reasons. First, the surface area of a wetted wall column is very limited, and so such a column would not be considered an efficient apparatus to use at the high flow rates of water in processes such as fracking. In wetted wall columns, the contact surface area between the gas and liquid phases is basically $\pi \cdot D \cdot L$ where $\pi = 3.142$, D is the inner diameter of the tube and L is the length of the tube. Thus, even if one uses multiple tubes, the total surface area would be limited, or the number of tubes needed to operate in an industrial use, such as at fracking flow rates, would be prohibitive. The second reason such columns have not been used in industrial applications is because the flow of liquid

down the inner surface of the tube is initially laminar and then gets turbulent beyond a certain length, as the liquid flows downwards due to gravity. Because the initial part of the flow is laminar, it will have poor mass transfer characteristics. And so, this initial entrance region with laminar flow has limited applicability in industrial applications wherein high mass transfer rates are desired.

[00325] Due to these limitations, wetted wall columns have been confined to laboratories and are basically used to teach the principles of mass transfer to chemical engineering students or to quantify the mass transfer coefficient for a given gas-liquid system. However, the particular separator (e.g., wetted wall column) of the present invention is structured in a novel manner that allows for its effective use in removing solvent on the scale needed.

[00326] To that end, the separator of the present invention may be, in one embodiment, a hollow cylindrical pipe having a top opening, a bottom opening, an inner wall, and an outer wall, and further including a contour disposed on at least a portion of the inner wall. The separator may be a wetted wall column. The contour may be, for example, a helical threaded feature disposed in, on, or associated with at least a portion of the inner wall of the tube. It should be noted that while this embodiment is described as a tube (which would be generally thought to have a circular or oval or similar cross-section), the separators described herein are not limited to tubes, but may include housings having multiple walls and cross-sections other than circular, oval, or similar (such as square, triangular, or trapezoidal cross-sections, for example).

[00327] A further aspect of the present invention provides an evaporator apparatus including one or more separators, which may be one or more wetted wall columns including a hollow cylindrical tube having a top opening, a bottom opening, an inner wall, and an outer wall, and including a contour (such as a helical threaded feature) disposed on, or in, or associated with, at

least a portion of the inner wall. The evaporating further contemplates, in some embodiments, the use of a wetted wall separation tube in the shape of a hollow cylinder or a pipe, or it can be a hollow frustoconical shape, or a hollow cylinder or a pipe having a frustoconical portion.

[00328] In certain embodiments, the tube includes an inner wall and an outer wall, wherein a contour is defined by at least a portion of the inner wall (or alternatively, may be positioned on, or otherwise associated with, the inner wall). In certain embodiments, the contour may include a helical threaded feature defined by at least a portion of the inner wall, or disposed on, or in, at least a portion of the inner wall. In some embodiments, the helical threads are of substantially the same dimensions throughout the portion of the inner wall where they are located; in other embodiments, helical threads of different dimensions occupy different continuous or discontinuous areas of the tube. The helical shape is useful in certain embodiments of the present invention, as it is easy to manufacture using a mandrel, and it also provides a gravity force for solids (which may be separated from any liquids) to travel along, instead of having obstructions that would allow the solids to build up within the separator.

[00329] In some embodiments, a series of fins defines at least a portion of the outer wall. In some embodiments, the tubes also include one or more weirs proximal to, or spanning the opening of one end of the tube. In some embodiments, the tubes also include a smooth inner wall portion proximal to one end of the tube.

[00330] In certain embodiments, one or more wetted wall separation tubes may be employed to carry out the evaporating described above. The method of evaporating the water miscible solvent from the aqueous mixture may include disposing the tube in a vertical position, flowing a salt slurry into the top opening, and allowing the slurry to proceed down the tube as aided solely by gravity. In some embodiments, a vacuum is applied to the top of the tube, or a flow of air or

another gas is applied through the bottom of the tube, or both. Movement of gas upward through the tube maximizes the evaporation rate of the water-miscible solvent. In some embodiments, the tube is heated in order to mitigate the loss of heat of evaporation. In some embodiments, a significant amount of the precipitated salt follow the path of the helical thread and proceeds in a circular pattern downward through the tube, while the water/water miscible solvent blend flows substantially vertically, such that the helices present multiple "weirs" or walls over which the water flows. This in turn causes turbulence in the vertical flow. The turbulent flow aids in the evaporation of the water miscible solvent. In some embodiments, the turbulent flow is substantially separate from the substantially laminar flow that proceeds within the helical threads. The water at the bottom of the tube is significantly free, or substantially free, of the water miscible organic solvent.

[00331] It is an advantage of the wetted wall separator tubes of the invention that the length of the tubes, and the number thereof employed in the evaporation process, are easily selected and optimized in order to achieve the separation of the selected water miscible solvent from the slurry formed in the separation. The general characteristics that are used to determine how to achieve such optimization are: (a) the mass transfer coefficient between the gas and liquid phase, which depends on the liquid flow rate per tube and the length of each tube (the liquid flow rate per tube = Q/N , where Q = total liquid flow rate, and N = number of vertical tubes); (b) the mass transfer coefficient, which gives the amount of organic solvent that can be evaporated per tube; and (c) the liquid flow rate per tube, which will be selected to prevent dry spots within the inner surface of the tube, as well as prevent a low mass transfer coefficient. Measuring or calculating these characteristics are within the knowledge of one of ordinary skill in the art.

[00332] One of ordinary skill in the art (with knowledge of the above characteristics) will then be able to determine a reasonable number of tubes for a selected length of tube in order to achieve the separation desired. By this manner, and as will be described in greater detail below with respect to systems for separation, one can then effectively separate a solvent from a liquid at the volumes and flow rates needed to treat liquids in industrial processes – which heretofore has not been achieved.

[00333] The separator (such as a wetted wall column including a contour feature) described herein overcomes the limitations of, for example, wetted wall columns of the prior art, which could not be used on an industrial scale for such separations. This is due at least to the following non-limiting list of novel features and aspects of the separator, system, and method of the present invention:

[00334] First, in the present separator, the tubes have a projection or projections inside the tube (e.g., contour, such as a helical threaded feature) that allow the liquid flow to get turbulent right away (as opposed to laminar flow) and additionally creates a very large surface area between the turbulent liquid flow and the gas phase (which enhances the volume and rate of evaporation of solvent – and thus separation of same – from liquid). Second, the contact surface area between the gas and liquid phases is not just $\pi \cdot D \cdot L$, as in the case of laminar flow, but significantly higher as the liquid flow is broken down by the projection or projections (i.e., contour or contours) into many small flows and creates mixing of the liquid as it flows downwards by gravity. Third, by having the contour or contours inside the tube, and corrugated fins outside (as will be described in greater detail below), a large surface area is created for heat transfer into the liquid phase. Thus, the separators (e.g., wetted wall columns) of the present invention achieve not only a very high mass transfer coefficient, but a high heat transfer coefficient for effective

heat transfer into the liquid phase. Fourth, a very large number of tubes can be fit inside a very small diameter shell; thus, various embodiments of the present invention contemplate and allow for a compact system. And fifth, if there are solids present in the liquid flow, the tubes will not get clogged, as in the case of plastic media packed towers. Rather, as described above, the contour or contours can be designed to allow for any solids present to proceed to an exit point of the separator.

[00335] In another aspect, the method of the present invention may further include isolating any solid salt (e.g., any precipitated or otherwise non-dissolved salt) after separating solvent from a slurry (such as via evaporation by using one or more wetted wall columns as described herein). In some embodiments, the flow within the helical threads is substantially laminar, and so the precipitated salt particles or crystals do not tend to re-mix with the water as the water miscible solvent is evaporated. Thus, the particles may be dispensed from the bottom of the tube (or tubes) in precipitated form. In such embodiments then, the precipitated salt from the slurry added to the top of the tube is substantially recovered at the bottom of the tube. The isolating of the salt may be carried out using conventional means, such as filtration. The water that is also recovered in the isolation thus has significantly reduced, or even substantially reduced, salt content compared to the solution of salt in water that was employed to form the aqueous mixture (i.e., the aqueous mixture is the mixture of salt water and salt that was in the feed to the system).

[00336] In some embodiments, the tubes may be surrounded by a source of heat to aid in the evaporation. In some embodiments, the water miscible organic solvent is collected by providing a condenser or other means of trapping the evaporated solvent that exits the top of the wetted wall separator tubes due to the flow of gas upward through the tubes. The evaporated solvent is significantly free, or substantially free, of evaporated water, which enables the isolation of

sufficiently pure solvent. The ability to collect the water miscible solvent enables the solvent to be incorporated in a closed system of solvent recycling within the overall precipitation and evaporation process.

[00337] The concept disclosed herein, namely, that of the separation of evaporated solvent from a liquid-solid slurry while maintaining the separation of the solid from the liquid, is applicable to other systems as well. For example, in wastewater remediation, anaerobic digesters are employed to digest waste products, and produce a substantial amount of ammonia gas which remains dissolved in the water. The separator tubes of the invention are useful to provide separation of the ammonia from the water, while maintaining separate flows of the solid waste from the liquid. At the end of the tube, the solid is easily isolated from the liquid and the ammonia is stripped away from the liquid.

[00338] It will be appreciated that depending on the type of gas-liquid-solid separation to be carried out, the ratio of liquid to solid in the slurry, and the flow rate selected for the slurry through the tube, the inner diameter of the tube, the helix angle of the helical thread, and the dimensions of the helical features will necessarily be different in order to effect the most efficient separation. However, as described above, once the relevant characteristics of the separation are calculated or measured (relative to a separator of the present invention) one of ordinary skill in the art would be able to make such a determination how to optimize a system to effect the most efficient separation.

[00339] As will be recognized by those of ordinary skill in the art, both the overflow and underflow of the illustrated embodiment of FIG. 12A will include solvent (the underflow will also include a larger amount of precipitated salt). The combined overflow, from each hydrocyclone, that contains the precipitated salt, is pumped into a degassing system (seen in FIG.

12B), and the overflow from the final hydrocyclone is pumped into a degassing system (seen in FIG. 12C). The apparatus of vessel for underflow and vessel for overflow may be of similar construction (as both are used for separation of solvent). Both the system of FIG. 12B and the system of FIG. 12C may use separator apparatus to remove solvent from underflow and overflow. The separator may include, in one embodiment, a wetted wall tube (such as a wetted wall static separator tube). Further, the separator may be structured to include (a) a housing having at least one wall defining an interior space, an open top end, and an open bottom end, wherein the at least one wall has an inner surface and an outer surface; and (b) a contour disposed on or defined by at least a portion of the inner surface of the at least one wall; and (2) wherein a flow path for an aqueous mixture is provided by at least a portion of the contour and the inner surface of the at least one wall. And, in embodiments where the separator is a wetted wall tube, the tube may include the contour described above.

[00340]a. Underflow

[00341]More specifically, and referring to FIG. 12B, a system 50 is shown that includes apparatus suitable for carrying out methods of various aspects of the invention for removal of solvent from underflow. In the embodiment shown in FIG. 12B, system 50 enables the evaporation of the water miscible organic solvent 26 from the slurry, and further enables the optional separation of precipitated salt from the water, wherein one optional means for separating the precipitated salt from the water is shown in FIG. 12B. Underflow from path 36 of FIG. 12A is directed via path 52 of FIG. 12B to the top of evaporation vessel 54, via opening 56 of the enclosed top chamber 58 of vessel 54, aided by pump 60. Vessel 54 includes inlet 56 for the underflow, that is, the incoming salt slurry; top chamber 58; bottom chamber 62; outlet 64 for the concentrated salt slurry; optional jacketed area 66 with inlet 68 and outlet 70 for jacketed temperature control via

addition of a heated fluid; and wetted wall separators 72 situated substantially vertically and disposed at least partially within top chamber 58 and bottom chamber 62.

[00342] Salt slurry, that is, the underflow 74 in path 36 from a separation system 10 such as that shown in FIG. 12A enters top chamber 58 by flowing along flow path 52 through inlet 56. When the level of underflow 74 in top chamber 58 reaches the level of the top openings 76 of the wetted wall separation tubes 72, it enters and flows down the hollow tubes 72, aided by gravity. As the liquid 74 proceeds down tubes 72, a lower pressure is applied at the top of the tubes 72 by applying a vacuum 78 along path 80 leading from the top chamber 58 of vessel 54. Optionally, instead of applying a vacuum, the lower pressure is applied in some embodiments by forcing an air flow from the bottom openings 82 of tubes 72, disposed within bottom chamber 62 of vessel 54, toward the top openings 76, such as by a blower (not shown). Application of lowered pressure aids in the evaporation of the water miscible solvent from the slurry, and the organic solvent is condensed and collected via path 80 and condensed via condenser 84, and the condensed water miscible solvent 26 is stored in storage tank 86. In some embodiments, this organic solvent is recycled back to the one or more sources such as sources 24n depicted in FIG. 12A, for reuse in a subsequent separation.

[00343] Within the vessel 54, the tubes 72 have openings 76 that project into top chamber 58 and openings 82 that project into bottom chamber 62. Between top chamber 58 and bottom chamber 62 of vessel 54, an optional jacketed area 66 surrounds tubes 72; the optional jacketed area 66 has inlet 68 and outlet 70. In some embodiments, a heated fluid is pumped into inlet 68, for example, by a liquid pump or heated gas pump (not shown) and exits via outlet 70. As evaporation occurs within tubes 72, loss of heat of evaporation is mitigated by adding heat to the jacketed area 66.

[00344] In some embodiments, the wetted wall separation tubes achieve evaporation of the water-miscible solvent from the salt slurry while maintaining substantial separation of the precipitated salt, that is, preventing subsequent redissolution of the salt in the water as the water miscible solvent is evaporated. This is achieved by a contour feature of the tubes as well as the inner diameter thereof. In embodiments, the wetted wall separator tubes of the invention are characterized primarily by inner diameter defining the inner wall, and height of the tube in combination with the contour feature defining at least a portion of the inner wall.

[00345] The rate of evaporation of the water miscible solvent from the salt slurry is determined by both the wetted wall separation tube itself and by additional factors. The tube properties affecting evaporation include the height of the tube, the contour dimensions of the inner wall of the tubes and the portion of the inner wall having the contour feature thereon, and the heat transfer properties of the tube – that is, tube material properties, thickness of the tube, and presence of heat transfer features present on the outer surface of the tube. Additional factors include the heat of vaporization of the water miscible solvent, external temperature control, such as by a jacketed area 66 shown in FIG. 12B, and the amount of pressure differential within the hollow separator tube between the top and bottom of the tube length. The height of the tubes useful in the evaporation is not particularly limited, and will be selected based on the amount of water miscible solvent entrained in the slurry and the heat of evaporation of the water miscible solvent. In some embodiments, the height of the wetted wall separator tubes useful in conjunction with the separation of water miscible solvent from a slurry of sodium chloride in water, using ethylamine as the water miscible solvent, is about 50 cm to 5 meters, or about 100 cm to 3 meters. In embodiments, the portion of the total length of the tube that includes the helical threaded features present on the inner wall thereof is between about 50% and 100% of the total

inner wall surface area, or about 90% to 99.9% of the total wall surface area, or about 95% to 99.5% of the total inner wall surface area.

[00346] b. Overflow

[00347] More specifically, and referring to FIG. 12C, a system 50' is shown that includes apparatus suitable for carrying out methods of various aspects of the invention for removal of solvent from overflow. In the embodiment shown in FIG. 12C, system 50' enables the evaporation of the water miscible organic solvent 26 from the overflow, (and further enables the optional separation of any precipitated salt that may be in the overflow, wherein one optional means for separating the precipitated salt from the water is shown in FIG. 12C). Overflow from path 42 of FIG. 12A is directed via path 52' of FIG. 12C to the top of evaporation vessel 54', via opening 56' of the enclosed top chamber 58' of vessel 54', aided by pump 60'. Vessel 54' includes inlet 56' for the underflow, that is, the incoming salt slurry; top chamber 58'; bottom chamber 62'; outlet 64' for the concentrated salt slurry; optional jacketed area 66 with inlet 68' and outlet 70' for jacketed temperature control via addition of a heated fluid; and wetted wall separators 72' situated substantially vertically and disposed at least partially within top chamber 58' and bottom chamber 62'.

[00348] Salt slurry, that is, the overflow in path 42 from a separation system 10 such as that shown in FIG. 12A enters top chamber 58' by flowing along flow path 52' through inlet 56'. When the level of overflow in top chamber 58' reaches the level of the top openings 76' of the wetted wall separation tubes 72', it enters and flows down the hollow tubes 72', aided by gravity. As the liquid 74' proceeds down tubes 72', a lower pressure is applied at the top of the tubes 72' by applying a vacuum 78' along path 80' leading from the top chamber 58' of vessel 54'. Optionally, instead of applying a vacuum, the lower pressure is applied in some embodiments by forcing an

air flow from the bottom openings 82' of tubes 72', disposed within bottom chamber 62' of vessel 54', toward the top openings 76', such as by a blower (not shown). Application of lowered pressure aids in the evaporation of the water miscible solvent from the slurry, and the organic solvent is condensed and collected via path 80' and condensed via condenser 84', and the condensed water miscible solvent 26 is stored in storage tank 86'. In some embodiments, this organic solvent is recycled back to the one or more sources such as sources 24n depicted in FIG. 12A, for reuse in a subsequent separation.

[00349] Within the vessel 54', the tubes 72' have openings 76' that project into top chamber 58' and openings 82' that project into bottom chamber 62'. Between top chamber 58' and bottom chamber 62' of vessel 54', an optional jacketed area 66' surrounds tubes 72'; the optional jacketed area 66' has inlet 68' and outlet 70'. In some embodiments, a heated fluid is pumped into inlet 68', for example, by a liquid pump or heated gas pump (not shown) and exits via outlet 70'. As evaporation occurs within tubes 72', loss of heat of evaporation is mitigated by adding heat to the jacketed area 66'.

[00350] In some embodiments, the wetted wall separation tubes achieve evaporation of the water-miscible solvent from the salt slurry while maintaining substantial separation of the precipitated salt, that is, preventing subsequent redissolution of the salt in the water as the water miscible solvent is evaporated. This is achieved by a contour feature of the tubes as well as the inner diameter thereof. In embodiments, the wetted wall separator tubes of the invention are characterized primarily by inner diameter defining the inner wall, and height of the tube in combination with the contour feature defining at least a portion of the inner wall.

