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(54) **Title:** A METHOD AND SYSTEM FOR RECOVERY OF ALKALI METAL HYDROXIDE AND OTHER CHEMICALS FROM WASTE

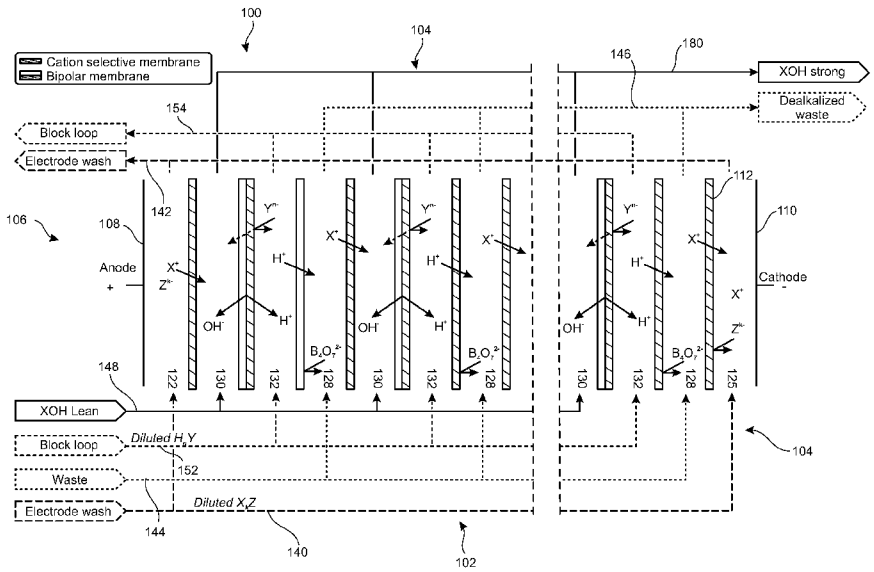

FIG. 1B

(57) **Abstract:** The present disclosure provides a method and system for recovery of alkali metal hydroxide (XOH) from waste comprising aqueous XBO_2 solution, the method comprising (i) subjecting the waste to a first electrodialysis process within a first electrodialysis unit that comprises at least one bipolar membrane, under conditions that provide a first XOH stream and a stream of de-alkalized waste and discharging the first XOH stream; and optionally mixing the de-alkalized waste with an acid H_nY, n being an integer and Y a counter anion to the alkali metal cation to form a slurry of boric acid and X_nY; (ii) removing solids from said slurry of boric acid and XnY to form a solid-free aqueous mixture of boric acid and X_nY; (iii) subjecting the solid-free aqueous mixture of boric acid and X_nY to a second electrodialysis process within a second electrodialysis unit comprising at

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least one bipolar membrane, the second electrodialysis unit being different from the first electrodialysis unit, under conditions that provides a second XOH stream and a stream of H_nY; and (iv) collecting the first XOH steam and the second XOH stream. The system comprises a first electrodialysis unit configured for receiving waste comprising aqueous XBO_2 solution, and for separately discharging a first XOH stream and dealkalized waste; and optionally a second electrodialysis unit, downstream to said first electrodialysis unit, configured for receiving saline boric acid comprising dissolved boric acid and X_nY, X representing an alkali metal cation, n representing an integer and Y representing an anion to said alkali metal cation, and for separately discharging a second XOH stream and aqueous solution of H_nY.

A METHOD AND SYSTEM FOR RECOVERY OF ALKALI METAL HYDROXIDE AND OTHER CHEMICALS FROM WASTE

TECHNOLOGICAL FIELD

The present disclosure relates to electrodialysis and the use of electrodialysis for recovery of chemical substances from waste.

BACKGROUND ART

References considered to be relevant as background to the presently disclosed subject matter are listed below:

H. I. Schlesinger, Herbert C. Brown, and A. E. Finholt "*The Preparation of Sodium Borohydride by the High Temperature Reaction of Sodium Hydride with Borate Esters*" Journal of the American Chemical Society 1953 75 (1), 205-209 DOI: 10.1021/ja01097a054

Handbook of Inorganic. Chemicals. Pradyot Patnaik, Ph.D. McGraw-Hill (pp. 117-118)

Gao, W., Fang, Q., Yan, H., Wei, X., & Wu, K. (2021). Recovery of Acid and Base from Sodium Sulfate Containing Lithium Carbonate Using Bipolar Membrane Electrodialysis. