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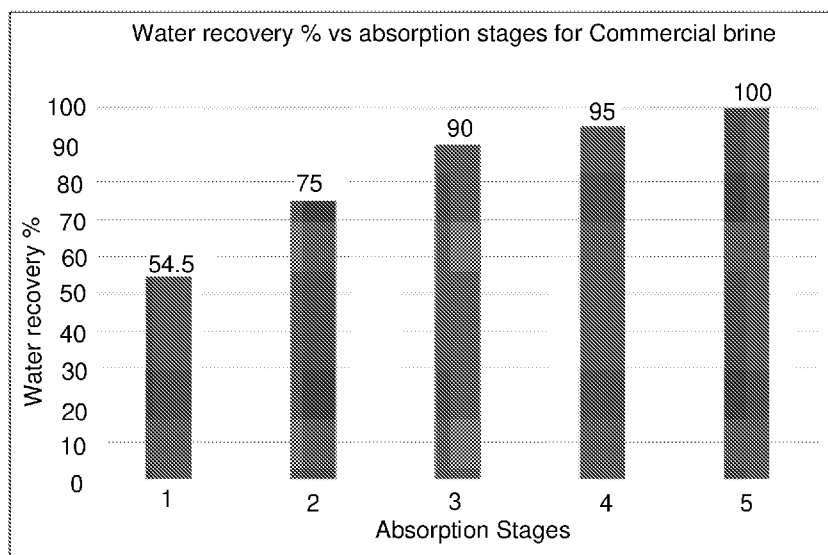
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(54) Title: A SALT RECOVERY SOLUTION AND PROCESSES OF USE THEREOF

Figure 1



(57) Abstract: The present invention relates to a salt recovery solution and to a process for separating a salt from an aqueous solution. The present disclosure also relates to a salt recovery solution and to its use to concentrate a salt or brine solution by recovering water therefrom. The salt recovery solution comprising at least two or more components independently selected from any combination of integers a), b), c) and d): where a) is a straight, branched or optionally substituted cyclic C₄-C₉ ether containing compound; b) is a straight chain or branched C₃-C₉ alkyl substituted by -OH; c) is a straight chain, branched or cyclic C₄-C₉ ketone or C₄-C₉ diketone; and d) is a straight chain or branched C₃-C₉ ester containing compound.



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A SALT RECOVERY SOLUTION AND PROCESSES OF USE THEREOF

FIELD OF THE INVENTION

[0001] The present disclosure relates to a salt recovery solution and to a process for separating a salt from an aqueous solution. The present disclosure also relates to a salt recovery solution and to its use to concentrate a salt or brine solution by recovering water therefrom.

BACKGROUND OF THE INVENTION

[0002] The extraction of salts from an aqueous solution is typically a high energy and time consuming process, requiring removal of water and salt crystallisation. As reported in 2016 by Tong et al. American Chemical Society 6846 DOI: 10.1021/acs.est.6b01000 Environ. Sci. Technol. 2016, 50, 6846–6855, Zero liquid discharge (ZLD) is an ambitious wastewater management strategy that eliminates any liquid waste leaving the plant or facility boundary, with the majority of water being recovered for reuse. Achieving ZLD, however, is generally characterized by intensive use of energy and high cost. As a result, ZLD has long been considered technically but not economically viable and has been applied only in limited cases. In recent years, greater recognition of the dual challenges of water scarcity and pollution of aquatic environments has revived global interest in ZLD. More stringent regulations, rising expenses for wastewater disposal, and increasing value of freshwater are driving ZLD to become a beneficial or even a necessary option for wastewater management. The global market for ZLD is estimated to reach an annual investment of at least \$100–200 million spreading rapidly from developed countries in North America and Europe to emerging economies such as China and India. Early ZLD systems were based on stand-alone thermal processes, where wastewater was typically evaporated in a brine concentrator followed by a brine crystallizer or an evaporation pond. The condensed distillate water in ZLD systems is collected for reuse, while the produced solids are either sent to a landfill or recovered as valuable salt by-products. Such systems, which have been in successful operation for 40 years and are still being built, require considerable energy and capital. Reverse osmosis (RO), a membrane-based technology widely applied in desalination, has been incorporated into ZLD systems to improve energy and cost efficiencies. However, RO, although much more energy efficient than thermal evaporation, can be applied only to feedwaters with a limited salinity range. Accordingly, other salt-concentrating technologies that can treat higher salinity feedwaters, such as electrodialysis (ED), forward osmosis (FO), and membrane distillation (MD), have emerged recently as alternative ZLD technologies to further concentrate wastewater beyond RO. Although ZLD holds great promise to reduce water pollution and augment

water supply, its viability is determined by a balance among the benefits associated with ZLD, energy consumption, and capital/operation costs.

[0003] It is an object of the present invention to provide a solution that overcomes these difficulties or to at least provide a useful alternative.

5 SUMMARY OF THE INVENTION

[0004] In a first aspect, the present invention provides a salt recovery solution suitable for recovering a salt from a salt containing aqueous solution, the salt recovery solution comprising at least two or more components independently selected from any combination of integers a), b), c) and d): where

- 10 a) is a straight, branched or optionally substituted cyclic C₄-C₉ ether containing compound;
- b) is a straight chain or branched C₃-C₉ alkyl substituted by -OH;
- c) is a straight chain, branched or cyclic C₄-C₉ ketone or C₄-C₉ diketone; and
- d) is a straight chain or branched C₃-C₉ ester containing compound;

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wherein at least one component of the salt recovery solution is substantially immiscible with an aqueous solution of sodium chloride at a 1 molar concentration at or above 20 degrees Celsius and at 1 atmosphere.

20 **[0005]** In one embodiment the ether containing compound may be a diether or polyether.

[0006] In one embodiment the C₄-C₉ ether containing compound is selected from one or more of 2-methyltetrahydrofuran, 3-methyltetrahydrofuran, 2-ethyltetrahydrofuran, 3-ethyltetrahydrofuran, dioxane, 2,2-dimethoxy propane, 2-phenoxyethanol, 1-ethoxypropane, and a C₄-C₉ glycol ether or combinations thereof.

25 **[0007]** In one embodiment the straight chain or branched C₃-C₉ alkyl substituted by -OH is selected from one or more of 1-butanol, 2, butanol and 1-pentanol or combinations thereof.

[0008] In one embodiment the C₄-C₉ glycol ether is selected from one or more of propylene glycol methyl ether, dipropyleneglycol dimethyl ether (and isomeric mixtures thereof), dipropylene glycol methyl ethyl acetate, dipropylene glycol n-propyl ether, propylene glycol n-butyl ether, 30 dipropylene glycol n-butyl ether, tripropylene glycol n-butyl ether, propylene glycol phenyl ether, propylene glycol diacetate or combinations thereof.

[0009] In one embodiment the C₄-C₉ ketone or diketone is selected from one or more of acetonylacetone, 2-butanone or cyclohexanone.

[0010] In one embodiment the C₃-C₉ ester is ethyl acetate or methyl acetate.

5 [0011] In one embodiment the salt recovery solution is a combination of 2-methyltetrahydrofuran and acetonylacetone.

[0012] In one embodiment the salt recovery solution is a combination of 2-methyltetrahydrofuran and 1-butanol.

[0013] In one embodiment the salt recovery solution is a combination of 2-methyltetrahydrofuran and 1-pentanol.

10 [0014] In one embodiment the salt recovery solution is a combination of ethyl acetate and 2-butanone.

[0015] In one embodiment the salt recovery solution is a combination of ethyl acetate and 2-methyltetrahydrofuran.

15 [0016] In one embodiment the salt recovery solution is a combination of ethyl acetate and 1-butanol.

[0017] In one embodiment the salt recovery solution is a combination of ethyl acetate and acetonylacetone.

[0018] In one embodiment the salt recovery solution is a combination of methyl acetate and 2-butanone.

20 [0019] In one embodiment the salt recovery solution is a combination of ethyl acetate and 2-phenoxyethanol.

[0020] In one embodiment the salt containing aqueous solution is an industrial brine.

[0021] In another aspect, the present invention provides a process for recovering a salt from an aqueous solution, the process including the step of

25 (a) adding the salt containing first aqueous solution to a salt recovery solution; and
(b) allowing the salt to precipitate on passage through the salt recovery solution.

[0022] In one embodiment the process is a zero-liquid discharge process.

[0023] In one embodiment the process is a counter current process.

[0024] In one embodiment the process is a non-membrane process.

[0025] In one embodiment the process is a non-osmotic process.

[0026] In another aspect, the present invention provides a process for concentrating a salt
5 containing aqueous solution, the process comprising the steps of:

(a) adding the salt containing aqueous solution to a salt recovery solution as defined above;
and

(b) allowing water from the salt containing aqueous solution to pass into the salt recovery
solution.

10 [0027] In one embodiment the precipitated salt forms part of an aqueous layer distinct from
the salt recovery solution.

[0028] In one embodiment the process is a non-membrane process.

[0029] In one embodiment the process is a non-osmotic process.

[0030] In one embodiment the process is a non-membrane and non-osmotic process.