[00351] The rate of evaporation of the water miscible solvent from the salt slurry is determined by both the wetted wall separation tube itself and by additional factors. The tube properties affecting

evaporation include the height of the tube, the contour dimensions of the inner wall of the tubes and the portion of the inner wall having the contour feature thereon, and the heat transfer properties of the tube – that is, tube material properties, thickness of the tube, and presence of heat transfer features present on the outer surface of the tube. Additional factors include the heat of vaporization of the water miscible solvent, external temperature control, such as by a jacketed area 66' shown in FIG. 12C, and the amount of pressure differential within the hollow separator tube between the top and bottom of the tube length. The height of the tubes useful in the evaporation is not particularly limited, and will be selected based on the amount of water miscible solvent entrained in the slurry and the heat of evaporation of the water miscible solvent. In some embodiments, the height of the wetted wall separator tubes useful in conjunction with the separation of water miscible solvent from a slurry of sodium chloride in water, using ethylamine as the water miscible solvent, is about 50 cm to 5 meters, or about 100 cm to 3 meters. In embodiments, the portion of the total length of the tube that includes the helical threaded features present on the inner wall thereof is between about 50% and 100% of the total inner wall surface area, or about 90% to 99.9% of the total wall surface area, or about 95% to 99.5% of the total inner wall surface area.

[00352] 4. *Separator Apparatus*

[00353] A detail of the apparatus used in the solvent separation process (liquid degassing) is shown in FIGS. 13A and 13B. Liquid degassing is a process in which the liquid containing a low boiling point organic solvent or a dissolved gas is pumped to the top of the degassing system vessel, and the liquid, which may contain a precipitated salt, flows down vertical, high surface area tubes, by gravity. Both the overflow and the underflow liquids (from FIG. 12A) are pumped to the top of such liquid degassing vessels, as shown in FIGS. 12B and 12C. As the

liquid flows down the high surface area tubes by gravity, a lower pressure is applied at the top of the tubes using a vacuum pump or even a gas blower. This allows the lower boiling point organic solvent to evaporate out of the water and salt solution, and this organic solvent is condensed and collected in storage tanks. This organic solvent may be recycled back to the in-line mixer 16 (FIG. 12A) to be re-used.

[00354] FIGS. 13A and 13B show a schematic detail of the interior and exterior of the high surface area tubes 48, which provide a high surface area between the liquid and gas phases, allowing all the organic solvent to be recovered by evaporation. To assist in this evaporation, some ambient air may be introduced at the bottom of the tubes into the liquid degassing vessels and this air is vented after the condenser, from the organic liquid storage tanks.

[00355] The evaporating of solvent contemplates, in some embodiments, the use of a wetted wall separation tube. The tube is in the shape of a hollow cylinder or a pipe, or it can be a hollow frustoconical shape, or a hollow cylinder or a pipe having a frustoconical portion. The tube includes an inner wall and an outer wall wherein a contour, such as a helical threaded feature, defines at least a portion of the inner wall. In some embodiments the helical threads are of substantially the same dimensions throughout the portion of the inner wall where they are located; in other embodiments, helical threads of different dimensions occupy different continuous or discontinuous areas of the tube. In some embodiments, a series of fins defines at least a portion of the outer wall. In some embodiments, the tubes also include one or more weirs proximal to, or spanning, the opening of one end of the tube. In some embodiments, the tubes 48 also include a smooth inner wall portion proximal to one end of the tube.

[00356] Further detail regarding the inner and outer wall features of the separation tubes are shown in FIGS. 13A and 13B. FIGS. 13A and 13B are a schematic representation of area of at

least one of the tubes 72 shown in FIG. 12B, depicting a section of the length of the tube as indicated, further bisecting the tube in a plane extending lengthwise through the center thereof. The features of FIGS. 13A and 13B are further defined by dimensions represented by lines a, b, and arrow lines 100, 102, 104, 112, 114, 116, 118, 124, 126, and 128 of FIG. 13A. Arrows 100, 102, 104, 112, 114, 116, 118, 124, 126, and 128 of FIG. 13A are used where appropriate to describe the various features and dimensions of the indicated section of wetted wall separation tubes. It will be appreciated that the detailed schematic diagram of FIGS. 13A and 13B are only one of many potential embodiments of the wetted wall separator tubes of the invention. Additional embodiments will be reached by optimization depending on the particular application to be addressed.

[00357] Referring to FIGS. 13A and 13B, one embodiment of a wetted wall separation tube 72 is defined by effective outer diameter 100 and effective inner diameter 102 which together define the effective thickness 104 of tube section. For purposes of separating an inorganic salt from water, the tube inner diameter 102 is between about 3 cm and 1.75 cm, or between about 2.5 cm and 1.9 cm. However, for other types of separations, the inner diameter 102 will be optimized to provide the required balance of flow differences between the solid phase and the liquid phase to maintain the solid within the helical grooves and allow the liquid to flow in substantially vertical fashion over the helix ribs when the selected slurry is added to the top opening 76 of wetted wall separation tubes 72. The inner diameter 102 of tube section defines inner wall 106 of tube section. Inner wall 106 includes a helical threaded section 108 defined by helix angle 110 which is defined in turn by lines a, b; helix pitch 112; helix rib height 114; helix base rib width 116, and helix top rib width 118. Helix "land" width is defined as the helix pitch 112 minus helix base rib width 116. Helical threaded section 108 of FIGS. 13A and 13B is

further defined for purposes of separating an inorganic salt from water as follows. In embodiments, the helix angle 110 is about 25° to 60° or about 30° to 50° , about 35° to 50° , or even about 38° to 48° . In embodiments, the helix pitch 112 is about 0.25 mm to 2 mm, or about 0.5 mm to 1.75 mm, or about 0.75 mm to 1.50 mm, or about 0.85 mm to 1.27 mm. In embodiments, the helix rib height 114 is about 25 μm to 2 mm, or about 100 μm to 1 mm, or about 200 μm to 500 μm . In some embodiments the helix rib height 114 is about 254 μm . In embodiments, the helix base rib width 116 is about 25 μm to 2 mm, or about 100 μm to 1 mm, or about 200 μm to 500 μm . In embodiments, the helix top rib width 118 is about 0 μm (defining a pointed tip with no "land") to 2 mm. In some embodiments, helix rib top width 118 is the same or less than helix rib base width 116. In some embodiments, the helix rib profile is triangular or quadrilateral. The helix rib profile shape is triangular in embodiments where helix top rib width 118 is 0; a square or rectangular shape where helix top rib width 118 is the same as the helix base rib width 116; or a trapezoidal shape where helix rib top width 118 is greater than 0 but less than the helix rib base width 116. While helix rib shapes wherein helix rib top width 118 is greater than helix base rib width 116 are within the scope of the invention, in some embodiments, such features are difficult to impart to the interior of a tube such as tubes 72. Further, the helix rib top can be tilted with respect to the approximate plane of the surrounding wall; that is, angled with respect to the vertical plane. Providing a tilted helix rib top will, in some embodiments, increase or decrease the degree of turbulence generated in the flow of the liquid as it proceeds vertically within the tube.

[00358] Additionally, while the shape of the helix ribs are not particularly limited and irregular or rounded shapes for example are within the scope of the invention, in embodiments it is advantageous to provide a regular feature in order to maintain laminar flow within the helix land

area. Further, in embodiments it is advantageous to provide an angular feature such as a trapezoidal or rectangular feature in order to incur some capillary pressure to maintain the laminar flow within the boundaries of the helix land area. However, it will be recognized by those of skill that machining techniques, such as those employed to machine a helical feature into the interior of a hollow metal tube, necessarily impart some degree of rounding to a feature where angles are intended. As such, in various embodiments the angularity of the features is subject to the method employed to form the helical threaded features that define the inner wall of 10 the wetted wall separation tubes of the invention.

[00359] Referring again to FIGS. 13A and 13B, as noted above, the effective outer diameter 100 and effective inner diameter 102 together define the effective thickness 104 of tube section. Effective thickness of the tube is, in various embodiments, about 0.1 mm to 10 mm, or about 0.25 mm to 3 mm, or 0.5 mm to 1 mm where the tube is fabricated from a metal, such as a stainless steel. However, the effective thickness of the tube is selected based on the material from which the tube is fabricated as well as heat transfer properties of the material and other features that will be described in more detail below, and also for convenience. It will be appreciated that an advantage of the wetted wall separator tubes of the invention is that the tubes do not include and are not contacted with moving machine parts, and are not subjected to harsh conditions or large amounts of abrasion, stress, or shear. Therefore, it is not necessary to provide very thick effective wall thickness of the tubes, nor is it necessary to fabricate the tubes from metal, in order to achieve the goal of evaporating the water miscible solvent from the slurry.

[00360] Referring again to FIGS. 13A and 13B, the outer diameter 100 of tube section defines outer wall 120 of tube section. Outer wall 120 may include a series of fins 122 protruding from outer wall 120, wherein the fins are defined by fin thickness 124 and fin height 126. The fins are

employed in embodiments for temperature control, for example by adding heat via the jacketed area 66 as shown in FIG. 12B, to increase the rate of heat transfer. In some embodiments (not shown), there is land between the fins; in other embodiments the fins do not have land area between them. The purpose of the fins inside the pipe is to break up the liquid flow into smaller streams and create turbulence, which increases the contact surface area between the gas and liquid phases. The purpose of the corrugated fins outside the tube is to increase the surface area between the fluid outside the tubes and the liquid flowing down inside the tubes, so we can heat/cool the liquid effectively.

[00361] The shape of the fins are not particularly limited and in various embodiments rounded, angular, rectilinear or irregularly shaped fins are useful. The dimensions of the fins are not particularly limited and are determined by employing conventional heat transfer calculations optimized for the targeted evaporation process. In some embodiments, the fins have fin thickness, or width, 124 of about 0.1 mm to 10 mm, or about 0.5 mm to 5 mm, or about 0.75 mm to 2 mm. In some embodiments, the fins have fin height 126 roughly the same as the fin thickness. The dimension of the fins is incorporated into the total width 128 of the tubes. In some embodiments, instead of fins encircling the tubes, discrete projections protrude from the outer walls in selected locations. In some embodiments, the fins or projections are present over a portion of the outer wall wetted wall separator tubes; in other embodiments the fins or projections are present over the entirety thereof. However, the presence of any fins or projections is optional and in some embodiments fins or projections are unnecessary to achieve effective evaporation of the water miscible solvent.

[00362] An additional optional feature of the wetted wall separator tubes of the invention includes an entry section proximal to the top openings of the tubes that facilitates and establishes a

suitable flow of the slurry entering the tube. The entry section 130 includes the top opening 76 and a first portion 132 of the inner wall 134 of the tube. A suitable flow is created when slurry enters the tube in a volume and flow pattern enter the helical threaded portion 136 of the tube in a manner wherein the solids tend to enter the helical threaded area beneath the entry section and flow in laminar fashion within the land area 138 between the helix ribs, and the bulk of the liquid phase tends to flow substantially vertically within the tube, further wherein the vertical flow is turbulent by virtue of passing over the helix rib features. The design of the entry section will vary depending on the nature of the slurry as well as the design of the helical thread situated further along the tube as the slurry proceeds vertically. For separation of a slurry of sodium chloride, we have found that the entry section optionally includes weirs 140 proximal to the top opening, and a smooth inner wall 134 extending from the top opening 76 to the onset of the helical threaded portion 136 of the tube. The weirs are designed to provide a substantially laminar flow of slurry at a suitable volume for flowing across and into the helical threaded area of the inner wall of the tube. In some embodiments, the weirs are rounded features, such as o-ring shaped features, placed proximal to and above the top opening, that facilitate slurry flow into the tube such that the flow proceeds in contact with the inner wall thereof. In other embodiments, the weirs are a series of walls, slotted features, or perforated openings disposed above and extended across the top opening, and shaped to provide flow of the slurry into the tube such that the flow proceeds in contact with the inner wall thereof. In some such embodiments, the weirs also regulate the rate of flow into the tube. The weirs are formed from the same or a different material or blend of materials than the tube itself, without limitation and for ease of manufacture, provision of a selected surface energy, or both.

[00363] In embodiments, the weirs are followed, in a portion of the tube proximal to and below the top opening, by a smooth inner wall section. The smooth inner wall section is characterized by a lack of a helical threaded feature or any other feature that causes disruption of the slurry in establishing a laminar downward flow within the tube. In embodiments, the smooth inner wall section extends vertically from the top opening of the tube to about 0.5 mm to 10 mm from the top opening of the tube, or about 1 mm to 5 mm from the top opening of the tube. Proximal to the smooth inner wall section in the vertical downward direction, the helical threaded portion of the inner wall begins. In some embodiments the smooth inner wall section has a substantially cylindrical shape; in other embodiments it has a frustoconical shape; that is, the smooth inner wall of the tube is frustoconical leading to the helical threaded inner wall portion. The frustoconical shape is not necessarily mirrored on the outer wall of the tube, though in embodiments it is. In general, where the smooth inner wall section has a frustoconical shape, the conical angle is about 1° to 10° from the vertical.

[00364] It will be understood that the fins 122 on the outer wall of the wetted wall separator tubes, as shown in FIGS. 13A and 13B, weirs, and a smooth inner wall section are optional features, and that the only feature necessary to the wetted wall separator tubes of the invention are the basic hollow cylinder or frustoconical shape having an inner wall and an outer wall wherein a helical threaded feature defines at least a portion of the inner wall. In embodiments, the helical threaded feature extends over a significant portion of the inner wall, and in other embodiments the helical threaded feature extends over substantially the entirety of the inner wall. In still other embodiments, the helical threaded feature extends over substantially the entirety of the inner wall except for the smooth inner wall portion of the tube as described above.

[00365] In the evaporation systems of the invention, such as the system 50 shown in FIG. 12B, there is at least one wetted wall separation tube 72. The number of tubes employed, in an array of tubes contained within an evaporation apparatus, is not limited and is dictated by the rate of delivery of slurry into the apparatus. In some embodiments, an evaporation apparatus of the invention includes between 2 and 2000 wetted wall separation tubes, disposed substantially vertically and parallel to each other and having the top openings 76 substantially in the same plane. In some embodiments where two or more tubes are present in an evaporation apparatus, the tubes are placed far enough apart from one another to provide for efficient heat transfer with the surrounding environment; where a jacketed area surrounds the tubes this spacing must account for efficient flow of the heat transfer fluid around and between the tubes. It will be appreciated that the number of tubes present in a particular evaporation apparatus of the invention will be adjusted based on the selected flow rate of slurry delivered by the precipitation apparatus such as the apparatus of FIG. 12A. In some embodiments, more than one evaporation apparatus 54 is connected to path 52, or chamber 58 is split into two or more chambers, in order to address total flow of slurry from flow path 52 into the tubes 72. Such compartmentalized control is useful because tubes 72 have a range of flow operability, that is, a minimum and a maximum flow capacity wherein turbulent wetted wall flow is achieved. Higher flow rates from flow path 52 require the use of more tubes, once the maximum flow capacity of one tube or one group of tubes is reached.

[00366] The wetted wall separation tubes of the invention are not particularly limited as to the materials used to form them. Layered or laminated materials, blends of materials, and the like are useful in various embodiments to form the wetted wall separation tubes of the invention.

Materials that form the inner wall and thus the helical threaded features are selected for machining

or molding capability, imperviousness to the materials to be contacted with the inner wall, durability to abrasion from the particulates in the slurries contacted with the inner wall, heat transfer properties, and surface energy of the material selected relative to the surface tension of the slurry to be contacted with the inner wall. In various embodiments, the wetted wall separator tubes of the invention are formed from metal, thermoplastic, thermoset, ceramic or glass materials as determined by the particular use and temperatures encountered. Metal materials that are useful are not particularly limited but include, in embodiments, single metals such as aluminum or titanium, alloys such as stainless steel or chrome, multilayered metal composites, and the like. It is important to select a metal for the inner wall of the tubes that is impervious to water, salt water, or the selected water miscible solvent. In some embodiments, metals have the additional advantage of providing excellent heat transfer, and so are the material of choice. In some embodiments, stainless steel is a suitable material for use in conjunction with the separation of sodium chloride from water. In some embodiments, it is advantageous to employ thermoplastic materials as part of, or as the entire composition of the tubes due to ease of machining or to minimize cost, or both. Further, in embodiments thermoplastics may be molded around a helically-shaped template and the helical threaded features imparted to the molded tubes are, in some embodiments, more defect-free than their metal counterparts. However, a thermoplastic selected to compose the inner wall of the tube must be substantially impervious to any effects of swelling or dissolution by water, salt water, or the selected water miscible solvent and substantially durable to the abrasion provided by movement of slurry particles within the tubes. Examples of suitable thermoplastics for some applications include polyimides, polyesters, polycarbonate, polyurethanes, polyvinylchloride, fluoropolymers, chlorofluoropolymers, polymethylmethacrylate, polyolefins, copolymers or blends thereof, and the like. The

thermoplastics further include, in some embodiments, fillers or other additives that modify the material properties in a way that is advantageous to the overall properties of the tube, such as by increasing abrasion resistance, increasing heat resistance, raising the modulus, or the like.

Thermosets are typically crosslinked thermoplastics wherein the crosslinking provides additional dimensional stability during e.g. temperature changes or any tendency of the polymer to dissolve or degrade in the presence of water, salt water, or the selected water miscible solvent. Radiation crosslinked polyolefins, for example, are suitable for some applications to form the inner wall or the entirety of a wetted wall separation tube of the invention. Ceramic or glass materials are also useful materials from which to form the wetted wall separation tubes of the invention and are easily machined to high precision in some embodiments.

[00367] The wetted wall separation tubes are particularly well suited for providing a means for evaporating the water miscible organic solvent from the salt slurry formed using the methods of the invention. It is an advantage of the wetted wall separation tubes that no moving parts reside within the tubes; and that the tubes are of simple design; and that the tubes contain no features that tend to collect and/or aggregate the slurry particles. The evaporation of the water miscible solvent is highly efficient using the wetted wall separation tubes of the invention, and the solid slurries particles are able to proceed in unfettered fashion downward through the tube. The wetted wall separation tubes provide a high surface area between the liquid and gas phases, allowing substantially all of the water miscible solvent to be recovered by evaporation and resulting in an overall efficient and rapid evaporation process. Because the salt crystals formed during the fractional addition of the water miscible solvent are small, they can be carried down the tubes along with some amount of liquid, in some embodiments in a substantially laminar flow that follows the helical threaded pathway.