15 [0031] In one embodiment the process concentrates the first aqueous solution by at least
20%. In other embodiments the process concentrates the first aqueous solution by at least 30%, or
by at least 40%, or by at least 50% or by at least 60%, or by at least 70% or by at least 80% or by at
least 90%.

[0032] In one embodiment the process is a minimal discharge process.

20 [0033] In one embodiment the process is a zero-liquid discharge process.

[0034] In one embodiment the aqueous solution is an industrial brine.

[0035] The foregoing brief summary broadly describes the features and technical
advantages of certain embodiments of the present invention. Further technical advantages will be
described in the detailed description of the invention and examples that follows.

25 [0036] Novel features that are believed to be characteristic of the invention will be better
understood from the detailed description of the invention when considered in connection with any
accompanying figures and examples. However, the figures and examples provided herein are

intended to help illustrate the invention or assist with developing an understanding of the invention, and are not intended to limit the invention's scope.

BRIEF DESCRIPTION OF THE DRAWINGS

[0037] Figure 1 shows schematically a plot of the water recovery percentage for each state of a 5 stage counter current absorption process for a commercial brine.

[0038] Figure 2 shows a process flow diagram providing five stages of absorption where water is absorbed from a brine/salt solution in 5 stages.

DETAILED DESCRIPTION OF THE INVENTION

[0039] The following description sets forth numerous exemplary configurations, parameters, and the like. It should be recognised, however, that such description is not intended as a limitation on the scope of the present invention but is instead provided as a description of exemplary embodiments.

DEFINITIONS

[0040] In each instance herein, in descriptions, embodiments, and examples of the present invention, the terms "comprising", "including", etc., are to be read expansively, without limitation. Thus, unless the context clearly requires otherwise, throughout the description and the claims, the words "comprise", "comprising", and the like are to be construed in an inclusive sense as to opposed to an exclusive sense, that is to say in the sense of "including but not limited to".

[0041] The term "about" or "approximately" usually means within 20%, more preferably within 10%, and most preferably still within 5% of a given value or range. Alternatively, the term "about" means within a log (i.e., an order of magnitude) preferably within a factor of two of a given value.

[0042] The term "minimal discharge" as used herein, means a salt water or brine treatment process where minimal effluent or discharge is left over.

[0043] The term "brine" or "brine solution" as used throughout the specification means an aqueous solution having a concentration of a salt in the water. The salt in the water could include sodium chloride, aluminium sulfate or the like, however, a wide range of salt solutions are envisaged that could include any number of a range of cations and anions. The concentration of the salt in the aqueous solution may range from about 3.5% (typical concentration of seawater) through to much higher concentrations, such as 25%, which would include a salt water solution used for brining foods.

Other brine waste water solutions from textile processing, the semiconductor industry or oil, mining and gas industry would also be applicable for use with the current salt recovery solution and processes defined herein.

[0044] As used herein, the term zero liquid discharge, as used throughout the specification, means a wastewater treatment process where no effluent, or discharge, is left over.

[0045] As used herein, the term “C₃-C₉ alkyl” refers to a fully saturated branched or unbranched hydrocarbon moiety, which may be a straight or a branched chain of a particular range of 3-9 carbons. Preferably the alkyl comprises 3 to 7 carbon atoms, or 3 to 6 carbon atoms. Representative examples of C₃-C₉ alkyl include, but are not limited to *n*-propyl, *iso*-propyl, *n*-butyl, *sec*-butyl, *iso*-butyl, *tert*-butyl, *n*-pentyl, isopentyl, neopentyl, *n*-hexyl, 3-methylhexyl, 2,2-dimethylpentyl, 2,3-dimethylpentyl, *n*-heptyl, and the like.

[0046] The term “C₄-C₉ ether containing compound” as used herein is a 4-, 5-, 6-, 7-, 8- or 9-membered saturated, unbranched, branched, or cyclic ether. Representative unbranched C₄-C₉ ether groups include, but are not limited to, methoxyethane, 1-methoxypropane, 1-methoxybutane, 1-methoxypentane, 1-methoxyhexane, 1-methoxyheptane and 1-methoxyoctane, ethoxyethane, 1-ethoxypropane, 1-ethoxybutane, 1-ethoxypentane, 1-ethoxyhexane, 1-ethoxyheptane, 1-propoxypropane, 1-propoxybutane, 1-propoxypentane, 1-propoxyhexane, 1-butoxybutane, 1-butoxypentane, Representative branched C₄-C₉ ether groups include, but are not limited to: 2-methoxypropane, 2-ethoxypropane, 1-isopropoxypropane, 1-isopropoxybutane, 1-isopropoxypentane, 1-isopropoxyhexane, 2-methoxy-2-methylpropane, 2,2-dimethoxypropane, 2-ethoxy-2-methylpropane, 2-methyl-2-propoxypropane, 1-(*tert*-butoxy)butane, 1-(*tert*-butoxy)pentane, 2-(*tert*-butoxy)-2-methylpropane, 2-isopropoxy-2-methylpropane, 2-(*tert*-butoxy)butane, 1-(*tert*-butoxy)-2,2-dimethylpropane. Representative cyclic C₄-C₉ ether groups include, but are not limited to: oxetane, tetrahydrofuran, 2-methyltetrahydrofuran, 3-methyltetrahydrofuran, 2-ethyltetrahydrofuran, 3-ethyltetrahydrofuran, 2-methyltetrahydro-2H-pyran, 3-methyltetrahydro-2H-pyran, 4-methyltetrahydro-2H-pyran, 2,4-dimethyltetrahydro-2H-pyran, 2-ethyltetrahydro-2H-pyran, 3-ethyltetrahydro-2H-pyran, 4-ethyltetrahydro-2H-pyran, oxepane, oxocane, oxanane, 1,3 dioxolane, dioxane, 1,4-dioxepane, 1,5-dioxocane, 1,5-dioxanane and 2-phenoxyethanol. In one embodiment, the C₄-C₉ ether containing compound may be substituted with one or more -OH. In one embodiment the C₄-C₉ ether containing compound may be a diether or a polyether, such as 2,2-dimethoxy propane.

[0047] The term “C₄- to C₉- ketone or diketone” refers to a C₄- to C₉- membered straight chain, branched or cyclic compound containing one or two ketone functional group. Representative examples of a C₄- to C₉- membered ketone include, but are not limited to butanone, pentanone, hexanone, cyclohexanone, 4-methylcyclohexanone, heptanone, 1,2-diketones, 2,3-pentandione, octanone, nonanone, heptane-2,6-dione, acetylacetone, and methylethylketone and the like.

[0048] The term “C₃-C₉ ester containing compound” as used herein is a 4-, 5-, 6-, 7-, 8- or 9-membered saturated, unbranched, branched, ester. Representative C₃-C₉ ester containing compounds as used herein include but are not limited to methyl acetate, ethyl acetate, propylacetate, methyl propionate, ethyl propionate, propyl propionate, butyl propionate, butyl butyrate, isopentyl acetate, 3,3-dimethylbutyl acetate, 3,3-dimethylbutyl propionate, isopropyl propionate, *tert*-butyl propionate; ethyl propionate, methyl pivalate, ethyl pivalate.

[0049] The term “C₄-C₉ glycol ether ” as used herein is a 4-, 5-, 6-, 7-, 8- or 9 -membered saturated, unbranched, branched, or glycol ether which includes without limitation from propylene glycol methyl ether, dipropylene glycol methyl ethyl acetate, dipropylene glycol dimethyl ether (and isomeric mixtures thereof), dipropylene glycol n-propyl ether, propylene glycol n-butyl ether, dipropylene glycol n-butyl ether, tripropylene glycol n-butyl ether, propylene glycol phenyl ether, propylene glycol diacetate.

[0050] The present disclosure provides a salt recovery solution suitable for recovering a salt from an aqueous solution, such as an industrial brine. The salt recovery solution as disclosed is suitable for brines that are quite acidic, although it is to be appreciated that the salt recovery solution described can be used across a wide pH range. The salt recovery solution as described is also suitable for use with brines that have very high dissolved salts that tend towards supersaturated solutions. Industrial brines can be very variable in nature. It is to be appreciated that any inorganic cation or inorganic anion and combinations thereof can create an inorganic salt and it is envisaged that this disclosure has application to all such salts. It is envisaged that a very wide range of salts may be recoverable from an aqueous solution using a salt recovery solution described herein. By way of a non-limiting example, a typical industrial brine may have a composition such as the following involving a number of different salts:

Salt	Concentration (g/L)
Aluminium sulfate(Al ₂ (SO ₄) ₃)	65.8
Calcium chloride (CaCl ₂)	2.0
Calcium sulfate (CaSO ₄)	1.5
Iron sulfate (FeSO ₄)	25.0

Magnesium sulfate (MgSO_4)	80.0
Total TDS, g/L	174.3

[0051] Recovering or precipitating salt from an industrial brine or an aqueous solution aids in releasing water within the brine or aqueous solution and frees the water for subsequent water recovery. The extraction or recovery of water from waste aqueous solutions is desirable, with the ultimate goal being to recover or extract substantially all the water from an aqueous system to lead to minimal liquid discharge or zero liquid discharge (ZLD). The salt recovery solutions as described act by extracting the water from the aqueous solution, in other words, the water migrates from the aqueous solution into the salt recovery solution. In doing so, the salt which had been dissolved in the aqueous solution and has now lost its solvent (water) precipitates out. The water that has migrated into the salt recovery solution can be separated and recovered from the salt. This leads to a viable energy efficient process of physically separating the salt and the water from a brine solution

[0052] The salt recovery solution comprises at least two or more components independently selected from any combination of integers a), b), c) and d) where:

- a) is a straight, branched or optionally substituted cyclic C_4 - C_9 ether containing compound;
- b) is a straight chain or branched C_3 - C_9 alkyl substituted by -OH; and
- c) is a straight chain or branched C_4 - C_9 ketone or C_4 - C_9 diketone; and
- d) is a straight chain or branched C_3 - C_9 ester containing compound;

wherein at least one component of the salt recovery solution is substantially immiscible with an aqueous solution of sodium chloride at a 1 molar concentration at or above 20 degrees Celsius and at 1 atmosphere.

[0053] A number of combinations of components have been found to be suitable as salt recovery solutions. These combinations include but are not limited to:

A combination of a substituted cyclic C_4 - C_9 ether containing compound and a C_4 - C_9 diketone;

A. A combination of a substituted cyclic C_4 - C_9 ether containing compound and a straight chain C_3 - C_9 alkyl substituted by -OH;

B. A combination of a C_3 - C_9 ester and a straight chain C_3 - C_9 alkyl substituted by -OH;

- 5 C. A combination of a C₃-C₉ ester and and a C₄-C₉ diketone;
- D. A combination of a substituted cyclic C₄-C₉ ether containing compound, a straight chain C₃-C₉ alkyl substituted by -OH; and a straight chain C₃-C₉ alkyl substituted by -OH;
- E. A combination of a substituted cyclic C₄-C₉ ether containing compound, a C₄-C₉ diketone and a straight chain C₃-C₉ alkyl substituted by -OH;
- 10 F. A combination of a substituted cyclic C₄-C₉ ether containing compound, a C₄-C₉ diketone and a C₃-C₉ alkyl substituted by -OH;
- G. A combination of 2-methyltetrahydrofuran and acetonylacetone;
- H. A combination of 2-methyltetrahydrofuran and 1-butanol;
- I. A combination of 2-methyltetrahydrofuran and 2-butanol;
- J. A combination of 2-methyltetrahydrofuran and 1-pentanol;
- K. A combination of 2-methyltetrahydrofuran and methylethylketone;
- L. A combination of ethyl acetate and acetonylacetone;
- M. A combination of ethyl acetate and 1-butanol;
- 15 N. A combination of 2-methyltetrahydrofuran, 1-butanol and acetonylacetone;
- O. A combination of 2-methyltetrahydrofuran; 1-butanol and 1-propanol;
- P. A combination of 2-methyltetrahydrofuran, 1-butanol and 3-methyl-1-butanol;
- Q. A combination of 2-methyltetrahydrofuran; 1-butanol and 1,4-butanediol;
- R. A combination of methyl acetate and 2-butanone;
- 20 S. A combination of ethyl acetate and di(propylene glycol) dimethyl ether (isomeric mixture);
- T. A combination of ethyl acetate and 2-phenoxyethanol;
- U. A combination of ethyl acetate and 2-dimethoxypropane;
- V. A combination of ethyl acetate and cyclohexanone; and
- 25 W. A combination of 2-methyltetrahydrofuran and methyl acetate.

[0054] The components as defined above create a solution into which water can readily migrate. The molar ratios of the components of the salt recovery solution can vary widely, however, there are preferred molar ratios that can be determined for each combination of components. The molar ratios can vary anywhere from 1:99 or 99:1 of the respective combination of components. More preferably, the molar ratio can be from about 1:50 or 50:1; or about 1:30 or 30:1; or about 1:10 or 10:1; or about 1:5 or 5:1; or about 1:3 or 3:1; or about 1:2 or 2:1 or about 1:1.

[0055] It is to be understood that it is possible to optimise the molar ratio combinations for the particular combination but also for a particular aqueous solution. In one embodiment the molar ratio combinations of some specific combinations for a simple salt solution comprising 300 g/litre of sodium chloride were found to be optimised as follows:

- A. A combination of 2-methyltetrahydrofuran and acetonylacetone, in a molar ratio of about 1:1 to about 1:10, or a molar ratio of about 2:1 to about 3:2;
- B. A combination of 2-methyltetrahydrofuran and 1-butanol, in a molar ratio of about 1:1 to about 1:10 or about 3:2 to about 3:7 or about 2:1 to about 3:2;
- C. A combination of 2-methyltetrahydrofuran and 1-pentanol in a molar ratio of about 1:1 to about 1:10 or a molar ratio of about 2:1 to about 3:2,
- D. A combination of ethyl acetate and 2-butanone in a molar ratio of about 1:1 to about 1:10.
- E. A combination of ethyl acetate and 2-methyltetrahydrofuran in a molar ratio of about 1:1 to about 1:10.
- F. A combination of ethyl acetate and 1-butanol in a molar ratio of about 1:1 to about 1:10.
- G. A combination of ethyl acetate and acetonylacetone in a molar ratio of about 1:1 to about 1:10.

[0056] The optimised molar ratios are those molar ratios that will lead to the quickest and most efficient passage or extraction of water from the salt containing aqueous solution into the salt recovery solution. This means that the zero liquid discharge target can be achieved more easily with an optimised molar ratio. The ZLD ratio is the amount of salt recovery solution that is needed to be added to extract all the water from the original aqueous solution. The lower the ZLD ratio the more efficient the extraction of water from the salt containing aqueous solution and the less salt recovery

solution required. A ZLD ratio of less than about 50 is preferred. While ZLD ratios higher than 50 will also work, it will just take greater volumes of salt recovery solution to achieve ZLD.

[0057] It is also to be appreciated that it is important when choosing the components for the salt recovery solution that minimal or no salt crossover is seen into the salt recovery solution. The purpose of the solution is to separate the salt from the water of the salt containing aqueous solution. Accordingly, the most desirable combinations will also be determined by those that exhibit minimal salt cross over at the molar ratios chosen. This will vary from salt recovery solution to salt recovery solution.

[0058] In another aspect, the present invention provides a process for concentrating a salt containing aqueous solution, the process comprising the steps of:

- (a) adding the salt containing aqueous solution to a salt recovery solution as defined above;
and
- (b) allowing water from the salt containing aqueous solution to pass into the salt recovery solution.

[0059] In one embodiment the process does not require a membrane to achieve the separation of the salt from the water.

[0060] In one embodiment the process is a non-osmotic process.

[0061] In one embodiment the process concentrates the first aqueous solution by at least 20%. In other embodiments the process concentrates the first aqueous solution by at least 30%, or by at least 40%, or by at least 50% or by at least 60%, or by at least 70% or by at least 80% or by at least 90%.

[0062] In one embodiment the process is a minimal discharge process, preferably a zero-liquid discharge process.

[0063] In one embodiment the aqueous solution is an industrial brine.

[0064] In a further embodiment the salt recovery solution is recovered by removing the water extracted into it. This process can be done using known techniques for removing water or releasing water from the salt recovery solution. Once the water has been removed from the salt recovery solution it can be recycled for use in a further separation process. The process may be converted into a continuous process. The process could be utilized on a large scale. Suitable processes for removing water or releasing water from the salt recovery solution are described in

PCT/NZ2020/050034, published as WO/2020/204733, the contents of the specification are herein incorporated by reference.

[0065] It is to be appreciated that the process may include the further step of adding an additive to the salt recovery solution to further release water held within the salt recovery solution.

5 In one embodiment the additive is citric acid. In one embodiment the citric acid is a concentrated solution of citric acid comprising between about 200-450gms of citric acid per litre of water. In another embodiment the citric acid is anhydrous citric acid added directly to the salt recovery solution.

[0066] It is to be appreciated that the molar ratio of the at least one component of a) to c) with the other component independently selected from a) to c) are present in a ratio of about 1:99 or 99:1. may be from about 1:99 or 99:1; or from about 1:50 or 50:1 or from about 1:10 or 10:1 or from about 1:5 or 5:1 or from about 1:3 or from about 3:1 or from about 1:2 or from about 2:1. In a preferred embodiment the molar ratio is about 1:1. A chemistry technician would be able to routinely determine the most suitable molar ratio depending on the purpose for which the salt recovery solution is to be employed.

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[0067] In a further embodiment the salt containing aqueous solution is salt water or a brine solution.

[0068] It is to be appreciated that the salt containing aqueous solution may need an optional pre-treatment step prior to being exposed to the salt recovery solution. Such pre-treatment may require a filtering step to remove any undissolved solids or clays, for example.

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EXAMPLES

[0069] The examples described herein are provided for the purpose of illustrating specific embodiments of the invention and are not intended to limit the invention in any way. Persons of ordinary skill can utilise the disclosures and teachings herein to produce other embodiments and variations without undue experimentation. All such embodiments and variations are considered to be part of this invention.