[00368] Referring once again to FIG. 12B, after evaporation from the wetted wall separation tubes 72, a concentrated salt slurry 150 exits tubes 72 at bottom openings 82 thereof. The precipitated salt and water, now substantially free of water miscible solvent, flow into bottom chamber 62 and exit outlet 64 as a concentrated salt slurry. In some embodiments, the salt crystals have been subjected to substantially laminar flow and do not tend to redissolve in the water as the water miscible solvent is removed from the turbulent flow. Thus, the crystals are easily isolated from the concentrated salt slurry exiting tubes 72 at bottom openings 82. The concentrated salt slurry is deposited into a collection apparatus 152. Collection apparatus 152 as shown is the same or similar to cylinder formers developed for papermaking applications, as will be appreciated by those of skill. Cylinder former 152 includes a horizontally situated cylinder 154 with a wire, fabric, or plastic cloth or scrim surface that rotates in a vat 156 containing the concentrated salt slurry 150 delivered from exit outlet 64. Water associated with the slurry 150 is drained through the cylinder 154 and a layer of precipitated salt is deposited on the wire or cloth, and exits collection apparatus 152 via pathway 158. The drainage rate, in some designs, is determined by the slurry concentration and treated water level inside the cylinder such that a pressure differential is formed. As the cylinder 154 turns and water is drained from the slurry, the precipitate layer that is deposited on the cylinder is peeled or scraped off of the wire or cloth, such as with a scraper blade 160 or some other apparatus, and continuously transferred, such as via a belt 162 or other apparatus, to receptacle 164. In some embodiments, during transport of the deposited layer of salt 166 to the receptacle 164, the salt is dried, such as by applying a hot air knife (not shown) across the belt 162 or by heating belt 162 directly, or by some other conventional means of drying salt crystals.

[00369] In some embodiments, water exiting collection apparatus 152 via pathway 158 may be sent to a subsequent treatment apparatus, such as ultrafiltration or nanofiltration, in order to remove the remaining salt or another impurity.

[00370] In some embodiments, the tubes are surrounded by a source of heat 66 to aid in the evaporation. In some embodiments, the water miscible organic solvent is collected by providing a condenser or other means of trapping the evaporated solvent that exits the top of the wetted wall separator tubes due to the flow of gas upward through the tubes. The evaporated solvent is significantly free, or substantially free, of evaporated water, which enables the isolation of sufficiently pure solvent. The ability to collect the water miscible solvent enables the solvent to be incorporated in a closed system of solvent recycling within the overall precipitation and evaporation process.

[00371] It will be appreciated that depending on the type of gas-liquid-solid separation to be carried out, the ratio of liquid to solid in the slurry, and the flow rate selected for the slurry through the tube, the inner diameter of the tube, the helix angle of the helical thread, and the dimensions of the helical features will necessarily be different in order to effect the most efficient separation.

[00372] The liquid degassing vessel is one method to achieve a high surface area between the gas and liquid phases. Other methods that could be used is a packed tower, with packing to increase the contact surface area between the gas and liquid phases, or even a spray tower in which the liquid is sprayed in the form of small droplets into the gas phase, which is maintained at a lower pressure. The low boiling point solvent would then transfer from the liquid to the gas phase.

[00373] Degassing of the organic solvent means that the organic solvent should have a low boiling point and preferably a low heat of vaporization. However, the energy of vaporization

needs to be supplied in order to convert the organic to the vapor state and remove it from the liquid water phase. In order to achieve a high removal efficiency for the organic, the boiling point difference between the organic and water should be as large as possible. Hence, some of the possible organics listed in Table 3 have a low boiling point when compared to water.

[00374] If the boiling point of the organic solvent and water are not very different, a multi-effect distillation column can be used to separate the organic from the water and achieve a high degree of separation for the solvent. As is known to those of ordinary skill in the art, multi-effect distillation is a distillation process that includes multiple stages. In each stage, the feed liquid (e.g., water) is heated (such as by steam) in tubes. Some of the liquid evaporates, and this steam flows into the tubes of the next stage, heating and evaporating more liquid. Each stage essentially reuses the energy from the previous stage. FIG. 14 shows an example of a multi-effect distillation column in which organic solvent is separated using two distillation columns operating at two different pressures. In this embodiment, one column operates at a higher pressure than the other column, and in the higher pressure column, the temperature of the condenser is higher than the temperature of the reboiler, which allows the heat evolved by the condensation of the vapors to be used to reboil the liquid in the reboiler.

[00375] More specifically, and referring to FIG. 14, the feed water, containing salts (monovalent, divalent, etc.), enter into feed pump 170 and then flows into settler vessel 172. The feed water may be any water prior to any contact with solvent – and as can be seen from the figure, and as will be described in greater detail below, the feed water will mix (in the illustrated embodiment) with recovered streams containing solvent. Additional solvent is added to the vessel 172 also, to make up any loss of organic solvent(. Such loss occurs, for example because any liquid removed from the settler vessel will likely include some amount of solvent, and so to maintain the amount

of solvent in the vessel, the solvent needs to be replenished. In the settler vessel 172, some of the divalent and monovalent salts are precipitated (due to the presence of solvent), and the resulting slurry of water and precipitated salts is removed through valve 174. Alternatively or additionally, some of this precipitated salt and water is recycled back to the starting point (i.e., feed point) using the recycle pump 176, where it is again directed into the settler vessel 172 via feed pump 170. The salt crystals that are present in this recycled slurry (of water and precipitated salt) assist in nucleating further salts (divalent, monovalent, etc.) from further incoming feed water, which promotes greater growth of salt crystals (upon solvent-induced precipitation from the feed water), which in turn promotes faster settling of precipitated salt in the settler, due to the increased crystal size.

[00376] The more clear portion of water from the settler, i.e., that portion having a lower concentration of salts (divalent, monovalent, etc.), will be located nearer to the top of the body of liquid in the tank 172, since the salt crystals will generally sink toward the bottom of the tank 172 (as described above). Thus, this more clear portion of water may be pumped by pump 178 into a first distillation column 180 (for removal of solvent), which may be set to operate at a lower pressure than a second distillation column 182. The organic solvent is removed as a pure compound or as an azeotropic composition with water as the top product, which is condensed, and collected in overhead product drum 184. A portion of the recovered solvent may then be returned back to the top of the first distillation column 180 as reflux, and the remaining portion may be recycled back to the settler tank 172 using pump 186. In this manner the organic solvent is recovered and recycled back to the settler 172 to precipitate more salt from the feed water.

[00377] The bottom product, (i.e., the portion that exits the bottom of the first distillation column 180) containing salts and water, may be partially reboiled back as water vapor (via the use of

first heat exchanger 194) and returned back to the bottom of this distillation column. The remaining portion of this bottom product may be withdrawn by pump 168 and fed into the second distillation column 182, which operates at a higher pressure than the first distillation column 180. The reason for operating the second distillation column 182 at a higher pressure than the first distillation column 180 is due to the fact that at a higher pressure, the boiling point (condensing temperature) of the pure water, produced in the top product of distillation column 182, will be higher than the boiling point of the bottom product of the first distillation column 180, and thereby the heat of condensation of water vapor exiting the top of second distillation column 182 can be used to partially vaporize the bottom product of first distillation column 180 (as shown in FIG. 14). This allows heat integration of the two distillation columns to minimize the net energy consumption within this process. The second distillation column 182 is operated at a pressure such that this heat transfer can occur economically with a reasonable temperature driving force and heat exchanger area.

[00378] The top product of second distillation column 182 is pure water, with no salt, and this water is pumped by pump 190 as the distilled water product. The bottom product of distillation column 182 includes mainly salt water. A portion of this bottom product may be partially reboiled back as water vapor (via the use of second heat exchanger 196) and returned back to the bottom of the second distillation column 182. The remaining portion of this salt water is pumped by pump 192 back to the settler to allow more salt to be precipitated.

[00379] By using the two distillation columns with heat integration, achieved by operating the second column 182 at a higher pressure than distillation column 180, the organic solvent is recovered and recycled back and salt is continuously precipitated from the feed water.

The salt slurry produced from the bottom of the settler can be further filtered, (filter not shown in FIG. 14), and the salt water, once separated from the wet salt, can also be recycled back to the settler.

[00380] 5. *Alternate Solvent Separation Methods*

[00381] Apart from the evaporation processes described above, other methods of separation of solvent may use non-vaporization processes to separate the organic solvent from the salt water solution.

[00382] One such separation method which does not require any vaporization of the solvent is a membrane process, in which the solvent is separated from the water using either a porous membrane, such as ultrafiltration or nanofiltration, or a dense membrane process, such as reverse osmosis. Thus, in various aspects and embodiments, the methods and apparatus of the present invention may use only one of these types of membranes, or any combination of these types of membranes. For effective membrane separation of the solvent from the water, a suitable membrane has to be used, i.e., one which can reject the solvent molecules and allow water (pure or salt water) to pass through. Of course, if a non-vaporization method is being used to separate the organic solvent from the water, then the energy ratio calculated in the above Table 4 is no longer applicable, since the energy ratio assumed that the solvent was going to be evaporated. However, in a membrane process using a dense membrane film, such as reverse osmosis, the osmotic pressure exerted by the solvent needs to be accounted for, and since a higher molecular weight solvent will exert a lower osmotic pressure than a lower molecular weight solvent, a higher molecular weight solvent may be useful in certain embodiments (as opposed to a lower weight solvent), such as where the concentrations of the two solvents would be the same (or similar) to achieve the same extent of salt separation. Further, in certain embodiments, a higher

molecular weight solvent may have greater potential to be separated and recycled back using ultrafiltration and/or nanofiltration, which have much lower operating pressure membranes than reverse osmosis (due to the more dense nature of the reverse osmosis membranes). Thus, in certain embodiments, the choice of solvent and membranes may further reduce the energy expenditure required.

[00383] As described above, any organic solvent that is miscible in water and changes the dielectric constant of the water solution to some extent can be used to cause salt precipitation to occur. In general, if the solvent has a large molecular weight then it can be separated from water using a reverse osmosis or even an ultrafiltration or nanofiltration membrane. In other words, larger molecules, depending on molecular weight would be rejected by the membrane, while water would pass through the membrane. As will be recognized by those of ordinary skill in the art, the larger the solvent molecule, the easier it is to remove it from the salt water using membranes. On the lower end, if distillation columns are being used, as in FIG. 14, then the solvent molecule can be small since then it can be easily boiled at a lower temperature. The rejected organic solvent can then be recycled back for reuse to precipitate more salt from the water.

[00384] Another embodiment of the present invention may use a reverse osmosis or a nanofiltration membrane to concentrate the salt in water to achieve almost a saturated salt in water condition in the membrane reject stream (i.e., before the addition of any solvent). Then the solvent precipitation process can be used for this salt-concentrated reject stream to precipitate the salt from the water.

[00385] Further, as will be described in greater detail below, when using membranes for separation, a concern is always the extent to which (and the rapidity with which) the membranes

may become fouled (e.g., clogged) to an extent that reduces their effectiveness such that they must be cleaned or replaced. Any time membranes must be cleaned or replaced, the system containing those membranes experiences down time, which is not cost efficient. As will be described in greater detail below, a further aspect of the present invention provides embodiments of separation systems using membranes that greatly reduce or eliminate the amount of membrane fouling. In certain embodiments, the methods and apparatus of the present invention may be used to prevent fouling or clean membranes during salt and solvent separation.

[00386] As described above, membranes that may be used in various aspects and embodiments of the present invention include ultrafiltration, nanofiltration, and reverse osmosis. Each of these will be described in greater detail below.

[00387] a. Ultrafiltration

[00388] Ultrafiltration is a variety of membrane filtration in which hydrostatic pressure forces a liquid against a semipermeable membrane. Suspended solids and solutes of high molecular weight are retained, while water and low molecular weight solutes pass through the membrane. Ultrafiltration is not fundamentally different from nanofiltration except in terms of the size of the molecules it retains.

[00389] The objective of ultrafiltration is to remove any particulates that may be present in the water while allowing all soluble species to get through the membrane. One of the main challenges in ultrafiltration is to maintain a high flux of water through the membrane, while minimizing the buildup of particulates on the membrane surface (i.e., prevention of membrane fouling (as described above)).

[00390] Ultrafiltration can be conducted using several membrane configurations, including: (1) hollow fiber membranes, (2) spiral wound membranes, (3) flat sheet membranes, and (4) tubular

membranes. Hollow fiber membranes include several hundred fibers installed within a cylindrical shell such that the feed water permeates through the membrane to the inside of the fibers. The particulates stay outside the fibers, and periodically through back-flushing and use of air and chemicals, the deposited particulates on the membrane surface are taken off the membrane surface and flushed away with the reject stream. In spiral wound membranes, flat membrane sheets are wound into a spiral, and spacers are used to separate the feed water from the permeate. Flat sheet membranes are installed as parallel sheets and have spacers to separate the feed water from the permeate. And tubular membranes, which are larger diameter tubes installed within a shell, operate much like the hollow fibers, except the tubes are longer and the number of tubes is (e.g., in the tens rather in the hundreds).

[00391] Of all the membrane configurations, hollow fibers are the most compact with the highest surface area per unit volume. However, since the particulates are deposited outside the hollow fibers, and there are several hundred and even thousands of these very small diameter hollow fibers installed within a small diameter cylindrical shell, the particulates get caught within the fibers and are difficult to dislodge from the outside of the fibers. Spiral wound membranes have a very narrow space between the spirally wound flat sheets, since the spacers are thin, and this causes the spaces between the flat sheets to get clogged with particulates easily. Flat sheet membranes are easier to clean, but have a large number of gaskets, with one gasket between each sheet and the membrane modules are not compact. Of all the membrane configurations, tubular membranes are perhaps the easiest to clean any particulate deposits off the membrane surface, though typical uses of tubular membranes will still result in membrane fouling. These various characteristics may be used by one of ordinary skill in the art to determine which membrane type

to use in various embodiments of the present invention. One embodiment of the invention may use spiral wound membranes, for example.

[00392] With reference to FIG. 15, the following is a description of an example of one possible embodiment of use of ultrafiltration to recover solvent following salt precipitation. As described above, if the organic molecule has a high molecular weight, such as a sugar, then a simple ultrafiltration membrane can be used to recover the solvent. The high TDS feed water is pumped by the feed pump 200 into the settler 202, wherein it mixes with the organic solvent, which results in the precipitation of salts, BOD, COD, etc. The settled solids are taken out from the bottom of the settler and the solid slurry is sent to a filter, not shown in FIG. 15, by a valve 204. Some of this solid slurry is diverted by the valve 204 into the recycle pump 206, which returns this slurry back to the inlet of the settler. The objective of recycling this solid slurry is that the precipitated salt crystals serve as nucleation sites for further crystal growth, and this allows the larger salt crystals to precipitate faster in the settler. The clear liquid from the settler is pumped by the pump 208 into a membrane unit, which is capable of separating the organic solvent from the salt water. If the organic solvent is a high molecular weight organic, such as sugar, then the membrane unit 210 can be an Ultrafiltration membrane unit, and this would allow the organic solvent to be separated at lower operating pressures than if a nanofiltration membrane or even a reverse osmosis membrane had to be used. The salt water passes through the membrane and is further treated to remove the salt using other membrane units, such as nanofiltration and/or reverse osmosis, not shown in FIG. 15. The organic solvent separated by the membrane unit 210 is simply recycled back to the settler.

[00393] More specifically, and referring to FIG. 15, the feed water, containing salts (monovalent, divalent, etc.), enter into feed pump 200 and then flows into settler vessel 202. (Additional

solvent is added to the vessel 202 also, to make up any loss of organic solvent. This make-up solvent is to make up for solvent losses when the salt slurry is sent to the filter, not shown in FIG. 15, wherein the wet salt is separated from the salt water, which is returned back to the settler. In the settler vessel 202, some of the divalent and monovalent salts are precipitated (due to the presence of solvent), and the resulting slurry of water and precipitated salts is removed through valve 204. Alternatively or additionally, some of this precipitated salt and water is recycled back to the starting point (i.e., feed point) using the recycle pump 206, where it is again directed into the settler vessel 202 via feed pump 200. The salt crystals that are present in this recycled slurry (of water and precipitated salt) assist in nucleating further salts (divalent, monovalent, etc.) from further incoming feed water, which promotes greater growth of salt crystals (upon solvent-induced precipitation from the feed water), which in turn promotes faster settling of precipitated salt in the settler, due to the increased crystal size.

[00394] The more clear portion of water from the settler 202, i.e., that portion having a lower concentration of salts (divalent, monovalent, etc.), will be located nearer to the top of the body of liquid in the tank 202, since the salt crystals will generally sink toward the bottom of the tank 202 (as described above). Thus, this more clear portion of water may be pumped by pump 208 to an ultrafiltration membrane 210 (for removal of solvent). The organic solvent is removed as it cannot pass through the membrane, and so the rejected solvent may be directed via pump 212 to be recycled back to the settler tank 202. In this manner the organic solvent is recovered and recycled back to the settler 202 to precipitate more salt from the feed water.

[00395] Thus, the solvent separated by the ultrafiltration membrane in FIG. 15 can be recycled back for reuse and the salt water that passes through the ultrafiltration membrane may then be further treated using a nanofiltration process or reverse osmosis process or combined

nanofiltration/reverse osmosis process. One benefit of the above-described solvent precipitation process is to reduce the salt concentration in the feed water, which will further reduce the osmotic pressure needed to use nanofiltration/reverse osmosis membranes to subsequently purify the water. The reject streams from the nanofiltration/reverse osmosis membranes containing solvent, can all be recycled back to the inlet of the solvent precipitation process, to again be used to precipitate salts from incoming water (or other liquid).

[00396] Further, as described above, in previously used membrane processes, problems arise with fouling of the membranes. Previously used strategies to keep the membrane surface clean include (1) air injection, which helps in dislodging any deposits off the membrane surface without causing any harm to the membrane surface, (2) back-pulsing by forcing the permeate backwards through the membrane into the feed side, while interrupting the feed flow, to dislodge any particulates deposited on the membrane pores, and (3) chemicals, such as citric acid to loosen any deposits on the membrane surface. However, there are drawbacks to each of these methods. For example, back-pulsing and chemical cleaning requires the use of several control valves, which have to open and close in order to isolate the membrane module temporarily for cleaning, so that the cleaning chemicals or the permeate do not mix with the feed flow.

[00397] Further, any of these previously used methods reduce the throughput of water through the membrane and hence their use has to be kept to a minimum, if possible. There are two kinds of particulates that can deposit on the membrane surface: (1) organic, such as sludge, bacterial growth, etc., and (2) inorganic precipitates of insoluble salts of metals such as calcium, magnesium, iron, etc. which form a hard scale that can only be dissolved by strong acids. Biological growth is usually prevented by using biocides such as hypochlorite, ozone dissolved in water, etc.