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Examples – Preparation and testing of a range of salt recovery solutions

[0070] The salt recovery solutions were all made using two components – component A and component B. For each type of salt recovery solution, the component A and component B were varied according to the molar ratios. The resulting solution was mixed with salt containing aqueous solution

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(brine). The ratio at which there was complete salt precipitation i.e., zero-liquid discharge (ZLD) condition was determined.

[0071] Standard salt solution was used as the aqueous solution. It was prepared by dissolving sodium chloride (NaCl) in water at a concentration of 300 000 ppm.

- 5 **[0072]** Compounds used in the formulation of salt recovery solution were: 2-Methyltetrahydrofuran (MeTHF), 1-butanol, 2,5-hexanedione (Acetylacetone), 1-pentanol, ethanol acetate and 2-butanone.

- 10 **[0073]** Apparatus used: After adding the brine solution to the salt recovery solution, the samples were mixed in vortex mixer for 30 seconds. After ensuring thorough mixing, these samples were centrifuged at 4000 rpm for 1 minute for the precipitated salts to settle at the bottom of the sample tubes.

The following table shows the different compounds used in preparing the salt recovery solutions:

Table 1: Different examples of salt recovery solution compositions:

Example No.	Component A	Component B
1	MeTHF	Acetylacetone
2	MeTHF	1-Butanol
3	MeTHF	1-Pentanol
4	Ethyl acetate	2-Butanone
5	Ethyl acetate	MeTHF
6	Ethyl acetate	1-Butanol
7	Ethyl acetate	Acetylacetone

15 **Example 1: MeTHF and Acetylacetone**

[0074] The salt recovery solution was prepared using MeTHF and acetylacetone. These individual components were combined at different molar ratios and the ZLD ratio for NaCl brine solution (300 000 ppm) was determined and shown below in Table 2.

Table 2:

Mole ratio of MeTHF	Mole ratio of acetonylacetone	Volume of MeTHF, mL	Volume of Acetonylacetone, mL	Volume of salt recovery solution, mL	Brine added, mL	ZLD ratio
0.10	0.90	0.87	9.13	10.00	1.30	7.69
0.20	0.80	1.77	8.23	10.00	1.10	9.09
0.33	0.67	3.01	6.99	10.00	0.85	11.70
0.40	0.60	3.64	6.36	10.00	0.80	12.50
0.50	0.50	4.62	5.38	10.00	0.70	14.29
0.60	0.40	5.63	4.37	10.00	0.60	16.67
0.67	0.33	6.32	3.68	10.00	0.50	20.00
0.75	0.25	7.21	2.79	10.00	0.35	28.57
0.85	0.15	8.30	1.70	10.00	0.30	33.33
0.95	0.05	9.42	0.58	10.00	0.20	50.00

Example 2: MeTHF and 1-Butanol

[0075] The salt recovery solution was prepared using MeTHF and 1-butanol. These individual components were combined at different molar ratios and the ZLD ratio for NaCl brine solution (300 000 ppm) was determined and shown below in Table 3:

Table 3

Mole ratio of MeTHF	Mole ratio of 1-butanol	Volume of MeTHF, mL	Volume of 1-butanol, mL	Volume of salt recovery solution, mL	Brine added, mL	ZLD ratio
0.10	0.90	3.20	26.00	13.00	1.00	13.00
0.20	0.80	5.00	18.30	11.00	1.00	11.00
0.30	0.70	7.50	16.01	12.00	1.00	12.00
0.40	0.60	10.00	13.72	12.00	1.00	12.00
0.50	0.50	12.50	11.43	12.00	0.80	15.00
0.60	0.40	15.00	9.14	12.00	0.80	15.00
0.70	0.30	17.50	6.85	15.00	0.80	18.75
0.80	0.20	20.00	4.58	17.00	0.20	85.00
0.90	0.10	22.50	2.27	17.50	0.20	87.50

Example 3: MeTHF and 1-Pentanol

[0076] The salt recovery solution was prepared using MeTHF and 1-pentanol. These individual components were combined at different molar ratios and the ZLD ratio for NaCl brine solution (300 000 ppm) was determined and show below in Table 4.

Table 4

Mole ratio of MeTHF	Mole ratio of 1-pentanol	Volume of MeTHF, mL	Volume of 1-pentanol, mL	Volume of salt recovery solution, mL	Brine added, mL	ZLD ratio
0.10	0.90	0.93	9.07	10.00	0.50	20.00
0.20	0.80	1.88	8.12	10.00	0.50	20.00
0.33	0.67	3.17	6.83	10.00	0.50	20.00
0.40	0.60	3.82	6.18	10.00	0.50	20.00
0.50	0.50	4.81	5.19	10.00	0.50	20.00
0.60	0.40	5.82	4.18	10.00	0.40	25.00
0.67	0.33	6.50	3.50	10.00	0.40	25.00
0.75	0.25	7.36	2.64	10.00	0.40	25.00
0.85	0.15	8.40	1.60	10.00	0.30	33.33
0.95	0.05	9.46	0.54	10.00	0.20	50.00

Example 4: Ethyl acetate and 2-Butanone

[0077] The salt recovery solution was prepared using ethanol acetate and 2-butanone. These individual components were combined at different molar ratios and the ZLD ratio for NaCl brine solution (300 000 ppm) was determined and shown below in Table 5.

Table 5:

Mole ratio of ethyl acetate	Mole ratio of 2-butanone	Volume of ethyl acetate, mL	Volume of 2-butanone, mL	Volume of salt recovery solution, mL	Brine added, mL	ZLD ratio
0.10	0.90	1.10	8.90	10.00	0.30	33.33
0.20	0.80	2.10	7.90	10.00	0.30	33.33

0.33	0.67	3.50	6.50	10.00	0.25	40.00
0.40	0.60	4.15	5.85	10.00	0.20	50.00
0.50	0.50	5.15	4.85	10.00	0.10	100.00
0.60	0.40	6.14	3.86	10.00	0.09	111.11
0.67	0.33	6.80	3.20	10.00	0.09	117.65
0.75	0.25	7.61	2.39	10.00	0.08	125.00
0.85	0.15	8.58	1.42	10.00	0.08	125.00
0.95	0.05	9.53	0.47	10.00	0.08	125.00

Example 5: Ethyl acetate and MeTHF

[0078] The salt recovery solution was prepared using ethanol acetate and MeTHF. These individual components were combined at different molar ratios and the ZLD ratio for NaCl brine solution (300 000 ppm) was determined and shown in Table 6.

Table 6:

Mole ratio of ethyl acetate	Mole ratio of MeTHF	Volume of ethyl acetate, mL	Volume of MeTHF, mL	Volume of salt recovery solution, mL	Brine added, mL	ZLD ratio
0.10	0.90	0.97	9.03	10.00	0.10	100.00
0.20	0.80	1.95	8.05	10.00	0.09	111.11
0.33	0.67	3.26	6.74	10.00	0.09	111.11
0.40	0.60	3.92	6.08	10.00	0.09	117.65
0.50	0.50	4.92	5.08	10.00	0.08	125.00
0.60	0.40	5.92	4.08	10.00	0.07	142.86
0.67	0.33	6.60	3.40	10.00	0.07	153.85
0.75	0.25	7.44	2.56	10.00	0.07	153.85
0.85	0.15	8.46	1.54	10.00	0.06	181.82
0.95	0.05	9.48	0.52	10.00	0.05	200.00

Example 6: Ethyl acetate and 1-Butanol

[0079] The salt recovery solution was prepared using ethyl acetate and 1-butanol. These individual components were combined at different molar ratios and the ZLD ratio for NaCl brine solution (300 000 ppm) was determined and shown in Table 7.

Table 7:

Mole ratio of ethyl acetate	Mole ratio of 1-butanol	Volume of ethyl acetate, mL	Volume of 1-butanol, mL	Volume of salt recovery solution, mL	Brine added, mL	ZLD ratio
0.10	0.90	1.06	8.94	10.00	0.75	13.33
0.20	0.80	2.11	7.89	10.00	0.70	14.29
0.33	0.67	3.48	6.52	10.00	0.45	22.22
0.40	0.60	4.15	5.85	10.00	0.45	22.22
0.50	0.50	5.16	4.84	10.00	0.50	20.00
0.60	0.40	6.16	3.84	10.00	0.38	26.32
0.67	0.33	6.81	3.19	10.00	0.35	28.57
0.75	0.25	7.62	2.38	10.00	0.25	40.00
0.85	0.15	8.58	1.42	10.00	0.20	50.00
0.95	0.05	9.53	0.47	10.00	0.10	100.00

5

Example 7: Ethyl acetate and Acetonylacetone

[0080] The salt recovery solution was prepared using ethyl acetate and acetonylacetone. These individual components were combined at different molar ratios and the ZLD ratio for NaCl brine solution (300 000 ppm) was determined and shown in Table 8.

10 Table 8:

Mole ratio of ethyl acetate	Mole ratio of acetonylacetone	Volume of ethyl acetate, mL	Volume of Acetonylacetone, mL	Volume of salt recovery solution, mL	Brine added, mL	ZLD ratio
0.10	0.90	0.85	9.15	10.00	1.10	9.09
0.20	0.80	1.72	8.28	10.00	1.10	9.09
0.33	0.67	2.94	7.06	10.00	0.75	13.33

0.40	0.60	3.57	6.43	10.00	0.70	14.29
0.50	0.50	4.54	5.46	10.00	0.50	20.00
0.67	0.33	6.25	3.75	10.00	0.35	28.57
0.75	0.25	7.14	2.86	10.00	0.30	33.33
0.85	0.15	8.25	1.75	10.00	0.25	40.00
0.95	0.05	9.41	0.59	10.00	0.20	50.00

Example 8: Methyl acetate and 2-Butanone

[0081] The salt recovery solution was prepared using methyl acetate and 2-butanone. These individual components were combined at different molar ratios and the ZLD ratio for NaCl brine solution (300 000 ppm) was determined and shown in Table 9.

Table 9:

Mole ratio of Methyl Acetate	Mole ratio of 2-Butanone	Volume of Methyl Acetate, mL	Volume of 2-Butanone, mL	Volume of salt recovery solution, mL	Brine added, mL	ZLD ratio
0.10	0.90	0.90	9.10	10.00	0.33	30.00
0.20	0.80	1.82	8.18	10.00	0.33	30.00
0.33	0.67	3.07	6.93	10.00	0.33	30.00
0.40	0.60	3.72	6.28	10.00	0.33	30.00
0.50	0.50	4.70	5.30	10.00	0.33	30.00
0.60	0.40	5.71	4.29	10.00	0.33	30.00
0.67	0.33	6.40	3.60	10.00	0.33	30.00
0.75	0.25	7.27	2.73	10.00	0.33	30.00
0.85	0.15	8.34	1.66	10.00	0.33	30.00
0.95	0.05	9.44	0.56	10.00	0.33	30.00

Example 9: Ethanol acetate and Di(propylene glycol) dimethyl ether, mixture of isomers

[0082] The salt recovery solution was prepared using ethanol acetate and Di(propylene glycol) dimethyl ether, mixture of isomers. These individual components were combined at different molar ratios and the ZLD ratio for NaCl brine solution (300 000 ppm) was determined and shown in Table 10.

Table 10:

Mole ratio of Ethanol Acetate	Mole ratio of Di(propylene glycol) dimethyl ether, mixture of isomers	Volume of Ethanol Acetate, mL	Volume of Di(propylene glycol) dimethyl ether, mixture of isomers, mL	Volume of salt recovery solution, mL	Brine added, mL	ZLD ratio
0.10	0.90	0.57	9.43	10.00	0.20	50.00
0.20	0.80	1.20	8.80	10.00	0.20	50.00
0.33	0.67	2.14	7.86	10.00	0.20	50.00
0.40	0.60	2.66	7.34	10.00	0.20	50.00
0.50	0.50	3.52	6.48	10.00	0.20	50.00
0.60	0.40	4.49	5.51	10.00	0.20	50.00
0.67	0.33	5.21	4.79	10.00	0.20	50.00
0.75	0.25	6.20	3.80	10.00	0.10	100.00
0.85	0.15	7.55	2.45	10.00	0.10	100.00
0.95	0.05	9.12	0.88	10.00	0.10	100.00

Example 10: Ethanol acetate and 2-Phenoxyethanol

[0083] The salt recovery solution was prepared using ethanol acetate and 2-Phenoxyethanol. These individual components were combined at different molar ratios and the ZLD ratio for NaCl brine solution (300 000 ppm) was determined and shown in Table 11.

Table 11:

Mole ratio of Ethanol Acetate	Mole ratio of 2-Phenoxyethanol	Volume of Ethanol Acetate, mL	Volume of 2-Phenoxyethanol, mL	Volume of salt recovery solution, mL	Brine added, mL	ZLD ratio
0.10	0.90	0.74	9.26	10.00	0.67	15.00
0.20	0.80	1.53	8.47	10.00	0.67	15.00
0.33	0.67	2.65	7.35	10.00	0.67	15.00
0.40	0.60	3.25	6.75	10.00	0.50	20.00
0.50	0.50	4.19	5.81	10.00	0.50	20.00
0.60	0.40	5.20	4.80	10.00	0.50	20.00

0.67	0.33	5.91	4.09	10.00	0.33	30.00
0.75	0.25	6.84	3.16	10.00	0.33	30.00
0.85	0.15	8.03	1.97	10.00	0.20	50.00
0.95	0.05	9.32	0.68	10.00	0.20	50.00

Example 11: Ethanol acetate and 2-Dimethoxypropane

[0084] The salt recovery solution was prepared using ethanol acetate and 2-Dimethoxypropane. These individual components were combined at different molar ratios and the ZLD ratio for NaCl brine solution (300 000 ppm) was determined and shown in Table 12.

Table 12:

Mole ratio of Ethanol Acetate	Mole ratio of 2-Dimethoxypropane	Volume of Ethanol Acetate, mL	Volume of 2-Dimethoxypropane, mL	Volume of salt recovery solution, mL	Brine added, mL	ZLD ratio
0.10	0.90	0.81	9.19	10.00	0.03	300.00
0.20	0.80	1.66	8.34	10.00	0.10	100.00
0.33	0.67	2.85	7.15	10.00	0.10	100.00
0.40	0.60	3.47	6.53	10.00	0.10	100.00
0.50	0.50	4.44	5.56	10.00	0.10	100.00
0.60	0.40	5.45	4.55	10.00	0.10	100.00
0.67	0.33	6.15	3.85	10.00	0.10	100.00
0.75	0.25	7.05	2.95	10.00	0.10	100.00
0.85	0.15	8.19	1.81	10.00	0.10	100.00
0.95	0.05	9.38	0.62	10.00	0.10	100.00

Example 12: Ethanol acetate and Cyclohexanone

[0085] The salt recovery solution was prepared using ethanol acetate and cyclohexanone. These individual components were combined at different molar ratios and the ZLD ratio for NaCl brine solution (300 000 ppm) was determined and shown in Table 13.

Table 13:

Mole ratio of Ethanol Acetate	Mole ratio of 2-Dimethoxypropane	Volume of Ethanol Acetate, mL	Volume of Cyclohexanone, mL	Volume of salt recovery solution, mL	Brine added, mL	ZLD ratio
0.10	0.90	0.95	9.05	10.00	0.20	50.00
0.20	0.80	1.91	8.09	10.00	0.20	50.00
0.33	0.67	3.21	6.79	10.00	0.20	50.00
0.40	0.60	3.86	6.14	10.00	0.20	50.00
0.50	0.50	4.85	5.15	10.00	0.20	50.00
0.60	0.40	5.86	4.14	10.00	0.20	50.00
0.67	0.33	6.54	3.46	10.00	0.20	50.00
0.75	0.25	7.39	2.61	10.00	0.10	100.00
0.85	0.15	8.42	1.58	10.00	0.10	100.00
0.95	0.05	9.47	0.53	10.00	0.10	100.00

Example 13: MeTHF and Methyl Acetate

[0086] The salt recovery solution was prepared using MeTHF and methyl acetate. These individual components were combined at different molar ratios and the ZLD ratio for NaCl brine solution (300 000 ppm) was determined and shown in Table 14.

Table 14:

Mole ratio of MeTHF	Mole ratio of Methyl Acetate	Volume of MeTHF, mL	Volume of Methyl Acetate, mL	Volume of salt recovery solution, mL	Brine added, mL	ZLD ratio
0.10	0.90	1.24	8.76	10.00	0.20	50.00
0.20	0.80	2.41	7.59	10.00	0.20	50.00
0.33	0.67	3.88	6.12	10.00	0.20	50.00
0.40	0.60	4.58	5.42	10.00	0.20	50.00
0.50	0.50	5.59	4.41	10.00	0.20	50.00
0.60	0.40	6.56	3.44	10.00	0.20	50.00

0.67	0.33	7.17	2.83	10.00	0.20	50.00
0.75	0.25	7.92	2.08	10.00	0.20	50.00
0.85	0.15	8.78	1.22	10.00	0.20	50.00
0.95	0.05	9.60	0.40	10.00	0.20	50.00

[0087] The results of these salt recovery solutions show that it is possible to get very effective salt recovery solutions with low ZLD ratios to effectively separate salt from water in a brine solution. These results demonstrate the potential and applicability of these salt recovery solutions to achieve ZLD with industrial brines with lower energy requirements. With many ZLD ratios shown to be below 50 and many below 30 these results are promising. While the ZLD ratios in Example 5 are greater than 50, it is to be appreciated that changes could be made to the components of Example 5, such as the addition of a further component to produce a ternary system that may significantly alter the ZLD potential.

Example 14: Modifying the salt recovery solution into a ternary system

In the examples 1 to 7 above, the salt recovery solutions were formulated to include two components (a binary system). In the following examples an additional component was added to see the effect of a ternary system on the ZLD ratios and the water absorption capacity of the resulting salt recovery solutions.