[00398] Thus, another aspect of the present invention is a method to reliably keep ultrafiltration membranes from clogging without significantly reducing the productivity of the membrane and requiring several control valves. This will be described in greater detail below.

[00399] b. Nanofiltration

[00400] As described above, nanofiltration may be used to separate salts and/or solvents from water. Alternatively, or additionally, nanofiltration may be used subsequent to an ultrafiltration process as described above. Nanofiltration is a cross-flow filtration technology which ranges somewhere between ultrafiltration and reverse osmosis. As previously mentioned, nanofiltration differs from ultrafiltration at least in the size of the molecules that are allowed to pass through the membrane. The nominal pore size of the membrane is typically about 1 nanometer.

However, nanofilter membranes are typically rated by molecular weight cut-off (MWCO) rather than nominal pore size. The MWCO is typically less than 1000 atomic mass units (daltons). The transmembrane pressure (pressure drop across the membrane) required is lower (up to 3 MPa) than the one used for reverse osmosis, reducing the operating cost significantly.

[00401] Nanofiltration is a membrane process that may be used by itself, or may be used sequentially after the ultrafiltration process. The objective of nanofiltration in various aspects of the present invention is to reject the majority of the divalent soluble ionic species that have not been previously precipitated or otherwise removed from the water.

[00402] As is known by those of ordinary skill in the art, every salt precipitated has a finite aqueous solubility, and these soluble species will not precipitate below their normal solubility. The concentration of salts in liquids such as produced/brackish water may be decreased by using the organic solvent precipitation process, as described above, (and the concentration of all the salts may be decreased to reduce their osmotic pressure). As is known to those of ordinary skill

in the art, the osmotic pressure, P_{osm} , of a solution can be determined experimentally by measuring the concentration of dissolved salts in solution via the equation, $\text{Posm} = 1.19 (T + 273) * \Sigma(mi)$, where Posm is osmotic pressure (in psi), T is the temperature (in °C), and $\Sigma(mi)$ is the sum of molar concentration of all constituents in a solution. An approximation for P_{osm} may be made by assuming that 1000 ppm of Total Dissolved Solids (TDS) equals about 11 psi (0.76 bar) of osmotic pressure. This approximation comes from the Van't Hoff equation, which is well known to those of ordinary skill in the art: $P'_{\text{osm}} (\text{atm}) = iMRT$, where P'_{osm} is in atm, M is the concentration of salt in gmoles/L, $R = 0.08205746 \text{ atm.L.K}^{-1}.\text{mol}^{-1}$, T is the temperature in degrees Kelvin, and i is the dimensionless Van't Hoff factor; 1.19 is the product of R and 14.7, which converts atm into psi, and 155 is the approximate average molecular weight of the divalent and monovalent salts; Each mole of salt yields about 2 ions, and hence the sum of molar concentrations is the sum of the concentration of the positive and negative ions from the salt. The Van't Hoff factor for NaCl is 2.

[00403] Further, as is known to those of ordinary skill in the art, the flow of water across a membrane (Q_w) depends on the difference between the feed pressure and the osmotic pressure, Posm : $Q_w = (AP - AP_{\text{osm}}) * K_w * S/d$, where Q_w is the rate of water flow through the membrane, AP is the hydraulic pressure differential across the membrane, AP_{osm} is the osmotic pressure differential across the membrane, K_w is the membrane permeability coefficient for water, S is the membrane area, and d is the membrane thickness. This equation is often simplified to: $Q_w = A * (\text{NDP})$, where A represents a unique constant for each membrane material type and NDP is the net driving pressure or net driving force for the mass transfer of water across the membrane. The constant "A" is derived from experimental data, and manufacturers supply the "A" value for their membranes.

[00404] As described above, the nanofiltration process may be used to remove some or all of the divalent soluble salts that have not been previously precipitated and/or otherwise removed. And so, to accomplish this, in nanofiltration, the feed pressure has to exceed the osmotic pressure of all the soluble divalent salts in the feed water.

[00405] As with ultrafiltration (or any other membrane process), it is important to keep the membrane surface clean (i.e., prevent membrane fouling) so that efficient separation can be achieved (while minimizing or eliminating downtime of a system due to membrane cleaning or replacement). Methods to combat fouling of nanofiltration membranes are: (1) air bubbles, which disturb the deposition layer of the salts on the membrane surface; (2) use of antifouling chemicals, which keep these salts in a dissolved state, even when they achieve high concentrations at the membrane surface; (3) back flow, by temporarily decreasing the feed pressure, which causes reverse flow through the membranes, and (4) low pH, i.e., acid conditions, since most salts have a high solubility at low pH. For example, in one embodiment of the present invention, both air injection and back flow may be used, by decreasing the feed pressure below the osmotic pressure of the salts, thereby causing reverse flow through the membranes.

[00406] For example, in one embodiment of such a process, one may drop the pressure in the system while liquid is still flowing through the membrane. The pressure may then be caused to drop below osmotic pressure. When this occurs, the osmotic pressure forces a backwards flow through the membrane because the higher concentration water is on the feed side of the membrane. The backwards flow caused by the osmotic pressure consists of low TDS water and dissolves any solids that may have started to precipitate in the membrane.

[00407] Further, since water is flowing backwards, some solids and high concentration water flow from the membrane into the feed side of the membrane. These are carried away in the reject stream as pumping of liquid through the entire system is ongoing. In other words, pressure is decreased on the feed side of the membrane below the osmotic pressure, so that water flows backwards from the permeate to the feed side of the membrane. In one embodiment, a reject valve may be opened to allow inlet water to flow through the membrane and out into the reject stream. The pressure in the feed side of the membrane decreases to less than that of the osmotic pressure across the membrane. The water all passes along the membrane surface but does not permeate the membrane due to osmotic pressure. Since the pressure on the feed side is less than the osmotic pressure across the membrane, water flows from the permeate side to the feed side where it joins the flow on the feed side and exits through the reject pressure control valve.

[00408] c. Reverse Osmosis

[00409] Reverse osmosis is a water purification technology that uses a semipermeable membrane. In reverse osmosis, an applied pressure is used to overcome osmotic pressure, a colligative property, that is driven by chemical potential, a thermodynamic parameter. The result is that the solute is retained on the pressurized side of the membrane and the pure solvent is allowed to pass to the other side. To be "selective," this membrane should not allow large molecules or ions through the pores (holes), but should allow smaller components of the solution (such as the solvent) to pass freely.

[00410] In a normal osmosis process, solvent naturally moves from an area of low solute concentration, through a membrane, to an area of high solute concentration. The movement of a pure solvent is driven to reduce the free energy of the system by equalizing solute concentrations

on each side of a membrane, generating osmotic pressure. Reverse osmosis is achieved by applying an external pressure to reverse the natural flow of pure solvent.

[00411] In various embodiments of the present invention, reverse osmosis may be used on its own, or may be used sequentially after the nanofiltration process, or may be used in a nanofiltration/reverse osmosis process following ultrafiltration. One objective of this process is to reject the monovalent ionic species in the water. These ionic species mainly includes salts of sodium, ammonium, and potassium.

[00412] Just like in nanofiltration, the osmotic pressure of the monovalent ions has to be overcome to allow water to flow through the membrane. Fouling of the membrane is combated by using all or some of the strategies used for nanofiltration. By reducing the concentration of the monovalent ions, the osmotic pressure that needs to be overcome during reverse osmosis has also been decreased substantially. This reduces power consumption, the fouling tendency of the membrane and the life of the membrane itself.

[00413] Thus, another possible implementation of the solvent precipitation process is to use an organic solvent that can be recovered using a nanofiltration/reverse osmosis membrane system. As shown in FIG. 16, the solvent can be recycled back, and the reduced concentration of salt in water can be further treated using nanofiltration/reverse osmosis process. In this case, the nanofiltration/reverse osmosis membranes used to reject the solvent mainly have a higher molecular weight cutoff than the membranes that are used subsequently in treating the water. Another possible implementation of the solvent precipitation process, shown in FIG. 16, is using an organic solvent that passes through the nanofiltration membrane, but the nanofiltration membrane is capable of rejecting some salt, and this means that the reject stream from the nanofiltration membrane will have a higher concentration of salt than the feed stream. This reject

stream can then be put into the solvent precipitation process, precipitating salt that can be filtered out. The amount of organic solvent needed to achieve a specific lower concentration of salt depends on the inlet salt concentration, as given by equation given earlier in this application, namely, $f = \alpha_{\min} + K\alpha$, where α is the mass fraction of solvent needed for precipitation, and f is the fraction of salt that is precipitated. For a salt saturated solution, $\alpha_{\min}$ is 0. However, for an under-saturated salt solution, $\alpha_{\min}$ is finite, and increases as the salt solution gets more and more under-saturated. Hence, if the feed water is under-saturated, then a nanofiltration membrane is used, as shown in FIG. 16, to concentrate the feed to a higher salt concentration, and hence the reject stream entering the settler, has a higher salt concentration, and hence will need lesser solvent to achieve a lower salt concentration. The salt slurry precipitated in the settler is removed from the bottom of the settler and is partly sent to a filter, not shown in FIG. 16, and partly recycled back to the settler feed by pump.

[00414] More specifically, and referring to FIG. 16, the feed water enters into feed pump 250 and then flows into a first nanofiltration membrane 252. As described above, the separation performed by the nanofiltration membrane will cause the salt concentration of the reject stream to be increased, and this reject stream is then sent into a settler vessel 254. Additional solvent (make-up solvent) is added to the vessel 254 also, to make up any loss of organic solvent. In the settler vessel 254, salts are precipitated (due to the presence of solvent), and the resulting slurry of water and precipitated salts is removed via pump 256 and sent through filter 258 to remove salt. The liquid (water) that passes through this filter 258 is then recycled back to be combined with additional feed water and be processed through first nanofiltration membrane 252.

[00415] The permeate stream that passes through first nanofiltration membrane 252 is then directed via pump 260 to a second nanofiltration membrane 262. The reject stream from this

second nanofiltration membrane is recycled back to be combined with feed water and begin the process again by passing through first nanofiltration membrane 252. The permeate stream that passes through second nanofiltration membrane 262 is then directed via pump 264 to a reverse osmosis membrane 266. The reject stream from this reverse osmosis membrane 266 is recycled back to be combined with feed water and begin the process again by passing through first nanofiltration membrane 252. The permeate stream passes through the reverse osmosis membrane as treated water.

[00416] The organic/water solution from the settler unit is pumped through a second nanofiltration system that rejects more salt and some organic, and finally the permeate from this nanofiltration membrane is fed into a reverse osmosis membrane that rejects the remaining salt and the remaining solvent. All the reject streams are recycled back, while the permeate stream from the reverse osmosis system is the treated, desalinated water. Since the required pressure difference across the nanofiltration membrane is based on the salt concentration in the feed and in the permeate, by allowing salt water to pass through with some salt rejection in the nanofiltration membranes, the pumps only have to generate the difference between the osmotic pressures of the feed and permeate streams. The following equation gives the net driving pressure across a nanofiltration membrane:

$$NDP = \left[\left(\frac{P_f + P_c}{2} \right) - (P_p) \right] - \left[\left\{ \left(\frac{TDS_f + TDS_c}{2} \right) - TDS_p \right\} \cdot 0.01 \frac{\text{psi}}{\text{mg / L}} \right]$$

where

NDP	=	net driving pressure (psi)
P_f	=	feed pressure (psi)
P_c	=	concentrate pressure (psi)
P_f	=	filtrate pressure (i.e., backpressure) (psi)
TDS_f	=	feed TDS concentration (mg/L)
TDS_c	=	concentrate TDS concentration (mg/L)
TDS_f	=	filtrate TDS concentration (mg/L)

[00417] Membrane systems, such as those described above, may also be used to remove solvent in the presence of salt (without fouling the membranes -- or minimizing the fouling of membranes) or may be used to remove both salts and solvent.

[00418] As will be described below in Examples 4 and 5, chemical formulations, such as n-Propyl-amine, can be used to precipitate salts from contaminated water. Subsequently, both the precipitated salts and the organic solvent will need to be removed from the resulting slurry. Membranes may be used for this process. To that end, n-Propyl-amine is rejected easier by membranes than multivalent salts are.

[00419] Various embodiments of the present invention may include a system that combines a number of the processes described above. For example, in one such embodiment, solvent may be used to precipitate a salt or salts from a liquid (such as water), followed by an ultrafiltration membrane separation process, and subsequently a nanofiltration/reverse osmosis separation process. In such an embodiment, an organic solvent, such as n-Propyl-amine, is to precipitate salts (divalent, monovalent, BOD, COD, etc.) from membrane reject streams, which contain a higher concentration of salts than the feed stream. The reject stream can then be pumped into a settler tank, wherein the organic solvent can be added to precipitate the salts and reduce the contaminants (salts, BOD, COD, etc.) concentration. Dwell time is provided by the settling tank for (1) crystal growth (as crystals grow they gain mass and settle), and (2) settling time (crystals with significant mass need time un-agitated to settle). This is similar to the process described

above with respect to FIG. 14. Following this dwell time, the outlet flow from the settling tank will be made up of at least (1) solids that have not reached enough mass to settle in the provided dwell time provided by the settling tank, and (2) water with a high concentration of n-Propyl amine.

[00420] Next, this water from the outlet flow of the settling tank may be subjected to ultrafiltration (such as via a 1/4" tube Ultra filter) – similar to the process shown in FIG. 15. More specifically, as water leaves the settling tank, it contains some nucleated low mass solids. These solids are then separated in the ultrafilter system because the nucleated solids are larger than the pores in the ultrafilter. Once they are rejected by the ultrafilter, they are recycled back to the inlet of the settling tank. The low mass solids returned to the inlet of the settling tank provide seeding nucleation sites for further crystal growth. As higher concentrations of solids are achieved in the tank from returning solids from other membrane processes, the crystals grow, thereby gaining mass and settling to the bottom of the tank.

[00421] The permeate from the ultrafilter system, however, is clear and passes to a nanofilter system (referred to here as Nanofilter Stage 1).

[00422] The purpose of Nanofilter Stage 1 is to reject a percentage of n-Propyl amine and multivalent salts. Nanofilter stage 1 functions as follows: First, water from the dissolved air flotation system is added to the permeate flowing from the Ultrafilter system and enters the Nanofilter Stage 1 nanomembrane filter system. In the particular embodiment of this example, the Nanofilter is a spiral wrapped filter with a membrane spacer of 43 mil thickness. The molecular weight cut off is in a range of 8,000 to 12,000 daltons, and in one embodiment that molecular weight cut off is 10,000 daltons.

[00423] During the Nanofilter Stage 1 process, n-Propyl amine, multivalent salts, and water are subjected to the membrane. n-Propyl amine is rejected to a greater extent than that of the water and multivalent salts. This means that the reject stream of the membrane increases in n-Propyl amine concentration. This also means that the n-Propyl amine concentration in the membrane pores decreases in concentration.

[00424] No water can enter the membrane pores that is not undersaturated. As an example of this, consider the following: Assume saturation of a multivalent salt is 100,000 mg/L. And assume concentration of n-Propyl amine in solution reduces the concentration of the multivalent salt to 75,000 mg/L. In the pores of the membrane, some of the multivalent salt has been rejected. And a greater percentage of the n-Propyl amine has been rejected. So, what we have is a solution that is unsaturated caused by both: (1) removal of n-Propyl amine, which causes water to have the capacity to hold more salt, and (2) removal of salt, which causes water to have the capacity to hold more salt.

[00425] Referring now to FIG. 17, crystals grow in the reject stream and the pores are saved from scaling as the divalent salts and the n-Propyl amine is reduced. When a high TDS (total dissolved solids) solution is pumped through Conventional membranes, fouling occurs within hours. And the system has to be flushed. Each time the system is flushed, recovery is less than 100 percent of previous flow. Pores get blocked and water cannot flow into the pores to unblock the pores. Further, with each passing flush, the membrane becomes more blocked and membrane has to be replaced after a short period of time. This is depicted in FIGS. 18-20. FIG. 17 shows the impact of the organic solvent on the fouling of the membrane due to salt deposition. The presence of the organic solvent on the feed side of the membrane and its presence within the membrane pores actually assists in keeping the salt in solution by forming an under-saturated

solution within the membrane. In conventional membranes, the fouling of the membrane due to the deposition of the soluble species on the surface and within the membrane results in a gradual decrease in membrane permeability, as shown in FIG. 18, wherein after each backflush cycle, the membrane water permeability increases but to the same extent as was present before the fouling began, and this gradual decline in permeability limits the number of backflush cycles before the membrane has to be replaced. FIG. 19 shows one of the membrane fouling mechanism, wherein the membrane pores get blocked with precipitated solids, while FIG. 20 shows the mechanism of solids deposition on the membrane surface, which causes decline in membrane permeability. When high TDS solution is pumped through the membranes in the process developed in this Example of the present invention, the reject flow is increased to flush crystals out of the reject stream. Full recovery is experienced with each flush as no pores have been blocked and the crystal build up that created the fouling has been removed. This is also depicted in FIGS. 18-20.

[00426] In other words, one major discovery of the solvent precipitation process is that the nanofiltration and even the reverse osmosis membranes will undergo less fouling due to salt deposition when an organic solvent is present in the feed. This is a major finding since fouling of reverse osmosis membranes currently is a major challenge for desalination applications. To fully understand this effect of solvent, we have to look at what causes a membrane that is being used for desalination to foul.

[00427] Reverse osmosis membranes have an asymmetrical structure with large pores on one side of the membrane, which decrease in size as you traverse the thickness of the membrane, with a dense layer on the opposite side of the membrane. Membrane fouling occurs due to salt deposition on the membrane surface, which can be periodically cleaned, and also within the

membrane structure. This salt deposition occurs due to selective permeation of water through the membrane, and is mainly caused by salt supersaturation, as water moves through the membrane to the permeate side. This is schematically shown in FIG. 21. Salt deposition within the membrane results in irreversible loss of membrane water permeability over time, eventually requiring membrane replacement.

[00428] With the presence of the solvent in the feed water, as in the case of the solvent crystallization process, as water selectively permeates through the membrane, the organic solvent concentration increases, and this results in salt crystallization occurring outside the membrane, as shown in FIG. 22. These fine salt crystals continue to flow with the feed water, eventually leaving the membrane module as the reject stream. The main point to emphasize is that before the salt can deposit inside the membrane, it crystallizes outside the membrane, thereby preventing the occurrence of supersaturation condition within the membrane structure, which results in salt deposition within the membrane, as in the case of normal operation of the membrane without an organic solvent.