[0088] Ternary salt recovery solutions were mixed with standard aqueous solution made up of NaCl at a concentration of 300 000 ppm. The ratio at which there was complete salt precipitation i.e., zero-liquid discharge (ZLD) condition was determined.

[0089] Some of the combinations (both binary and ternary systems) were also tested against synthetic commercial brine sample whose composition matched closely to that of a mining waste stream.

[0090] The following ternary salt recovery solutions were prepared as set out in Table 15. The salt recovery solution was made up of three compounds – compound A, compound B and compound C. In this example, compound A was MeTHF and compound B was 1-butanol. The additional Compound C used was - acetonylacetone, 1-propanol, 1-pentanol, 3-methyl-1-butanol and 1,4-

butanediol. The following table shows the different compounds selected as part of the salt recovery solution composition:

Table 15:

Compound A	Compound B	Compound C
MeTHF	1-Butanol	Acetylacetone
MeTHF	1-Butanol	1-Propanol
MeTHF	1-Butanol	1-Pentanol
MeTHF	1-Butanol	3-Methyl-1-butanol
MeTHF	1-Butanol	1,4-Butanediol

- 5 **[0091]** The molar ratio of Compound C was varied from 0.1 to 0.3 and its effect on the water absorption capacity of the salt recovery solution was determined. The ZLD ratio of the ternary salt recovery solution was determined for standard NaCl brine at a concentration of 300 000 ppm.

[0092] A brine sample was prepared comprising sodium chloride (NaCl) in deionised water at a concentration of 300 000 ppm.

- 10 **[0093]** 5 mL of the salt recovery solution was taken in centrifuge tubes. The brine sample was added in the increments of 100uL and the ZLD ratio was determined. The following Table 16 shows the various mole ratios of the compounds in the salt recovery solution and its ZLD ratio for standard NaCl brine:

Table 16:

Compound A	Compound B	Compound C	Mole ratio of Compound A: Compound B: Compound C	Volume of salt recovery solution, mL	Brine added, mL	ZLD ratio for NaCl brine (300 000 ppm)
MeTHF	1-Butanol	Acetylacetone	0.5: 0.4: 0.1	5	0.35	14.3
MeTHF	1-Butanol	Acetylacetone	0.5: 0.3: 0.2	5	0.36	13.9
MeTHF	1-Butanol	Acetylacetone	0.5: 0.2: 0.3	5	0.4	12.5
MeTHF	1-Butanol	1-Propanol	0.5: 0.4: 0.1	5	0.4	16.7
MeTHF	1-Butanol	1-Propanol	0.5: 0.3: 0.2	5	0.45	16.7

MeTHF	1-Butanol	1-Propanol	0.5: 0.2: 0.3	5	0.47	25.0
MeTHF	1-Butanol	1-Pentanol	0.5: 0.4: 0.1	5	0.3	16.7
MeTHF	1-Butanol	1-Pentanol	0.5: 0.3: 0.2	5	0.3	16.7
MeTHF	1-Butanol	1-Pentanol	0.5: 0.2: 0.3	5	0.2	25.0
MeTHF	1-Butanol	3-Methyl-1-butanol	0.5: 0.4: 0.1	5	0.3	16.7
MeTHF	1-Butanol	3-Methyl-1-butanol	0.5: 0.3: 0.2	5	0.3	16.7
MeTHF	1-Butanol	3-Methyl-1-butanol	0.5: 0.2: 0.3	5	0.25	20.0
MeTHF	1-Butanol	1,4-Butanediol	0.5: 0.4: 0.1	5	0.4	12.5
MeTHF	1-Butanol	1,4-Butanediol	0.5: 0.3: 0.2	5	0.4	12.5
MeTHF	1-Butanol	1,4-Butanediol	0.5: 0.2: 0.3	5	1	5.0

[0094] It can be seen from Table 16 that the ZLD ratio can be changed quite markedly with the addition of a third component, when comparing against the ZLD ratio observed for the two component system MeTHF and 1-Butanol at 0.5:0.5 molar ratio having a ZLD of 15 (see Table 3 of Example 2 above). The ternary system of MeTHF, 1-Butanol and 1,4-butanediol at molar ratios of 0.5:0.2:0.3 respectively provided a ZLD ratio of 5, which appears to be extremely promising.

[0095] A synthetic brine solution, which mimics low pH commercial brines from a mining waste stream was prepared using aluminium sulfate ($\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$), calcium chloride (CaCl_2), calcium sulfate (CaSO_4), iron sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) and magnesium sulfate (MgSO_4). The composition of the synthetic commercial brine comprised mostly sulfate salts with a pH of 1.74. The composition was as shown in Table 17.

Table 17: Composition of synthetic commercial brine

Salt	Concentration (g/L)
Aluminium sulfate($\text{Al}_2(\text{SO}_4)_3$)	65.8
Calcium chloride (CaCl_2)	2.0
Calcium sulfate (CaSO_4)	1.5
Iron sulfate (FeSO_4)	25.0
Magnesium sulfate (MgSO_4)	80.0
Total TDS, g/L	174.3

[0096] Some of the binary and ternary systems trialled above were tested against the synthetic commercial brine. The brine solution was added to the salt recovery solution in increments of 100 µl to the volumes shown below in Table 18 until the point when the brine solution was passing through the salt recovery solution and forming a “heavy brine layer” under the salt recovery solution.

- 5 Heavy brine is simply the brine solution depleted in water. The samples were mixed in a vortex mixer for 30 seconds. After ensuring thorough mixing, the samples were centrifuged for 1 minute for the precipitated salts to settle at the bottom of the sample tubes. The ZLD ratios were determined by calculating the ratio between volume of salt recovery solution (ml) divided by the brine added (ml). The results are shown in Table 18.

10 Table 18: Different variations of salt recovery solution combinations

Compound A	Compound B	Compound C	Mole ratio of Compound A: Compound B: Compound C	Volume of salt recovery solution, mL	Brine added, mL	ZLD ratio
MeTHF	Acetylacetone	-	1:2	10	1.50	6.67
MeTHF	1-Butanol	-	1:2	10	0.85	11.76
MeTHF	Ethyl acetate	-	1:2	10	0.15	66.67
Ethanol Acetate	1-Butanol	-	1:2	10	0.85	11.76
MeTHF	1-Butanol	Acetylacetone	0.5: 0.3: 0.2	5	0.40	12.50
MeTHF	1-Butanol	1-Propanol	0.5: 0.3: 0.2	5	0.40	12.50
MeTHF	1-Butanol	1-Pentanol	0.5: 0.3: 0.2	5	0.30	16.67
MeTHF	1-Butanol	3-Methyl-1-butanol	0.5: 0.3: 0.2	5	0.30	16.67
MeTHF	1-Butanol	1,4-Butanediol	0.5: 0.3: 0.2	5	0.90	5.56
Methyl Acetate	2-Butanone	-	3:2	10	0.50	20
Ethanol Acetate	Di(propylene glycol) dimethyl ether, mixture of isomers	-	3:2	10	0.20	50
Ethyl Acetate	2-Phenoxyethanol	-	1:2	10	0.50	20
Ethyl Acetate	2-Dimethoxypropane	-	3:2	10	0.167	60

Ethyl Acetate	Cyclohexanone	-	2:1	10	0.33	30
MeTHF	Methyl Acetate	-	3:2	10	0.33	30

[0097] It can be seen from the results in the table that a wide range of ZLD ratios were observed with the synthetic commercial brine. The ZLD ratios are all very promising, with the exception of the combination of ethyl acetate and MeTHF and the combination of ethyl acetate and 2,2-dimethoxypropane. However, it is anticipated that further refinement of the ethyl acetate and MeTHF system and the of ethyl acetate and 2,2-dimethoxypropane may be possible by converting into a ternary system, which might result in a lower ZLD ratio for similar synthetic brines. It is to be appreciated that a range of combinations could be useful and suitable depending on the application and results to be achieved. For example, it is envisaged that quaternary combinations may also be suitable for some applications.

With reference to Figure 1, it is to be appreciated that different countercurrent absorption processes can also be utilised. Figure 1 shows a 5-stage stage countercurrent absorption process to reach full crystallization, the ratio of salt recovery solution to brine was confirmed at 40:1 in a cascading configuration to reduce the amount of salt recovery solution (absorption) needed. The salt recovery solution was ethyl acetate to butanol. The brine was a commercial brine having a range of chlorides and sulphates, a pH of less than 2 and a density of 1.13 g/ml after filtration through a 0.45um membrane.

Figure 1 shows the water recoveries at each different absorption stages. At the fifth stage, full crystallization is achieved. By using five stages of absorption, the ZLD ratio was determined to be 40:1, which is significantly lower than the ZLD ratio of a single stage absorption (700:1). The ratio of 40:1 was obtained through many trials to optimize the salt recovery solution ratio, for five stages of countercurrent absorption. The ZLD ratio was the lowest ratio in which the brine reached full crystallization.

With reference to Figure 2 a process flow diagram is illustrated that shows how a 5 stage countercurrent absorption process might be set up. The brine or salt tank feeds into absorption stage 1, and once water has been absorbed from the brine into the salt recovery solution, the brine is then fed into absorption stage 2 to recover further water from the now water depleted brine. This cycle is repeated until all the water has been recovered from the brine. As shown in Figure 1, 5 stages of water recovery or absorption were required to achieve ZLD.