[00429] The system may include one nanofiltration membrane, or more than one nanofiltration membrane. Each additional Nanofiltration Membrane system functions the same as the Stage 1 filter, removing more n-Propyl amine and divalents. The only difference is control of membrane system to assure saturation of salts is reached in the reject stream. Referring to FIG. 23, controls for the membranes 350 may include: (1) a proportion flow control valve 352, (2) a pressure transducer 354, (3) a first flow meter 356 in the membrane inlet flow, (4) a second flow meter 358 in the membrane permeate flow, (5) a TDS meter or meter to detect n-Propyl amine concentration 360, (6) a variable drive system 362 for a delivery pump 364, and (7) a level sensor 366 for tank control.

[00430] Referring to FIG. 23, the proportion flow control valve 352 opens: (1) to reject stream back pressure drops, and (2) to reject stream flow increases. This assures a complete flush of crystal build up in the reject stream of the membrane.

[00431] The pressure transducer is on a reject circuit for PLC to control reject back pressure and flush cycles.

[00432] Knowing the TDS, the concentration of n-Propyl amine, the flows, and pressure of reject stream, a control system can function the pump to operate and maximum pressure efficiency and use the proportional valve to control pressure required to obtain necessary permeate flow. Also flush cycles can be obtained and performed.

[00433] The system and apparatus may also include a reverse osmosis membrane. The reverse osmosis membrane is used to reject the remainder of the n-Propyl amine, to reject traces of divalent salts, and to reject the remainder of the monovalent salts.

[00434] Solids removal and flushing of solids to recover n-Propyl amine: Solids from the settling tank are delivered to a filter press with the capability of flushing the solids with a fluid that is to be defined via testing of filter press companies. 150,000 mg/L water is likely the best flushing water for the following reasons: (1) It will not dissolve significant solids in the flushing process; (2) It is readily available from the reverse osmosis reject stream; and (3) It will not deposit significant amount of solids when subjected to n-Propyl amine.

[00435] One will also have to allow for handling of contaminants that build up in the plant that do not precipitate. Products that do not precipitate will be of two classes: (1) products such as alkanes (e.g., hexane), and (2) products such as biocides. More specifically, products such as alkanes (hexane) will build up until they float on top of the water in the settling tank and form a layer. A mechanism can be put in place to recognize the presence of the layer and it can be

decanted via port on the side of the vessel. And, products such as biocides will build up in concentration and pass through all filter except the reverse osmosis membrane. A maximum concentration will be decided upon and the reverse osmosis reject stream will be “blown down” when concentration reach the targeted maximum. The reverse osmosis reject stream contains the biocides and has the least concentration of n-Propyl amine. This makes it the target for the blow down point. If large amounts of biocides are delivered and blow down requirements grow, it may be necessary to add a small tight membrane to separate the n-Propyl amine from the biocide.

[00436] EXAMPLES

[00437] The following Examples further exemplify the principles of the various aspects of the present invention described above.

[00438] 1. *Examples Regarding the Separation of an Element, such as Strontium, from a Liquid*

[00439] a. Background

[00440] As described above, typically produced/brackish water can contain strontium together with calcium and other inorganic contaminants. Typically concentration of calcium in the feed water is much higher than strontium, with $\text{Ca}^{++}/\text{Sr}^{++}$ ratio in the range of 10-50, and since these two contaminants are very similar in terms of the aqueous solubility of their salts, it is difficult to separate strontium preferentially.

[00441] An aspect of this invention is the initial separation of strontium from produced/brackish water with little or no precipitation of calcium, even though the concentration of calcium is much higher than strontium. The basic idea, as described above, is the preferential precipitation of strontium from the water by pre-mixing the water with seed crystals of strontium sulfate. This

approach can be used to preferentially precipitate any insoluble salt from water that contains a mixture of several salts with very similar solubilities, like salts of calcium and strontium.

[00442] The chemical precipitation reactions in this case are:



[00445] The total amount of soluble sulfate species (Na_2SO_4 , MgSO_4) added may be in accordance with the stoichiometric amount needed to precipitate the strontium. To initially form the seed crystals of strontium sulfate, about 10-50% of the total amount of soluble sulfate needed stoichiometrically is added. These seed crystals are added to the water to preferentially precipitate the strontium sulfate. The seed crystals can also be introduced from outside by using a mineral like celestite or by precipitating from a pure solution of strontium chloride using a soluble sulfate, as given by reaction (2.1).

[00446] The amount of seed crystals determines the rate of precipitation of strontium sulfate. However, it does not affect the yield of strontium sulfate precipitated from the water.

[00447] Typically, embodiments of the invention can be practiced between the temperatures of 10-150°C, with the higher temperature being used when the liquid is under pressure. The rate of precipitation decreases as the temperature decreases, and vice versa.

[00448] b. Example 1

[00449] 500 mL of produced water containing 442 mg/L strontium chloride and 6,200 mg/L calcium chloride (giving a $\text{Ca}^{++}/\text{Sr}^{++}$ wt ratio of 14.0 and molar ratio of 20.0) was used in this Example. The temperature was maintained at 25°C, and small amounts of sodium sulfate (Na_2SO_4) were added and mixed with 500 mL of the water in a constantly stirred beaker. The total amount of sodium sulfate added was 280 mg. Approximately 10 minutes after each

incremental addition, the concentration of Sr^{++} was measured and the wt % strontium removed was calculated by the difference from the initial amount present in the water. Table 5 gives the % of the sodium sulfate that was used for precipitating strontium.

[00450] TABLE 5

Sample	% Na_2SO_4 added	Wt removed % Sr^{++}
1	0	0
2	30	41.916
3	40	54.32
4	50	65.8
5	60	75.6
6	70	85.26
7	80	95.2
8	90	100
9	100	100
10	120	100

[00451]c. Example 2: Selective Precipitation of Strontium

[00452] Water containing strontium was first reacted with sulfuric acid based on the inlet strontium concentration, with 40% excess sulfuric acid being added to complete the formation of Strontium sulfate in the water. The pH of the water was below 3.0.

[00453] 1 L of produced water containing 442 mg/L strontium chloride, 6,200 mg/L calcium chloride, and 30 mg/L barium chloride (giving a $\text{Ca}^{++}/\text{Sr}^{++}$ wt ratio of 14.0 and molar ratio of 20.0) was used in this Example. The temperature was maintained at 25° C.

[00454] The chemical precipitation reaction is as follows:



[00457] After the reaction was complete, which took about 1 hour, the pH was increased to a range between 3.5 to 4.0, which caused the strontium sulfate and barium sulfate to precipitate while any calcium sulfate formed remained in solution. 1 L of produced water containing 442 mg/L strontium chloride, 6,200 mg/L calcium chloride, and 30 mg/L barium chloride (giving a $\text{Ca}^{++}/\text{Sr}^{++}$ wt ratio of 14.0 and molar ratio of 20.0) was used in this Example. The temperature was maintained at 25° C.

[00458] 7.81 mL of 0.5M sulfuric acid (Sigma Aldrich, Product #38294) was added to the 1 L of produced water and the flask was shaken thoroughly. White precipitate was formed, which was filtered and analyzed. The filtered water was also analyzed for strontium. This method allowed the barium and strontium to be removed while keeping the calcium in solution.

[00459] Analysis of the filtered water shows that the strontium concentration was 0.3 mg/L and analysis of the white precipitate obeyed the mass balance, since its dry weight was 79.7 g with 243.2 mg/Kg of barium and 3009 mg/Kg of strontium in the precipitate, indicating that all of the

barium and almost all of the strontium had been precipitated as sulfates, while the calcium sulfate remained in solution.

[00460] 2. *Examples Regarding System and Apparatus for Separation of Salt and Solvent*

[00461] a. Example 3

[00462] An experimental evaporation setup 952 was built as shown in FIG. 24. Referring to FIG. 24, a 900 mm length of corrugated PVC pipe 954 having an outer diameter of 32 mm and nominal inner diameter of 25.4 mm (CORRFOAM®, obtained from ILPEA Industries of Cleveland, OH) was mounted vertically and attached to a trough 956 and collection tank 958. A feed tank 960 containing a solution 962 of 300 – 500 ppm ammonia in water was attached to a liquid pump 964 and tubing 966 was used to connect the feed tank 960 and liquid pump 964 to the chamber 956. Chamber 956 was further attached to vacuum pump 968. The pipe 954 was perforated 970 near the bottom but above collection tank 958 and a valve 972 attached to the perforation as a means to control the amount of air to be pulled upwards through the tube 954 by vacuum pump 968. Corrugated PVC pipe 954 had base inner diameter of 27.94 mm, corrugation rib height of 4.32 mm, corrugation rib width, at rib top, of 1.91 mm, and corrugation rib pitch of 3.68 mm.

[00463] The ammonia solution 962 was drawn from the feed tank 960 by liquid pump 964 and dispensed into chamber 956 at a series of selected rates ranging from 20 mL/min to 280 mL/min, and the solution was allowed to flow into and downward within pipe 954 and into collection tank 958. The amount of air allowed into the pipe 954 during the liquid flow was about 1-2 mL/min, such that by turning on the vacuum pump 968 a vacuum level of about 300 mm Hg was maintained in the pipe 954 at steady-state operation. The temperature of the environment surrounding the setup was 25°C.

[00464] Ammonia analyzers (AAM631 Aztec 600 ISE, available from ABB Inc. of Warminster, PA) were used to measure the concentration of ammonia in the water. One analyzer was used to measure the ammonia level in the trough 956, and a second analyzer was used to measure ammonia in the collection tank 958.

[00465] The inlet and outlet ammonia concentrations, together with pH and temperature measurements allowed the determination of the loss of ammonia from the water during the test. The results are shown in Table 6. The data in Table 6 was used to determine the liquid-phase mass transfer coefficient, and the dimensionless mass transfer number was plotted versus the Reynolds Number, wherein the Reynolds Number is calculated according to the equation: $Re = 4Q/\nu W$, where Q is the liquid flow rate, ν is the kinematic viscosity, and W is the pipe perimeter.

[00466] The experiment was repeated with a PVC pipe (also obtained from ILPEA Industries of Cleveland, OH) without interior corrugation – that is, having a substantially smooth inner wall - and the measurements were used to determine the liquid-phase mass transfer coefficient, and the dimensionless mass transfer number was plotted versus the Reynolds Number. Mass transfer number as a function of the Reynolds Number for the control experiment is shown in FIG. 25, where mass transfer number is: kLz/DL , where kL is the mass transfer coefficient, z is the height of the PVC pipe, and DL is diffusivity of ammonia in water.

Table 6. Ammonia measured in the influent and effluent water for corrugated and plain PVC pipe.

Corrugated Tube						
Influent Water (100 mL/min)			Effluent Water			% NH ₃ -N Removal
pH	Temperature (°C)	NH ₃ -N (mg/L)	pH	Temperature (°C)	NH ₃ -N (mg/L)	
8.0	22	28.8	8.0	16	18.2	37
8.6	21	26.6	8.1	17	15.8	41
9.3	23	26.2	8.6	18	5.3	80
9.7	21	30.0	9.1	16	2.1	93
10.8	22	25.5	10.1	17	0.6	98

Plain Tube						
Influent Water (100 mL/min)			Effluent Water			% NH ₃ -N Removal
pH	Temperature (°C)	NH ₃ -N (mg/L)	pH	Temperature (°C)	NH ₃ -N (mg/L)	
8.0	22	32.0	8.0	22	31.4	1.9
8.6	21	28.9	8.1	21	27.3	5.5
9.3	23	26.2	8.6	19	25.6	2.3
9.7	21	32.1	9.1	22	31.0	3.4
10.8	22	23.8	10.1	20	22.9	3.8

[00467] Data for the corrugated pipe gave mass transfer coefficient (kL) values which were 10-20 times higher than the values obtained for the smooth pipe. This showed that using a corrugated pipe produced significant turbulence in the liquid film, which enhanced the rate of mass transfer of the ammonia from the water into the gas phase.

[00468] b. Example 4: Salt Precipitation Via Use of Organic Solvent

[00469] This Example demonstrates the precipitation of a salt out of solution via the use of an organic solvent. To that end, water saturated with table salt was prepared by dissolving salt in hot water in a container until un-dissolved salt was observed at the bottom of the container. Then, the salt solution was allowed to cool to room temperature, allowing additional salt to precipitate. The salt-saturated solution was then decanted. The salinity and pH of this salt solution was then measured, and had a salinity of 293,000 ppm and a pH of 6.95.

[00470] 40 mL of this saturated salt solution was then mixed with differing amounts of isopropyl amine [obtained from, and commercially available from, Sigma-Aldrich company, St. Louis, MO (Product No.: 109819)]. After each addition of propylamine, the salt was allowed to precipitate and 40 ml of liquid was decanted off from the top. Table 7 shows the change in the salinity of the decanted salt water, as more and more propylamine was added.

Table 7. Change in Salinity of Salt Water after addition of Propylamine.

Specific Gravity of Propylamine		0.69				
Amt of Salt-Saturated Water (mL)	Initial Propylamine (mL)	Propylamine added (mL)	pH	Specific Gravity	Vol % Propylamine	Decant Salinity (ppm)
40	0	0	6.95	1.2	0.00	293,000
40	0	4.44	9.9	1.149	9.99	253,000
40	0	10	10.23	1.082	20.00	215,000
40	0	17.1	10.31	1.005	29.95	168,000
40	0	40	10.68	0.895	50.00	135,000
40	0	120	10.84	0.782	75.00	88,000

[00471] As can be seen from the results in Table 7, as the amount of propylamine was increased in the salt water, more salt precipitated, thereby reducing the salinity in the decanted water. The pH increased since propylamine ionized in water to produce hydroxyl ions in water. By using 75 vol% of propylamine, the salinity in salt water was reduced from the initial value of 293,000 ppm to 88,000 ppm

[00472] c. Example 5: Pilot Scale System for Salt Precipitation via Organic Solvent, with Subsequent Removal of Precipitated Salt and Solvent from Water

[00473] i. Background

[00474] As described previously, the methods and apparatus of the present invention may be used in reclamation of water contaminated with various materials (during subsurface geological operations, for example). Thus, ultimately, systems including such methods and apparatus will need to operate at volumes and flow rates dictated by such operations. In order to demonstrate the viability of such methods and apparatus, a pilot-scale system was designed, constructed, and tested.

[00475] The system was designed to handle input water (i.e., water entering the system) having saturation levels of (1) naturally occurring radioactive material (e.g., radium, strontium, barium – materials that can become radioactive during processes such as fracking), (2) multivalent salts, (3) monovalent salts, and/or (4) organic materials. The output water (i.e., water exiting the system following treatment) is cleaned to designed specifications, which can be designed to meet potable water requirements.

[00476] Although not tested in the pilot system of this Example, the input water may be pretreated prior to introduction into the pilot system, such as with a dissolved air flotation method (e.g., that described in U.S. Application Serial No. 61/786,942, incorporated by reference herein) to remove materials such as iron and emulsified oils.

[00477] The water (whether subjected to pretreatment or not) may be subjected to a precipitation process to remove salts (such as that described in the present application, and for example, as shown in Example 4, above). To accomplish this, chemical formulations having the ability to change the amount of solids that water can dissolve have been developed. By “developed” it is meant that mixtures of organic solvents can be developed and used, just like a single organic, such as n-Propyl-amine. In other words, the organic solvent is not limited to being a single chemical only. Further, the use of the organic solvent or these organic solvents does alter the amount of solids (salt, BOD, COD, etc.) that water can dissolve and hence precipitation of solids (salts, BOD, COD, etc.) occurs.

[00478] One such chemical formulation is n-Propyl amine. As n-Propyl amine is added to water, an equilibrium between the n-Propyl amine and salt is established in the water. The more n-Propyl amine that is added, the more equilibrium is pushed towards precipitating the salts. Salts

will not start to precipitate until the n-Propyl amine has pushed equilibrium to full saturation of the salts in the water.

[00479] The precipitation of salts and the subsequent reclamation of water by steps including for example, removing salt from the salt slurry that results from salt precipitation, can be accomplished in the pilot scale system of this Example. The pilot scale system is further shown schematically in FIG. 26. The numbered units in the process flow diagram of FIG. 26 are as follows:

400	Tank for mixing salt into water
402	Heater to heat water to aid in salt mixing process
404	Tank for holding salt water
406	Pump to supply salt water
408	Variable speed drive salt water supply pump
410	Gauge pressure 1, (working pressure to supply salt water)
412	Flow meter, (salt water supply flow)
414	Pump to supply isopropyl amine
416	Variable speed drive for isopropyl amine delivery pump
418	Valve relief to maintain rail pressure for isopropyl amine delivery
420	Flow meter, (isopropyl amine flow)
422	Retention coil (a coil of pipe to allow time for crystal growth)
424	Hydrocyclone
426	Flow meter, (down flow from hydrocyclone)
428	Flow meter, (isopropyl amine flow)

430	Retention coil (a coil of pipe to allow time for crystal growth)
432	Gauge pressure, (working pressure to hydrocyclone)
434	Hydrocyclone
436	Flow meter, (down flow from hydrocyclone)
438	Pump to boost pressure
440	Variable speed control for boost pump
442	Flow meter, (isopropyl amine flow)
444	Retention coil (a coil of pipe to allow time for crystal growth)
446	Gauge pressure, (working pressure to hydrocyclone)
448	Hydrocyclone
450	Flow meter, (down flow from hydrocyclone)
452	Flow meter, (isopropyl amine flow)
454	Retention coil (a coil of pipe to allow time for crystal growth)
456	Gauge pressure, (working pressure to hydrocyclone)
458	Hydrocyclone
460	Flow meter , down flow from Hydrocyclone
462	Reactor vessel
464	Pump to control level in reactor
466	Switch level to control Reactor level
468	Reactor vessel
470	Pump to control level in reactor
472	Switch level to control Reactor level

474	Tank for precipitate
476	Tank for salt water with reduced salt concentration
478	Pump Vacuum to vaporize Isopropyl amine
480	Variable speed drive for Vacuum pump
482	Gauge Vacuum , Reactor vessel and pressure
484	Compressor to compress Isopropyl amine
486	Drive variable speed for compressor
488	Valve check, pressure check
500	Gauge pressure, Compressor working pressure
502	Shell and Tube heat exchanger to condense Isopropyl amine
504	Tank for holding liquid isopropyl amine
506	Gauge pressure vacuum pump outlet
508	Pump Cooling water
510	Tank Cold water
512	Pressure relief for compressor case
514	Valve check salt water supply
516	Valve check isopropyl amine supply
518	Valve check isopropyl amine supply
520	Valve check isopropyl amine supply
522	Valve check isopropyl amine supply
524	Tank compressor intake liquid protection
526	Tank vacuum pump intake liquid protection

528	Valve tank shutoff
530	Valve tank shutoff
532	Valve bypass
534	Valve salt water feed shutoff
536	Valve retention coil bypass
538	Valve underflow control
540	Valve flow direction control
542	Valve flow direction control
544	Gauge pressure 0-160 psi
546	Valve underflow control
548	Valve flow direction control
550	Valve flow direction control
552	Valve flow direction control
554	Valve flow direction control
556	Valve flow direction control boost pump feed
558	Valve retention coil bypass
560	Valve underflow control
562	Valve Chemical flow control
564	Valve Chemical flow control
566	Valve Chemical flow control
568	Valve Chemical flow control
570	Valve flow direction control

572	Valve flow direction control
574	Valve retention coil bypass
576	Valve underflow control
578	Valve vacuum isolation
580	Valve chemical tank isolation
582	Valve chemical tank isolation
584	Valve reactor tank isolation
586	Valve reactor tank isolation
588	Valve chemical tank isolation
590	Valve compressor suction isolation
592	Valve chemical tank isolation

[00480]ii. Procedures

[00481]The operating procedure for the pilot-scale system with reference to FIG. 26 was as follows:

[00482]First, an influent (of a saturated salt solution) was prepared in tank 400. To accomplish this, tank 400 was filled with water and heated to 30°C. NaCl was then added to the water in the tank 400, and mixed until no more salt saturated (i.e., similar to the process described above in Example 4). The salinity of the water after salt quit dissolving was measured at 295,000 ppm. In this Example, the salinity was determined by diluting a sample of the salt water 40:1 and testing by conductivity. This process is well known to those of ordinary skill in the art as being useful as a measure of salt concentration when only one salt is being used, as in this Example (NaCl).