The present invention and its embodiments have been described in detail. However, the scope of the present invention is not intended to be limited to the particular embodiments of any process, manufacture, composition of matter, compounds, means, methods, and/or steps described in the specification. Various modifications, substitutions, and variations can be made to the disclosed material without departing from the spirit and/or essential characteristics of the present invention. Accordingly, one of ordinary skill in the art will readily appreciate from the disclosure that later modifications, substitutions, and/or variations performing substantially the same function or achieving substantially the same result as embodiments described herein may be utilized according to such related embodiments of the present invention. Thus, the following claims are intended to encompass within their scope modifications, substitutions, and variations to combinations, kits, compounds, means, methods, and/or steps disclosed herein.

CLAIMS

1 A salt recovery solution suitable for recovering a salt from a salt containing aqueous solution,
the salt recovery solution comprising at least two or more components independently
5 selected from any combination of integers a), b), c) and d): where

a) is a straight, branched or optionally substituted cyclic C₄-C₉ ether containing
compound;

b) is a straight chain or branched C₃-C₉ alkyl substituted by -OH;

c) is a straight chain, branched or cyclic C₄-C₉ ketone or C₄-C₉ diketone; and

10 d) is a straight chain or branched C₃-C₉ ester containing compound;

wherein at least one component of the salt recovery solution is substantially immiscible with
an aqueous solution of sodium chloride at a 1 molar concentration at or above 20 degrees
Celsius and at 1 atmosphere.

2 The salt recovery solution as claimed in claim 1, wherein the ether containing compound is a
15 diether or polyether.

3 The salt recovery solution as claimed in claim 1 or claim 2, wherein the C₄-C₉ ether containing
compound is selected from one or more of 2-methyltetrahydrofuran, 3-
methyltetrahydrofuran, 2-ethyltetrahydrofuran, 3-ethyltetrahydrofuran, dioxane, 1-
ethoxypropane, and a C₄-C₉ glycol ether or combinations thereof.

20 4 The salt recovery solution as claimed in any one of claims 1 to 3, wherein the straight chain or
branched C₃-C₉ alkyl substituted by -OH is selected from one or more of 1-butanol, 2, butanol
and 1-pentanol or combinations thereof.

5 The salt recovery solution as claimed in any one of claims 1 to 4, wherein the C₄-C₉ glycol ether
is selected from one or more of propylene glycol methyl ether, dipropylene glycol methyl ethyl
25 acetate, dipropylene glycol n-propyl ether, propylene glycol n-butyl ether, dipropylene glycol
n-butyl ether, tripropylene glycol n-butyl ether, propylene glycol phenyl ether, propylene
glycol diacetate or combinations thereof.

6 The salt recovery solution as claimed in any one of claims 1 to 5, wherein the C₄-C₉ ketone or
diketone is selected from one or more of acetonylacetone, 2-butanone or cyclohexanone.

30 7 The salt recovery solution as claimed in any one of claims 1 to 6, wherein the C₃-C₉ ester is
methyl acetate or ethyl acetate.

- 8 The salt recovery solution as claimed in claim 1, wherein the salt recovery solution is a combination of 2-methyltetrahydrofuran and acetonylacetone.
- 9 The salt recovery solution as claimed in claim 1, wherein the salt recovery solution is a combination of 2-methyltetrahydrofuran and 1-butanol.
- 5 10 The salt recovery solution as claimed in claim 1, wherein the salt recovery solution is a combination of 2-methyltetrahydrofuran and 1-pentanol.
- 11 The salt recovery solution as claimed in claim 1, wherein the salt recovery solution is a combination of ethyl acetate and 2-butanone.
- 12 The salt recovery solution as claimed in claim 1, wherein the salt recovery solution is a combination of ethyl acetate and 2-methyltetrahydrofuran.
- 10 13 The salt recovery solution as claimed in claim 1, wherein salt recovery solution is a combination of ethyl acetate and 1-butanol.
- 14 The salt recovery solution as claimed in claim 1, wherein the salt recovery solution is a combination of ethyl acetate and acetonylacetone.
- 15 15 The salt recovery solution as claimed in any one of claims 1 to 14, wherein the salt containing aqueous solution is an industrial brine.
- 16 A process for recovering a salt from an aqueous solution, the process comprising the step of adding the salt containing first aqueous solution to a salt recovery solution as defined in any one of claims 1 to 15; and allowing the salt to precipitate on passage through the salt recovery solution.
- 20 17 The process as claimed in claim 16, wherein the process is a zero-liquid discharge process.
- 18 The process as claimed in claim 16 or claim 17 wherein the process is a counter current process.
- 19 The process as claimed in any one of claims 16 to 18, wherein the process is a non-membrane process.
- 25 20 The process as claimed in any one of claims 16 to 18 wherein the process is a non-osmotic process.
- 21 A process for concentrating a salt containing aqueous solution, the process comprising the steps of:
- 30 (a) adding the salt containing aqueous solution to a salt recovery solution as defined in any one of claims 1 to 15; and
- (b) allowing water from the salt containing aqueous solution to pass into the salt recovery solution.

- 22 The process as claimed in claim 21, the process being a non-membrane process.
- 23 The process as claimed in claim 21 or claim 22, the process being a non-osmotic process.
- 24 The process as claimed in any claim 21, the process being a non-membrane and non-osmotic process.
- 5 25 The process as claimed in any one of claims 21 to 24, wherein the process concentrates the first aqueous solution by at least 20%.
- 26 The process as claimed in any one of claims 21 to 25, wherein the process concentrates the first aqueous solution by at least 30%.
- 10 27 The process as claimed in any one of claims 21 to 26, wherein the process concentrates the first aqueous solution by at least 40%.
- 28 The process as claimed in any one of claims 21 to 27, wherein the process concentrates the first aqueous solution by at least 50%.
- 29 The process as claimed in any one of claims 21 to 28, wherein the process concentrates the first aqueous solution or by at least 60%.
- 15 30 The process as claimed in any one of claims 21 to 29, wherein the process concentrates the first aqueous solution or by at least 70%.
- 31 The process as claimed in any one of claims 21 to 30, wherein the process concentrates the first aqueous solution or by at least 80%
- 20 32 The process as claimed in any one of claims 21 to 31, wherein the process concentrates the first aqueous solution by at least 90%.
- 33 The process as claimed in any one of claims 21 to 32 wherein the process is a minimal discharge process.
- 34 The process as claimed in any one of claims 21 to 33 wherein the process is a zero-liquid discharge process.
- 25 35 The process as claimed in any one of claims 21 to 34 wherein the aqueous solution is an industrial brine.