[00483] Once a saturated solution was achieved, this solution was transferred from tank 400 to tank 404, and four liters of isopropyl amine were added into tank 504 via pump 414. At this point, all valves on the system were closed.

[00484] Next, the circulation pump 508 was started and cooling water was circulated from tank 510 through heat exchanger 502. Certain valves were then opened to create a flow path for Step 1 of this Example. More specifically, valve 534 was opened to allow influent (the salt solution) to flow to hydrocyclone 424. Valves 538 and 584 were opened to direct underflow from hydrocyclone 424 to flow through flow meter 426 through reactor 468 to tank 474. Valves 540 and 586 were opened to direct overflow to pass through reactor 462 to holding tank 476. And valves 578, 590, and 592 were opened to create flow path for gases to flow.

[00485] Next, a vacuum pump 478 and compressor 484 were prepared for Step 1 of the procedure. A vacuum pressure of 11 inches Hg was drawn on reaction vessels 462 and 468 using vacuum pump 478 (with readout on gauge 482). And, at this point, compressor speed was run to maintain 1 psi pressure between vacuum pump 478 and compressor 484 (with readout on gauge 506). This targets the ideal outlet pressure for the vacuum pump.

[00486] Pump 406 (influent pump) was started and a flow rate of 0.85 gpm was established (readout on flow meter 412). Additionally, pump 414 (chemical pump) was started and a flow rate of 0.15 gpm was established (readout on flow meter 420). And the flow rate for underflow hydrocyclone 424 was 0.1 gpm (readout on flow meter 426). In this Example, it was found that a pressure of 92 psi (on pump 406, read on gauge 410) was achieved under these conditions (i.e., to flow .85 gpm water and .15 gpm isopropyl amine with underflow of hydrocyclone 424 set at .1 gpm).

[00487] After achieving steady state conditions, it was found that the compressor operated at 53 psi and a flow rate of 2.1 scfm (per compressor rate chart based on rpm and pressure). In the experiment of this Example, rate and pressure were used to estimate the volume of the chemical being recovered, and this was calculated on this first pass to be 35%. [This calculation was made because (1) .15 gpm of isopropyl amine in gaseous state equates to approximately 6 scfm, and thus (2) the volume of isopropyl amine being recovered is $2.1 \text{ scfm} / 6 \text{ scfm} * 100$, which equals approximately 35%.]

[00488] After this was done, the overflow and underflow from hydrocyclone 424 were checked by taking samples from the liquid entering tanks 474 and 476. The underflow was observed to have a small amount of precipitate. After decanting, the underflow fluid tested to 275,000 ppm NaCl. The overflow was observed to have more precipitated salt than the underflow, since small salt crystals were floating, instead of sinking. This was believed to be due to evaporation of organic solvent into vapor form, which was sticking to the salt crystals, thereby making them lighter. The overflow was decanted and tested to 273,000 ppm NaCl. It is believed that the differences were probably due to fluctuations in the accuracy of testing.

[00489] These results of this Step 1 were then compared to previous testing (shown above in Table 7 of Example 4) that indicates that 15 percent isopropyl amine should yield a reduction of salinity to approximately 234,000 ppm. This would equal a reduction of 61,000 ppm (295,000 starting point minus 234,000). The underflow yielded a reduction of 20,000 ppm (295,000 minus 275,000) which is approximately 33% of 61,000. The overflow yielded a reduction of 22,000 ppm (295,000 minus 273,000) which is approximately 36% of 61,000. The results from Step 1 thus showed a higher ppm of NaCl than was expected, which showed that not all of the chemical was being removed from the influent.

[00490] A second flow was then tested under adjusted conditions. In this step, valve E was opened to add a 24 second retention time to the fluid before it entered the hydrocyclone. Thus, this increased dwell time was used to allow salt crystals additional time to grow and gain mass, to allow the hydrocyclone to separate the salt more efficiently. The second pass was then run under the same remaining conditions as in Step 1, above.

[00491] Following this step, it was observed that slightly more precipitate was present in the underflow than on previous step. This indicates that it is possible that crystals were slightly larger than previously (and that more precipitation occurred in the underflow when more time was given for crystal growth). However, the hydrocyclone was unable to separate the precipitate from the fluid. And, recovery of chemical did not change.

[00492] The retention coil bypass 422 was then closed by opening valve 536. Flow from pump 406 was decreased to .75 gpm using flow meter 412 and variable speed control 408. Flow from pump 414 was increased to .25 gpm using flow meter 420 and variable speed control 416. The system was allowed to reach a steady state. Liquid entering into tanks 474 and 476 was observed and recorded, and a sample was taken from liquid entering into tanks 474 and 476. Following these steps, isopropyl amine content was increased from 15% of total volume being passed through the hydrocyclone to 25%. An expected ppm from Table 7 (Example 4) would indicate a target of 192,000 ppm. More salt precipitate was present in the overflow than in the underflow. Same process was used to prepare samples for conductivity testing.

[00493] The compressor reached a steady state flow rate of 3.7 scfm. Conductivity measurements were then taken on samples of the under flow and overflow, and the underflow and overflow values were 259,000 ppm and 260,000 ppm respectively.

[00494] The flow from hydrocyclone 424 underflow was then increased to .2 gpm using flow meter 426 and valve 538. The system was allowed to reach a steady state. Liquid entering into tanks 474 and 476 was observed and recorded, and a sample of liquid entering into tanks 474 and 476 was taken. When measurements were again run on these samples, it was determined that the hydrocyclone performance did not change significantly from the previous passes.

[00495] The retention coil bypass 422 was then opened by closing valve 536, and the system was allowed to reach a steady state. Liquid entering into tanks 474 and 476 was observed and recorded, and a sample of liquid entering into tanks 474 and 476 was taken. This time, the retention coil was activated to give 22 extra seconds of retention time for salt crystals to grow. All other settings remained as they were prior to these steps. It was observed that an equal amount of salt was passed from the underflow and the overflow.

[00496] Retention coil bypass 422 was then closed by opening valve 536. Flow from pump 406 was set to .7 gpm using flow meter 412 and variable speed control 408. Flow through pump 414 was adjusted to .15 gpm (flow meter 420). Hydrocyclone 424 underflow was adjusted to .1 gpm using flow meter 426 and valve 562. Flow of isopropyl amine was adjusted through flow meter 428 to .05 gpm using valve 564. Hydrocyclone 434 underflow was adjusted to .05 gpm using valve 546. Valve 556 was opened to direct flow through pump 438. The speed through pump 438 was controlled with variable speed control 440 was used to maintain flow rates through hydrocyclones 448 and 458. Valve 572 was opened to direct flow through hydrocyclone 458. Valve 540 was closed to force flow to go through all hydrocyclones. The underflow for hydrocyclone 448 was set at .05 gpm (readout on flow meter 450). The underflow for hydrocyclone 458 was set at .05 gpm (readout on flow meter 460). The flow rate through pump 414 was set to .05 gpm (readout on flow meter 442). The flow rate through pump 414 was set to

.05 gpm (readout on flow meter 452). Pump 406 pressure was 110 psi (gauge 410). Pressure into hydrocyclone 434 was 96 psi (gauge 432). Pressure into hydrocyclone 448 was 86 psi (gauge 446). And pressure into hydrocyclone 458 was 70 psi (gauge 446). All hydrocyclones were run in series.

[00497] Samples were then taken from the underflow and overflow after running through the hydrocyclones. From Table 7 (Example 4), the final concentration should be 168,000 ppm, a reduction of 56.9% of total salt in solution. Equivalent precipitate was observed in both underflow and overflow. Underflow sample was tested to have 254,000 ppm while the overflow sample was tested to have 256,000 ppm. The compressor ran steady state at 3.6 scfm. It does not appear that incremental usage of hydrocyclones would make much difference. Salt precipitate showed up in both underflow and overflow samples. Each sample was decanted and let sit to evaporate solvent. Vacuum pressure was increased to 18 inches Hg. System was allowed to reach a steady state.

[00498] The previous tests were repeated to see if increased recovery of the chemical would be experienced. The results were that the compressor rate increased from 3.6 to 4.7 scfm. There was an increase in vacuum of 7 inches Hg. The increase in flow of chemical was 1.1 scfm.

[00499] All of the retention coils were then opened to see if separation of precipitates from fluid would increase significantly. However, no significant change was observed.

[00500] Thus, there were two objectives for the pilot scale test of Example 2: (1) to show that the organic solvent, n-Propyl-amine, could be used to reduce the salt concentration in the water due to salt precipitation; and (2) the salt crystals could be separated by hydrocyclones. The experimental test proved the first objective, namely, that the use of organic solvent can reduce the salt concentration. However, it also showed that the hydrocyclones were unable to separate

the fine salt crystals, since evaporation of the solvent caused the crystals to float instead of sinking and leaving with the bottoms flow in the hydrocyclone. The fact that n-propyl-amine has a low boiling point and can easily evaporate was the cause of hydrocyclone failure and hence by using a larger molecular weight organic, that has a higher boiling point, this evaporation of the organic can be eliminated and then the hydrocyclones can easily separate the precipitated salt. Further, an adjustment of dwell times has been shown to allow the salt crystals to grow to a size where they settle more rapidly, and so the system may be optimized as needed (which is within the skill of one of ordinary skill in the art).

[00501]d. Example 6: Other Methods of Separating Solvent from Water

[00502] Another possible implementation of the solvent precipitation process is to use a non-vaporizing separation system, such as a membrane. If the organic molecule has a high molecular weight, such as a sugar, then a simple ultrafiltration membrane can be used to recover the solvent, as shown in FIG. 15. As is described in more detail above, the feed water is pumped by a pump 200 into the settler tank 202, wherein the organic solvent causes precipitation of the soluble species (salts, BOD, COD, etc.), and these precipitates settle down in the settler. Some of the slurry from the bottom of the settler is recycled back by pump 206 to the feed of the settler, to make the salt crystals serve as nuclei for further salt precipitation and allow the salt crystals to grow in size and hence settle faster in the settler. The clear liquid from the settler is pumped by pump 208 into an ultrafiltration membrane, wherein the solvent is separated by the membrane and recycled back, while the salt water permeates through the membrane and is further processed to separate the salt from the water. The solvent precipitation process is able to reduce the salt concentration to manageable levels, and the organic solvent being used is recycled back. The slurry that is taken out of the system by valve 204, which is not recycled

back to the settler, is further filtered using a conventional filter, not shown in FIG. 15, wherein the solids are separated from the salt solution and the salt solution is recycled back to the settler. Since there is some loss of solvent with the wet solids that are separated by the filter, not shown in FIG. 15, make-up solvent is added to the settler. The solvent can be recycled back and the salt water that passes through the ultrafiltration membrane can be further treated using a nanofiltration/reverse osmosis process. The main advantage of this solvent precipitation process is to reduce the salt concentration in the feed water, which will further reduce the osmotic pressure needed to use nanofiltration/reverse osmosis membranes to subsequently purify the water. The reject streams from the nanofiltration/reverse osmosis membranes can all be recycled back to the inlet of the solvent precipitation process.

[00503] Another possible implementation of the solvent precipitation process is to use an organic solvent that can be recovered using a nanofiltration/reverse osmosis membrane system. As shown in FIG. 16, the solvent can be recycled back, and the reduced concentration of salt in water can be further treated using nanofiltration/reverse osmosis process. In this case, the nanofiltration/reverse osmosis membranes used to reject the solvent mainly have a higher molecular weight cutoff than the membranes that are used subsequently in treating the water.

[00504] Another possible implementation of the solvent precipitation process, shown in FIG. 16, is using an organic solvent that passes through the nanofiltration membrane, but the nanofiltration membrane is capable of rejecting some salt, and this means that the reject stream from the nanofiltration membrane will have a higher concentration of salt than the feed stream. The amount of organic solvent needed to achieve a specific lower concentration of salt depends on the inlet salt concentration, as given by equation given earlier in this application, namely, $f = \alpha_{\min} + K\alpha$, where α is the mass fraction of solvent needed for precipitation, and f is the fraction

of salt that is precipitated. For a salt saturated solution, $\alpha_{\min}$ is = 0. However, for an under-saturated salt solution, $\alpha_{\min}$ is finite, and increases as the salt solution gets more and more under-saturated. Hence, if the feed water is under-saturated, then a nanofiltration membrane is used, as shown in FIG. 16, to concentrate the feed to a higher salt concentration, and hence the reject stream entering the settler, has a higher salt concentration, and hence will need lesser solvent to achieve a lower salt concentration. The salt slurry precipitated in the settler is removed from the bottom of the settler and is partly sent to a filter, not shown in FIG. 16, and partly recycled back to the settler feed by pump. This reject stream can then be put into the solvent precipitation process, precipitating salt that can be filtered out.

[00505] The organic/water solution from the settler unit is pumped through a second nanofiltration system that rejects more salt and some organic, and finally the permeate from this nanofiltration membrane is fed into a reverse osmosis membrane that rejects the remaining salt and the remaining solvent. All the reject streams are recycled back, while the permeate stream from the reverse osmosis system is the treated, desalinated water. Since the required pressure difference across the nanofiltration membrane is based on the salt concentration in the feed and in the permeate, by allowing salt water to pass through with some salt rejection in the nanofiltration membranes, the pumps only have to generate the difference between the osmotic pressures of the feed and permeate streams. The following equation gives the net driving pressure across a nanofiltration membrane:

$$NDP = \left[\left(\frac{P_f + P_c}{2} \right) - (P_p) \right] - \left[\left\{ \left(\frac{TDS_f + TDS_c}{2} \right) - TDS_p \right\} \cdot 0.01 \frac{\text{psi}}{\text{mg / L}} \right]$$

where

NDP	=	net driving pressure (psi)
P_f	=	feed pressure (psi)
P_c	=	concentrate pressure (psi)
P_p	=	filtrate pressure (i.e., backpressure) (psi)
TDS_f	=	feed TDS concentration (mg/L)
TDS_c	=	concentrate TDS concentration (mg/L)
TDS_p	=	filtrate TDS concentration (mg/L)

[00506] If the total dissolved solids (TDS) in the feed, concentrate (reject) and filtrate is high, the net driving pressure (NDP) which has to be generated by the feed pump can be a reasonable number, which means that the operating electrical cost for the process can be acceptable to give an economical process.

[00507] One major discovery of the solvent precipitation process is that the nanofiltration and even the reverse osmosis membranes will undergo less fouling due to salt deposition when an organic solvent is present in the feed. This is a major finding since fouling of reverse osmosis membranes currently is a major challenge for various applications (such as desalination applications). To fully understand this effect of solvent, we have to look at what causes a membrane that is being used for desalination to foul.

[00508] Reverse osmosis membranes have an asymmetrical structure with large pores on one side of the membrane, which decrease in size as you traverse the thickness of the membrane, with a dense layer on the opposite side of the membrane. Membrane fouling occurs due to salt deposition on the membrane surface, which can be periodically cleaned, and also within the membrane structure. This salt deposition occurs due to selective permeation of water through the membrane, and is mainly caused by salt supersaturation, as water moves through the membrane to the permeate side. This is schematically shown in FIG. 21. The reverse osmosis membrane 650 includes a dense membrane 652, and a portion 654 of lesser density. Portion 654 includes a

first surface 656, which is a porous surface having relatively large pores, and a second surface 658 at an interface with the dense membrane. The second surface 658 has smaller pores than the first surface. As water moves through the membrane (as seen in FIG. 21) salt gets deposited within the membrane, resulting in eventual fouling of the membrane. This salt deposition within the membrane results in irreversible loss of membrane water permeability over time, eventually requiring membrane replacement.

[00509] However, one aspect of the present invention is the prevention of this membrane fouling. With the presence of the solvent in the feed water, due to the solvent precipitation process of the present invention, as water selectively permeates through the membrane, the organic solvent concentration increases (because the solvent cannot pass through the membrane – thus, the solvent builds up, and there is an increased concentration of solvent on the reject side of the membrane). This increased solvent concentration results in salt crystallization occurring outside the membrane 660 (i.e., on the reject side of the membrane, as shown in FIG. 22. These fine salt crystals continue to flow with the feed water, eventually leaving the membrane module in the reject stream. The main point here is that before the salt can deposit inside the membrane, it crystallizes outside the membrane and is disposed of in the reject stream, thereby preventing the occurrence of supersaturation condition within the membrane structure, which results in salt deposition within the membrane, as in the case of normal operation of the membrane without an organic solvent. Thus, the membrane does not foul.