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Figure 1

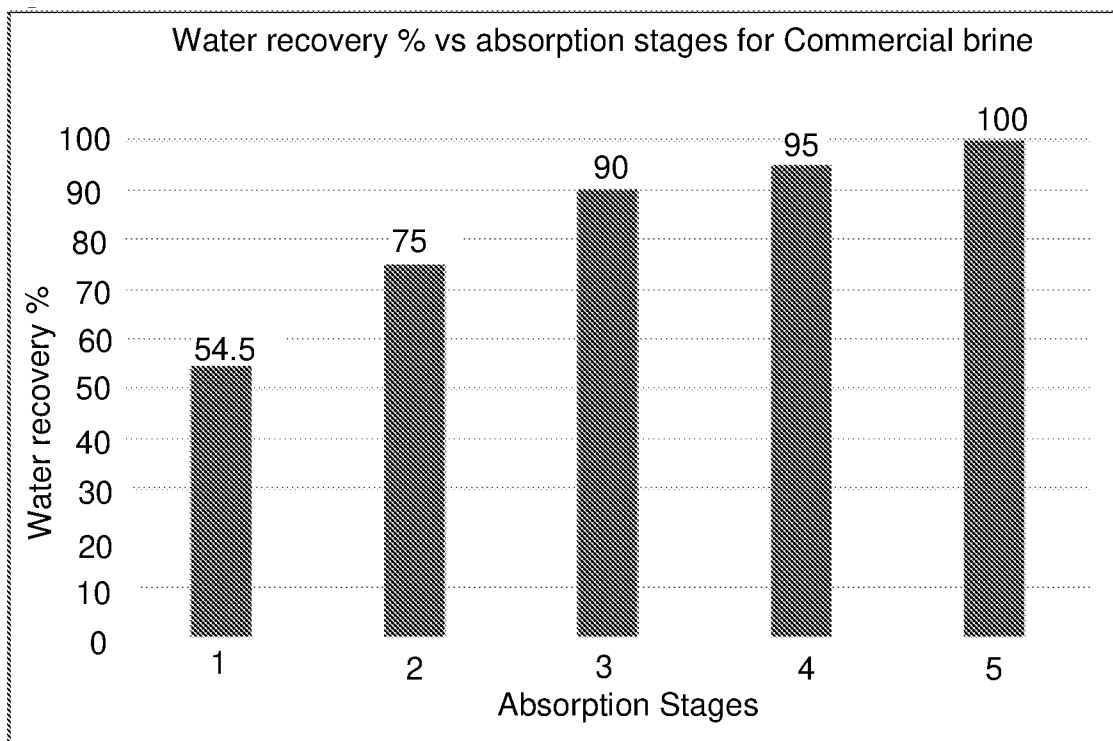
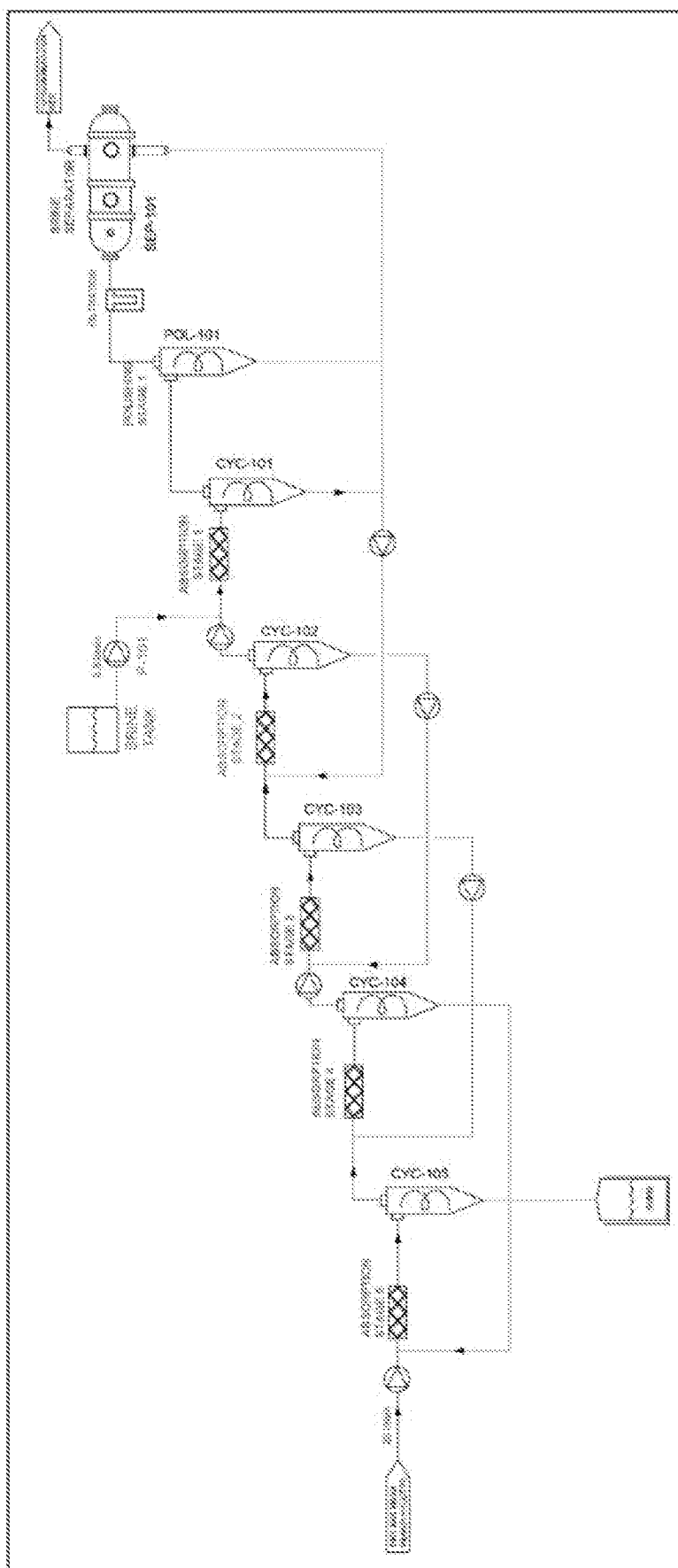


Figure 2



INTERNATIONAL SEARCH REPORT

International application No.

PCT/NZ2021/050105

A. CLASSIFICATION OF SUBJECT MATTER

C02F 1/26 (2006.01) C02F 103/08 (2006.01) B01D 11/04 (2006.01) C01D 3/06 (2006.01)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

Databases: CAplus, CAS Registry, CBNB, CEABA, CIN, COMPENDEX, Google, COMPENDEX, IFIALL, NTIS, PATENW, PQSCITECH, SCISEARCH, TULSA2.

Keywords: zero liquid discharge, salt, desalt, salting out, desalinate, sodium chloride, NaCl, brine, extract, exchange, recover, partition, solvent, 2-methyltetrahydrofuran, 3-methyltetrahydrofuran, 2-ethyltetrahydrofuran, dioxane, 1-ethoxypropane, propylene glycol methyl ether, dipropylene glycol methyl ether, dipropylene glycol mono-n-propyl ether, 1,2-dipropylene glycol 1-monobutyl ether, 1-(2-butoxy-1-methylethoxy)-2-propanol, tripropylene glycol n-butyl ether, 1-phenoxy-2-propanol, propylene glycol diacetate, 1-butanol, 2-butanol, 1-pentanol, acetylacetone, 2-butanone, cyclohexanone, methyl acetate, ethyl acetate.

Applicant and inventor searches were conducted in IP Australia's internal databases.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	Documents are listed in the continuation of Box C	

☒ Further documents are listed in the continuation of Box C☒ See patent family annex

* Special categories of cited documents:	
"A" document defining the general state of the art which is not considered to be of particular relevance	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"D" document cited by the applicant in the international application	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E" earlier application or patent but published on or after the international filing date	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&" document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

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INTERNATIONAL SEARCH REPORT		International application No.
C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		PCT/NZ2021/050105
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 2009200349 A (HITACHI CHEMICAL CO LTD) 03 September 2009 see: example 1; paragraph beginning with: "The organic solvent used ..."	1-7, 14, 15, 21-24, 33-34
X	JP H04266845 A (JAPAN SYNTHETIC RUBBER CO LTD) 22 September 1992 see: [0009]-[0012]; Example 4	1-4, 6, 7, 11, 13, 15, 21-24, 33-35
X	WO 2013/016491 A1 (VERTEX PHARMACEUTICALS INCORPORATED) 31 January 2013 see: [00122]	1, 3, 7, 12, 15
X	GUO, C. <i>et al.</i> , 'Structural Characteristic Integrated Computer-Aided Molecular Design for Phenols Removal Considering Synergistic Effect', <i>Industrial & Engineering Chemistry Research</i> , 2018, vol. 57, pp. 11374-11380. see: Abstract; Figure 2	1, 4-6, 15
X	US 5486314 A (WACK et al.) 23 January 1996 see: Example 5	1, 3, 5, 15
X	LI, H-B. <i>et al.</i> , 'Preparative isolation and purification of salidroside from the Chinese medicinal plant <i>Rhodiola sachalinensis</i> by high-speed counter-current chromatography', <i>Journal of Chromatography A</i> , 2001, vol. 932, pp. 91-95. see: Table 1	1, 4, 7, 13, 15
X	WALSHAM, J. G., 'Prediction of Flash Points for Solvent Mixtures', <i>Advances in Chemistry</i> , 1973, vol. 124, chapter 5, pp. 56-69 see: Table II - Blends 2, 4, 9, 12, 13, 15-18, 20, 22, 23, 27-29, 36, 43-45, 47, 48	1, 3, 4, 6, 7, 15

INTERNATIONAL SEARCH REPORT		International application No. PCT/NZ2021/050105	
Information on patent family members			
This Annex lists known patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.			
Patent Document/s Cited in Search Report		Patent Family Member/s	
Publication Number	Publication Date	Publication Number	Publication Date
JP 2009200349 A	03 September 2009	JP 2009200349 A	03 Sep 2009
		JP 5176136 B2	03 Apr 2013
JP H04266845 A	22 September 1992	JP H04266845 A	22 Sep 1992
WO 2013/016491 A1	31 January 2013	WO 2013016491 A1	31 Jan 2013
		AR 087344 A1	19 Mar 2014
		AR 087345 A1	19 Mar 2014
		AR 087346 A1	19 Mar 2014
		AU 2012286853 A1	02 May 2013
		EP 2736893 A1	04 Jun 2014
		TW 201313697 A	01 Apr 2013
		TW 201315467 A	16 Apr 2013
		TW 201317223 A	01 May 2013
		US 2014206888 A1	24 Jul 2014
		US 2014235703 A1	21 Aug 2014
		US 2014235704 A1	21 Aug 2014
		US 2014235705 A1	21 Aug 2014
		WO 2013016490 A1	31 Jan 2013
		WO 2013016492 A1	31 Jan 2013
		WO 2013016499 A1	31 Jan 2013
		WO 2013016501 A1	31 Jan 2013
US 5486314 A	23 January 1996	US 5486314 A	23 Jan 1996
		CA 2100053 A1	08 Feb 1994
		EP 0587917 A1	23 Mar 1994
		EP 0587917 B1	04 Jan 1995
		JP H06108097 A	19 Apr 1994
End of Annex			
Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001. Form PCT/ISA/210 (Family Annex)(July 2019)			