[00510] Preliminary testing of a membranes with ethylamine as the organic solvent has shown that the rate of water permeation through the membrane gradually declined when there was no solvent present, while with 15 vol % ethylamine in the feed, there was no decrease in the permeate flux with time.

[00511] Bench-scale experiments were also conducted to determine the separation of ethylamine from water using a membrane system. Studies on ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) were conducted. The membranes used in this study are given in Table 8.

Table 8. Membrane Characteristics – Separation of Monoethanolamine from Water.

Membrane	Ultrafiltration (UF)	Nanofiltration (NF)	Reverse Osmosis (RO)
Material	Cellulose Acetate	Polyamine	Polyamide
Configuration	Tubular	Tubular	Tubular
pH max	2.0 -7.25	1.2-11	1.1-14
Max. Temperature (deg C)	80	80	80
Maximum Pressure (bar)	30	45	64
Apparent Retention	2000 MW	60% CaCl ₂	99% NaCl
Hydrophilicity	5	4	3
Solvent Resistance	+	++	+++

Note: Solvent Resistance: + low, +++ high

[00512] Experimental work was conducted using monoethanolamine (MEA) using the membranes listed in the table. Various concentrations of salt water containing 15%, 30%, 50% by volume of monoethanolamine were used in the testing. The concentrations of monoethanolamine in the feed, permeate and reject were determined using a UV-Spectrophotometer. The Rejection Coefficient of the membrane was calculated as follows:

$$R = \frac{(C_p - C_b)}{C_b}$$

where C_p = permeate concentration and C_b is the bulk concentration.

[00513] The experimental apparatus for this study is shown in FIG. 27. It consists of a feed tank 700, in which the mixture of organic and salt water are added, a high pressure recycle pump 702, a flat membrane cell 704, in which the UF, NF or RO membrane can be used, and the sampling

ports 706, 708, 710 to determine the feed, reject and permeate concentrations of organic in the liquid.

[00514] The membrane cell is a cross-flow system in which the permeate flows perpendicular to the feed flow direction. A single piece of rectangular membrane is installed in the base of the cell. A stainless steel support membrane is used as a permeate carrier. The two cell components are assembled using the stainless steel studs as guides. Hand nuts are used to assemble the membrane cell and tighten the rectangular O-ring on the edges of the flat sheet membrane.

[00515] The feed is pumped to the feed inlet of the membrane cell, which is located at the bottom of the cell. The feed flows tangentially across the membrane surface, and the fluid velocity can be controlled by the user. The permeate is collected from the center of the cell at the top and is collected in a separate vessel. The reject flow from the membrane is recycled back to the feed tank.

[00516] The test system parameters are as follows:

Effective membrane area:	140 cm ² (22 inch ²)
Maximum Pressure:	69 bars (1,000 psig)
Maximum operating temperature:	177 deg C (360 deg F)
Holdup volume:	70 mL
O-rings:	Viton
pH range:	Membrane dependent
Materials of Construction:	
Membrane cell body:	316L stainless steel
Top and Bottom plates:	316L stainless steel
Membrane Support:	20 micron sintered 316L stainless steel
Connections:	
Feed:	¼ inch FNPT
Reject:	¼ inch FNPT
Permeate:	1/8 inch FNPT

[00517] The flow superficial velocity in the membrane cell versus volumetric flow rates is shown in FIG. 28. As the spacer height is increased the superficial velocity for the flow decreases.

[00518] A detailed view of the membrane cell 750, showing the spacer 752, O-ring 754, membrane 756 and flow chambers 758, 760 is shown in FIG. 29. The diagram shows the two chambers for the feed/reject 760 and permeate 758 flows. The feed spacer 752 thickness or height can be varied to obtain different feed flow velocity on the surface of the membrane. The spacer height selected for all the experimental data was 47 mils and the volumetric flowrate was 6 L/min.

[00519] The configuration shown in FIG. 29 also includes a permeate outlet 762, permeate carrier 764, shim 766, feed inlet 768, pressure guage 770, reject flow control valve 772, and reject outlet 774.

[00520] Ethanolamine was bought from Sigma-Aldrich company, St Louis, MO (Product Number E9508), Formula C_2H_7NO , CAS-No.: 141-43-5. Salt water used in the experiments had the following composition analysis:

Analyte Name	Analysis Method Reference	Result	MDL	Units	Analyst	Analyzed Date	Time Started
pH	4500 H+ B	5.53	N/A	s.u.	DER	6/7/2013	5:00:00 PM
Calcium, Total (N)	EPA 200.7	17100	0.149	mg/L	CDG	6/13/2013	9:50:00 AM
Iron, Total	EPA 200.7	94.0	0.016	mg/L	CDG	6/21/2013	10:16:00 AM
Sodium, Total (N)	EPA 200.7	64700	0.602	mg/L	CDG	6/13/2013	9:50:00 AM
Strontium, Total	EPA 200.7	1380	0.002	mg/L	CDG	6/19/2013	3:17:00 PM
Sulfate	HACH 8051	266	0.897	mg/L	DER	6/8/2013	10:32:00 AM
Alkalinity, Bicarbonate (HCO ₃) N	SM 2320 B	52.5	2.0	mg/L	DER	6/9/2013	10:31:00 AM
Alkalinity, Carbonate (CO ₃) N	SM 2320 B	<2.0	2.0	mg/L	DER	6/9/2013	10:31:00 AM
Alkalinity, Tot(CaCO ₃) - Screen	SM 2320 B	52.5	2.0	mg/L	DER	6/9/2013	10:31:00 AM
Chloride	SM 4500 Cl C	200000	1.7	mg/L	VNR	6/14/2013	3:04:00 PM

* All analytes R - samples should be stored and transported on ice or with ice packs.
 * pH Q - measured upon receipt to the laboratory.
 * Aliquot for Metals (Ca, Fe, Sr, Na) split and preserved with HNO₃ upon receipt to the laboratory to pH <2.
 * Sulfate and Chloride F
 * Calcium, Sodium and Strontium F
 * Alkalinity N
 * Calcium B
 * Iron F

Table 9 gives the effect of operating pressure and feed concentration on permeate flux using RO membrane (cross-flow velocity = 6 L/min and pH = 3)

Table 9. Effect of operating pressure and feed concentration on RO membrane flux.

Operating Pressure (bar)	Monoethanolamine concentration (v/v)		
	15%	30%	50%
	Membrane Flux (L/h.m ²)		
7.5	12	10	8
13	25	20	18
20	40	36	30
25	45	40	35

As can be seen, the permeate flux increases with operating pressure, and as the Monoethanolamine concentration is increased from 15 vol% to 50 vol%, there is a decrease in membrane flux. The corresponding fluxes for the NF and UF membranes are given in Tables 10 and 11, respectively.

Table 10. Effect of operating pressure and feed concentration on NF membrane flux.

Operating Pressure (bar)	Monoethanolamine concentration (v/v)		
	15%	30%	50%
	Membrane Flux (L/h.m ²)		
7.5	42	39	36
13	61	57	54
20	106	96	90
25	120	110	100

Table 11. Effect of operating pressure and feed concentration on UF membrane flux.

Operating Pressure (bar)	Monoethanolamine concentration (v/v)		
	15%	30%	50%
	Membrane Flux (L/h.m ²)		
7.5	62	59	54
13	82	76	72
20	147	140	137
25	167	160	154

The membrane rejections for the RO, NF and UF membranes are given in Tables 12, 13, and 14, respectively.

Table 12. Effect of operating pressure and feed concentration on RO membrane rejection coefficient. (Cross-flow velocity = 6 L/min; pH = 3)

Operating Pressure (bar)	Monoethanolamine concentration (v/v)		
	15%	30%	50%
	Rejection Coefficient		
7.5	0.995	0.992	0.990
13	0.998	0.996	0.995
20	1.0	0.997	0.995
25	1.0	0.997	0.995

Table 13. Effect of operating pressure and feed concentration on NF membrane rejection coefficient. (Cross-flow velocity = 6 L/min; pH = 3)

Operating Pressure (bar)	Monoethanolamine concentration (v/v)		
	15%	30%	50%
	Rejection Coefficient		
7.5	0.65	0.62	0.60
13	0.72	0.70	0.68
20	0.78	0.74	0.72
25	0.82	0.80	0.78

Table 14. Effect of operating pressure and feed concentration on UF membrane rejection coefficient. (Cross-flow velocity = 6 L/min; pH = 3)

Operating Pressure (bar)	Monoethanolamine concentration (v/v)		
	15%	30%	50%
	Rejection Coefficient		
7.5	0.35	0.33	0.30
13	0.44	0.40	0.37
20	0.49	0.45	0.42
25	0.54	0.50	0.48

[00521] Clearly, from the data shown in the Examples above, ethanolamine can be separated from salt water using UF, NF and RO. The separation efficiency decreases as we go from a porous membrane, i.e., UF and NF to a dense film, such as in RO. The highest separation efficiency

would be attained by RO. By staging in sequence the UF, NF and RO membranes, it is possible to achieve a very high removal efficiency for the solvent, in this case, ethanolamine.

[00522] While the present invention has been disclosed by reference to the details of preferred embodiments of the invention, it is to be understood that the disclosure is intended as an illustrative rather than in a limiting sense, as it is contemplated that modifications will readily occur to those skilled in the art, within the spirit of the invention and the scope of the amended claims.

We claim:

1. A method of separating a neutrally buoyant material from a liquid, the method comprising
 - (a) pressurizing a first liquid with a gas at a first pressure to form a pressurized liquid;
 - and
 - (b) contacting the pressurized liquid with a second liquid, the second liquid including a neutrally buoyant material dispersed therein, the second liquid being maintained at a second pressure that is lower than the first pressure,wherein the contacting includes a gradient pressure change from the first pressure to the second pressure, such that the gradient pressure change results in the formation of nanobubbles having an average diameter of about 10 nm to 100 nm.
2. The method of claim 1 wherein the first liquid is water.
3. The method of claim 2 wherein the water includes a hydrophobically modified water soluble polymer dispersed or dissolved therein.
4. The method of claim 1 wherein the hydrophobically modified water soluble polymer comprises repeat units derived from monomers including acrylamide, acrylate, methacrylate, or combinations thereof.
5. The method of claim 1 wherein the second liquid is water.

6. The method of claim 5 wherein the water further includes one or more dissolved solids.
7. The method of claim 6 wherein the water is hard water, brackish water, or produced water.
8. The method of claim 1 wherein the neutrally buoyant material is oil or an oily mixture.
9. The method of claim 1 wherein the pressure difference between the first pressure and the second pressure is about 0.1 MPa to 1 MPa.
10. The method of claim 1 wherein the second pressure is about 0.101 MPa.
11. The method of claim 1 wherein the nanobubbles result in flotation of the neutrally buoyant material to the surface of the contacted first and second liquids via association of the neutrally buoyant material with the nanobubbles.
12. The method of claim 11 wherein at least 90 wt% to 100 wt% of the total weight of neutrally buoyant material floats to the surface of the contacted first and second liquids.
13. The method of claim 11 further comprising removing the neutrally buoyant material from the surface of the contacted first and second liquids.

14. The method of claim 1, wherein the neutrally buoyant material has an average density that is between about 95% and about 105% of the density of the second liquid.
15. The method of claim 1, wherein the neutrally buoyant material is dispersed, emulsified, gelled, or agglomerated within the second liquid.
16. The method of claim 1, wherein the neutrally buoyant material is a single compound, a range of related compounds, or a heterogeneous mixture of compounds.
17. The method of claim 1, wherein the neutrally buoyant material includes a single phase or multiple phases.
18. The method of claim 1, wherein the first liquid is a single compound.
19. The method of claim 1, wherein the first liquid is a mixture of different compounds.
20. The method of claim 19, wherein the first liquid is chosen from an aqueous solution of an alcohol, and a solution of a hydrophobically modified water soluble polymer in water.
21. The method of claim 1, wherein the nanobubbles have a density that is 90% or less of the density of the first liquid.

22. The method of claim 1, wherein the gas is air.
23. The method of claim 1, wherein the gas is chosen from carbon dioxide, nitrogen, helium, argon, and air enriched with one or more of N₂, CO₂, O₂, He, and Ar.
24. The method of claim 1, further comprising associating a hydrophobically modified water soluble polymer with the nanobubbles, by dispersing a hydrophobically modified water soluble polymer in the first liquid.
25. The method of claim 1, wherein dispersing the hydrophobically modified water soluble polymer in the first liquid further comprises mixing, tumbling, shaking, or sonicating the first liquid having the hydrophobically modified water soluble polymer therein.
26. The method of claim 1, wherein the first liquid is a mixture of water and a second liquid.
27. The method of claim 1, wherein the first liquid is a mixture of liquids that does not include water.

28. A method of forming nanobubbles, the method comprising
- (a) dissolving a hydrophobically modified water soluble polymer in a liquid to form a solution,
 - (b) pressurizing the solution with a gas to form a pressurized solution, and
 - (c) reducing the pressure applied to the pressurized solution by employing a gradient pressure change sufficient to form nanobubbles out of solution, the nanobubbles having an average diameter of about 10nm to 100nm.
29. The method of claim 28, wherein the hydrophobically modified water soluble polymer comprises repeat units derived from monomers chosen from an acrylamide, an acrylate, a methacrylate, and combinations thereof.
30. The method of claim 29, wherein the monomers comprise acrylamide and dodecylacrylate.
31. The method of claim 28, wherein the hydrophobically modified water soluble polymer has a majority by weight of content that is dispersible or dissolvable in the liquid.
32. The method of claim 28, wherein the hydrophobically modified water soluble polymer has about 0.01wt% to about 5wt%, based on the dry weight of the polymer, of hydrophobic moieties covalently bonded to the polymer backbone.

33. The method of claim 32, wherein the hydrophobic moieties covalently bonded to the polymer backbone are pendant from, incorporated within, or present at the termini of the polymer backbone.

34. The method of claim 32, wherein the hydrophobic moieties includes hydrocarbon, siloxane, fluorocarbon, or a combination thereof.

35. The method of claim 28, wherein the hydrophobically modified water soluble polymer includes at least one hydrophobic moiety.

36. The method of claim 35, wherein the at least one hydrophobic moiety is nonpolar.

37. The method of claim 36, wherein the at least one hydrophobic moiety is a linear alkane moiety.

38. The method of claim 35, wherein the at least one hydrophobic moiety is present within the backbone of the polymer.

39. The method of claim 35, wherein the at least one hydrophobic moiety is an endgroup, and is present substantially only at the termini of the polymer.

40. The method of claim 28, wherein the hydrophobically modified water soluble

polymer includes a minor amount of covalently attached hydrophobic moieties.

41. The method of claim 28, wherein the hydrophobically modified water soluble polymer is chosen from a synthetic polymer, a naturally occurring polymer, and a synthetically modified naturally occurring polymer.

42. The method of claim 28, wherein the hydrophobically modified water soluble polymer is chosen from a linear polymer, a branched polymer, a hyperbranched polymer, and a dendritic polymer.

43. The method of claim 1, wherein the hydrophobically modified water soluble polymer includes hydrophobic moieties pendant to the polymer backbone.

44. The method of claim 43, wherein the hydrophobic moieties are incorporated into the polymer via copolymerization at about 0.01 mole% to 1 mole% of the repeat units of the polymer.

45. The method of claim 44, wherein the incorporation includes the copolymerization of water soluble monomers and hydrophobic vinyl monomers.

46. The method of claim 45, wherein the water soluble monomers are chosen from acrylic acid, methacrylic acid, acrylate salts, methacrylate salts, acrylamide, and methacrylamide.

47. The method of claim 46, wherein the water soluble monomers are copolymerized with one or more of acrylate esters, methacrylate esters, N-functional acrylamide, N,N-difunctional acrylamide, N-functional methacrylamide, or N,N-difunctional methacrylamide monomers having hydrophobic moieties present as the ester or N-functional group(s).

48. The method of claim 43, wherein the hydrophobic moieties are chosen from linear, cyclic, or branched alkyl, aryl, or alkaryl moieties having between 6 and 24 carbons; perfluorinated or partially fluorinated versions of these moieties, and fluorinated alkyl groups having one or more heteroatoms, including perfluoroalkylsulfonamidoalkyl moieties; dialkylsiloxane, diarylsiloxane, or alkylarylsiloxane moieties having between 3 and 10 siloxane repeat units; and the like.

49. The method of claim 43, wherein the hydrophobic moieties include dodecyl, perfluorooctyl, or dimethyltrisiloxane moieties.

50. The method of claim 28, wherein the hydrophobically modified water soluble polymer is synthesized from acrylamide and 1 mole% or less of dodecylacrylamide, N, N-dihexylacrylamide, or dodecylmethacrylate, or dodecylacrylate.

51. The method of claim 28, wherein the amount of the hydrophobically modified water soluble polymer employed in the water is about 0.001 wt% to about 3 wt% in water.

52. An apparatus that achieves separation and removal of neutrally buoyant materials from liquid, the apparatus comprising:

a source of pressurized gas;

a pressurized tank situated to receive a pressurized solution of a first liquid, wherein the pressurized tank is connected to the source of pressurized gas;

an element attached to the pressurized tank and adapted to deliver the pressurized solution into a second liquid; and

a receiving vessel for holding the second liquid having a neutrally buoyant material dispersed therein, wherein the element is disposed within the receiving vessel.

53. The apparatus of claim 52, further comprising a skimmer disposed within the receiving vessel and adapted to remove a separated layer from the surface of a liquid present within the receiving vessel.

54. The apparatus of claim 52, wherein the first liquid further includes a hydrophobically modified water soluble polymer disposed therein.

55. The apparatus of claim 52 wherein the element for delivering the pressurized solution may include one or more headers or one or more eductors.

56. A composition comprising

a) seed crystals composed substantially of a target insoluble salt to be formed from a soluble salt;

b) a reagent capable of forming the target insoluble salt from the soluble salt, when the composition is in the presence of the soluble salt; and

c) water.

57. The composition of claim 56, wherein the seed crystals have an average particle size of about 30 to 100 microns.

58. The composition of claim 56, wherein the reagent is a water soluble sulfate salt.

59. The composition of claim 58, wherein the water soluble sulfate salt is substantially free of protonated sulfate adducts including sulfuric acid and metal hydrogen sulfates.

60. The composition of claim 56, wherein the water soluble sulfate salt is chosen from sodium sulfate, potassium sulfate, lithium sulfate, ammonium sulfate, and magnesium sulfate.

61. The composition of claim 56, wherein the reagent includes more than one soluble metal sulfate.

62. The composition of claim 56, further comprising one or more of surfactants, thermal stabilizers, water soluble polymers, water dispersible polymers, water soluble cosolvents, pH buffers, and adjuvants.

63. The composition of the slurry, wherein the pH of the composition is between about 6 and about 7.5.

64. The composition of claim 56, wherein the composition is substantially free of calcium salts.

65. The composition of claim 56, further comprising sodium chloride.

66. A slurry composition comprising
- a) a water soluble sulfate salt,
 - b) seed crystals consisting essentially of strontium sulfate, the seed crystals having an average particle size of about 30 to 100 microns; and
 - c) water.
67. The slurry composition of claim 66 wherein the composition consists essentially of the recited substituents.
68. The slurry composition of claim 66 wherein the water soluble sulfate salt is sodium sulfate, potassium sulfate, magnesium sulfate, ammonium sulfate, lithium sulfate, or a combination of two or more thereof.
69. The slurry composition of claim 66 further comprising sodium chloride.

70. A method of separating a first soluble salt from a water product that contains the first soluble salt and a second soluble salt, the method comprising:

- a) adding a composition to a water product containing a first soluble salt and a second soluble salt, the composition comprising seed crystals composed substantially of a target insoluble salt to be formed from the first soluble salt; and
- b) collecting the target insoluble salt.

71. The method of claim 70, wherein the seed crystals have an average particle size of about 30 to 100 microns.

72. The method of claim 70, wherein the composition further comprises a reagent capable of forming the target insoluble salt from the first soluble salt.

73. The method of claim 72, wherein the composition further comprises water.

74. The method of claim 70, wherein the first soluble salt is a strontium salt.

75. The method of claim 70, wherein the target insoluble salt is strontium sulfate.

76. The method of claim 70, wherein the second soluble salt is a calcium salt.

77. A method of separating strontium from a water product, the method comprising
- a) forming a slurry composition comprising a water soluble sulfate salt, seed crystals consisting essentially of strontium sulfate, and water, wherein the seed crystals have an average particle size of about 30 to 100 microns;
 - b) adding the slurry composition to a water product, the water product including at least one soluble strontium salt and one soluble calcium salt; and
 - c) collecting strontium sulfate.
78. The method of claim 77 wherein the ratio of calcium:strontium in the water product is between about 0.010:1 and 1000:1 on a weight:weight basis.
79. The method of claim 77 wherein precipitation of 90% to 100% by weight of measurable strontium dissolved in water is collected in the form of strontium sulfate, further wherein the precipitant includes less than about 0.1 to 10 % calcium sulfate by weight.
80. The method of claim 77 further comprising washing the collected strontium sulfate with water.
81. The method of claim 77, further comprising partitioning a portion of the collected strontium sulfate and forming seed crystals from the partitioned strontium sulfate.

82. An apparatus for separating a first soluble salt from a water product that contains the first soluble salt and a second soluble salt, the apparatus comprising:

- a) a source of a water product that contains a first soluble salt and a second soluble salt;
- b) a tank for dispensing a composition into the water product to form a combined flow, the composition comprising seed crystals composed substantially of a target insoluble salt to be formed from the first soluble salt;
- c) an in-line mixer adapted to mix the combined flow;
- d) a precipitator vessel adapted to receive the mixed combined flow and separate treated water and a concentrated slurry of the target insoluble salt from the combined flow; and
- e) a collecting apparatus adapted to receive the concentrated slurry of the target insoluble salt, to collect the target insoluble salt.

83. The apparatus of claim 82, wherein the seed crystals of the composition have an average particle size of about 30 to 100 microns.

84. The apparatus of claim 82, wherein the composition further comprises a reagent capable of forming the target insoluble salt from the first soluble salt.

85. The apparatus of claim 84, wherein the composition further comprises water.

86. The apparatus of claim 82, wherein the first soluble salt is a strontium salt.

87. The apparatus of claim 82, wherein the target insoluble salt is strontium sulfate.
88. The apparatus of claim 82, wherein the second soluble salt is a calcium salt.

89. An apparatus for collecting strontium sulfate from a water product, the water product including at least one soluble strontium salt and one soluble calcium salt, the apparatus comprising at least

- a) a source of the water product;
- b) a tank for dispensing a slurry composition of claim 1 into the water product to form a combined flow;
- c) an in-line mixer adapted to mix the combined flow;
- d) a precipitator vessel adapted to receive the mixed combined flow and separate treated water and a concentrated slurry of strontium sulfate from the combined flow; and
- e) a collecting apparatus adapted to receive the concentrated slurry of strontium sulfate to collect the strontium sulfate.

90. A system for separating a solvent from an aqueous mixture, the system comprising:

(a) a separator including:

i. a housing having at least one wall defining an interior space, an open top end, and an open bottom end, wherein the at least one wall has an inner surface and an outer surface; and

ii. a contour disposed on or defined by at least a portion of the inner surface of the at least one wall;

(b) wherein a flow path for an aqueous mixture is provided by at least a portion of the contour and the inner surface of the at least one wall.

91. The system of claim 90, wherein the aqueous mixture includes water and a solvent.

92. The system of claim 90, wherein the aqueous mixture includes, water, a solvent, and precipitated salt.

93. The system of claim 90, wherein the contour is continuous from substantially the open top end of the separator to the open bottom end of the separator.

94. The system of claim 93, wherein the contour is substantially of a single cross-sectional dimension along the length of the contour.

95. The system of claim 93, wherein a cross-sectional dimension of the contour varies along the length of the contour.

96. The system of claim 93, wherein a cross-sectional shape of the contour is substantially the same along the length of the contour.

97. The system of claim 93, wherein a cross-sectional shape of the contour varies along the length of the contour.

98. The system of claim 90, further comprising a vacuum source operatively coupled to the open top end of the separator.

99. The system of claim 90, further comprising a gas source operatively coupled to the open bottom end of the separator.

100. The system of claim 98, further comprising a gas source operatively coupled to the open bottom end of the separator.

101. The system of claim 90, wherein the at least one wall forms a cylindrical tube structure.

102. The system of claim 101, wherein the open top end and the open bottom end define the tube length, wherein the tube length is about 50 cm to 5 meters.

103. The system of claim 101, wherein the contour is a helical threaded feature.

104. The system of claim 103, wherein the helical threaded feature is disposed on about 50% to 100% of the inner wall surface area.

105. The system of claim 90, wherein the at least one wall defines an inner diameter of about 3 cm to 1.75 cm.

106. The system of claim 103, wherein the helical threaded feature comprises a helix angle of about 25° to 60°.

107. The system of claim 103, wherein the helical threaded feature comprises a rib area and a land area defining a pitch, wherein the pitch is about 0.25 mm to 2 mm.

108. The system of claim 103, wherein the helical threaded feature comprises a rib area and a land area, wherein the rib area has a profile that is substantially triangular or quadrilateral.

109. The system of claim 108, wherein the rib area defines a helix rib base width, wherein the helix rib base width is about 25 μm to 2 mm.

110. The system of claim 108, wherein the rib area is quadrilateral and defines a helix rib top width, wherein the helix rib top width is about 25 μm to 2 mm.

111. The system of claim 90, further comprising a second wall having an inner surface and an outer surface, wherein the second wall is positioned such that the inner surface of the second

wall faces the outer surface of the at least one wall, and wherein an interior space is defined between the second wall and the at least one wall.

112. The system of claim 111, wherein the at least one wall and the second wall together define a two-wall thickness, and wherein the two-wall thickness is about 0.1 mm to 10 mm.

113. The system of claim 111, wherein the second wall comprises one or more fins extending away from the outer surface of the second wall.

114. The system of claim 90, wherein the separator further comprises an entry section proximal to the open top end, the entry section comprising a smooth inner wall section.

115. The system of claim 114, wherein the entry section is frustoconical, wherein the conical angle is about 1° to 10° from the vertical.

116. The system of claim 90, wherein the separator comprises one or more wires extending across the open top end.

117. A method of separating water soluble salts from an aqueous solution, the method comprising

- a. adding a water miscible solvent to a solution of salt in water to form an aqueous mixture, wherein the mass ratio of the water miscible solvent to the total volume of aqueous mixture is about 0.05 to 0.3, and wherein the water miscible solvent is characterized by
 - i. infinite solubility in water at 25°C;
 - ii. a boiling point of greater than 25°C at 0.101 MPa;
 - iii. a heat of vaporization of about 0.5 cal/g or less; and
 - iv. no capability to form an azeotrope with water;
- b. separating a salt slurry from the aqueous mixture; and
- c. evaporating the water miscible solvent from the salt slurry to form a concentrated salt slurry.

118. A method of separating water soluble salts from an aqueous solution, the method comprising

- a. adding a water miscible solvent to a solution of salt in water to form an aqueous mixture, wherein the mass ratio of the water miscible solvent to the total volume of aqueous mixture is about 0.05 to 0.3, and wherein the water miscible solvent is characterized by
 - i. infinite solubility in water at 25°C;
 - ii. a boiling point of greater than 25°C at 0.101 MPa;
 - iii. a heat of vaporization of about 0.5 cal/g or less; and
 - iv. no capability to form an azeotrope with water;
- b. separating a salt slurry from the aqueous mixture; and
- c. evaporating the water miscible solvent from the salt slurry to form a concentrated salt slurry.

119. The method of claim 118, wherein the salt is sodium chloride.

120. The method of claim 118, wherein the solution is a brine.

121. The method of claim 120, wherein the brine is produced by a mining operation.

122. The method of claim 121, wherein the brine has been pretreated to remove one or more materials comprising oily residues, gel particles, suspended solids, strontium, calcium, or two or more thereof.

123. The method of claim 118, wherein the mass ratio of the water-miscible solvent to the total volume of aqueous mixture is achieved over two to twenty individual repetitions of steps a. and b. such that the final mass ratio after the two to twenty repetitions is about 0.05 to 0.3.

124. The method of claim 118, wherein the separating is accomplished by using a one or more hydrocyclone apparatuses.

125. The method of claim 118, wherein the evaporating is carried out in one or more wetted wall separator tubes.

126. The method of claim 125, the evaporating further comprising a source of air flow through the tubes, a source of vacuum attached to the tubes, or both.

127. The method of claim 118, wherein about 70% to 95% by weight of the salt present in the water solution is separated.

128. The method of claim 125, wherein about 90% to 99.9% of the water miscible solvent is evaporated.

129. A wetted wall separator tube comprising a hollow cylindrical pipe having a top opening, a bottom opening, an inner wall, and an outer wall, and comprising a helical threaded feature disposed on at least a portion of the inner wall.

130. The wetted wall separator tube of claim 129, wherein the top opening and bottom opening define the tube length, wherein the tube length is about 50 cm to 5 meters.

131. The wetted wall separator tube of claim 129, wherein the helical threaded feature is disposed on about 50% to 100% of the inner wall surface area.

132. The wetted wall separator tube of claim 129, wherein the inner wall defines an inner diameter of about 3 cm to 1.75 cm.

133. The wetted wall separator tube of claim 129, wherein the helical threaded feature comprises a helix angle of about 25° to 60°.

134. The wetted wall separator tube of claim 129, wherein the helical threaded feature comprises a rib area and a land area defining a pitch, wherein the pitch is about 0.25 mm to 2 mm.

135. The wetted wall separator tube of claim 129, wherein the helical threaded feature comprises a rib area and a land area, wherein the rib area has a profile that is substantially triangular or quadrilateral.

136. The wetted wall separator tube of claim 135, wherein the rib area defines a helix rib base width, wherein the helix rib base width is about 25 μm to 2 mm.
137. The wetted wall separator tube of claim 135, wherein the rib area is quadrilateral and defines a helix rib top width, wherein the helix rib top width is about 25 μm to 2 mm.
138. The wetted wall separator tube of claim 129, wherein the inner wall and outer wall together define a wall thickness, and wherein the wall thickness is about 0.1 mm to 10 mm.
139. The wetted wall separator tube of claim 129, wherein the tube formed from a metal or a thermoplastic, or a combination of two or more thereof.
140. The wetted wall separator tube of claim 139, wherein the metal is stainless steel.
141. The wetted wall separator tube of claim 129, wherein the outer wall comprises one or more fins extending away from the outer wall.
142. The wetted wall separator tube of claim 129, wherein the tube further comprises an entry section proximal to top opening, the entry section comprising a smooth inner wall section.
143. The wetted wall separator tube of claim 142, wherein the entry section is frustoconical, wherein the conical angle is about 1° to 10° from the vertical.

144. The wetted wall separator tube of claim 129, wherein the tube comprises one or more weirs extending across the top opening.

145. An evaporator apparatus comprising one or more wetted wall separator tubes of claim 129.

146. The evaporator apparatus of claim 145, further comprising a jacketed area equipped to accept and circulate a heated fluid, wherein the jacketed area surrounds a portion of the wetted wall separator tubes.

147. The evaporator apparatus of claim 145, wherein a vacuum source is in disposed in fluid communication with the top opening of the one or more wetted wall separation tubes.

148. The evaporator apparatus of claim 145, wherein a source of gas pressure is disposed in fluid communication with the bottom opening of the one or more wetted wall separation tubes.

149. The evaporator apparatus of claim 145, wherein the apparatus comprises between 2 and 2000 wetted wall separation tubes, wherein the tubes are arranged substantially vertically and wherein the top openings thereof are arranged in substantially planar fashion.

150. The evaporator apparatus of claim 145, further comprising a collection apparatus attached to the evaporator apparatus and situated to collect precipitated solids exiting the bottom opening of the one or more wetted wall separation tubes.

151. The evaporator apparatus of claim 145, further comprising a condenser apparatus attached to the evaporator apparatus and situated to condense a water miscible solvent exiting the top opening of the one or more wetted wall separation tubes.

152. A method of precipitating a water soluble salt or water soluble salts from water, the method comprising:

adding a water-miscible solvent to a water solution including an inorganic salt, wherein the water-miscible solvent is characterized by:

- a. infinite solubility in water at 25°C;
- b. a boiling point of greater than 25°C at 0.101 MPa;
- c. a heat of vaporization of about 0.5 cal/g or less; and
- d. no tendency to azeotrope with water;

wherein the mass ratio of the water-miscible solvent to the total volume of aqueous mixture is about 0.05 to 0.3.

153. The method of claim 152, wherein the inorganic salt is sodium chloride.

154. The method of claim 152, wherein the water solution is brine.

155. The method of claim 154, wherein the brine is water produced by a mining operation.

156. The method of claim 155, wherein the brine has been pretreated to remove one or more materials comprising oily residues, gel particles, suspended solids, strontium, calcium, or a mixture of two or more thereof.

157. The method of claim 152, wherein the water-miscible solvent is an organic solvent or inorganic solvent.

158. The method of claim 152, wherein the water-miscible solvent is a mixture of two or more solvents.

159. The method of claim 152, wherein the water-miscible solvent is chosen from methylamine, dimethylamine, trimethylamine, ethylamine, acetaldehyde, methylformate, isopropylamine, propylene oxide, dimethoxymethane, t-butylamine, propionaldehyde, N-propylamine, allylamine, diethylamine, acetone, s-butylamine, or a mixture of two or more thereof.

160. The method of claim 159, wherein the water-miscible solvent is ethylamine.

161. A method of precipitating and concentrating water soluble salts from water, the method comprising

- a. forming an aqueous mixture by adding a water-miscible solvent to a water solution of an inorganic salt, the water-miscible solvent characterized by infinite solubility in water at 25°C, a boiling point of greater than 25°C at 0.101 MPa, a heat of vaporization of about 0.5 cal/g or less, and no tendency to azeotrope with water, wherein the mass ratio of the water-miscible solvent to the total volume of aqueous mixture is about 0.05 to 0.3;
- b. separating precipitated salt from the aqueous mixture; and
- c. evaporating the water-miscible solvent from the water.

162. The method of claim 161, wherein the inorganic salt is sodium chloride.

163. The method of claim 161, wherein the water solution is brine.

164. The method of claim 163, wherein the brine is water produced by a mining operation.

165. The method of claim 164, wherein the brine has been pretreated to remove one or more materials comprising oily residues, gel particles, suspended solids, strontium, calcium, or a mixture of two or more thereof.

166. The method of claim 161, wherein the mass ratio of the water-miscible solvent to the total volume of aqueous mixture is achieved over two to twenty individual repetitions of steps a. and b. such that the final mass ratio after the two to twenty repetitions is about 0.05 to 0.3.

167. The method of claim 161, wherein the separating is accomplished by using a hydrocyclone apparatus.

168. The method of claim 161, wherein the evaporation is carried out in high surface area tubes, the evaporation further comprising a source of air flow through the tubes, a source of vacuum attached to the tubes, or both.

169. The method of claim 161, wherein between about 70% and 95% by weight of the salt present in the water solution is separated.

170. The method of claim 161, wherein about 90% to 99.9% of the water miscible solvent is evaporated.

171. The method of claim 161, wherein the water-miscible solvent is an organic solvent or inorganic solvent.

172. The method of claim 161, wherein the water-miscible solvent is a mixture of two or more solvents.

173. The method of claim 161, wherein the water-miscible solvent is chosen from methylamine, dimethylamine, trimethylamine, ethylamine, acetaldehyde, methylformate, isopropylamine, propylene oxide, dimethoxymethane, t-butylamine, propionaldehyde, N-

propylamine, allylamine, diethylamine, acetone, s-butylamine, or a mixture of two or more thereof.

174. The method of claim 173, wherein the water-miscible solvent is ethylamine.

175. A method of separating a salt or salts from a solution containing dissolved salts and a solvent, comprising:

passing a solution including a liquid, dissolved salts, and a solvent through a membrane having a first side and a second side and is adapted to have a structure or configuration that does not allow the solvent to pass through the first side of the membrane;

wherein solvent concentration increases on the first side of the membrane, and such increased solvent concentration precipitates the salt out of the solution.

176. The method of claim 175, further comprising recapturing the rejected solvent for reuse in precipitating a salt.

177. The method of claim 175, wherein the membrane is chosen from an ultrafiltration membrane, a nanofiltration membrane, and a reverse osmosis membrane.

178. A method of preventing the fouling of a membrane, comprising:
- providing a solvent on a first side of a membrane, wherein the solvent is provided at a concentration capable of precipitating a salt out of solution; and
- passing a solution having a soluble salt therein through said first side of said membrane;
- wherein said solution first contacts said solvent, and said salt precipitates out of solution prior to passing through said first surface of said membrane and into said membrane.
179. The method of claim 178, further comprising, removing said salt from said solvent.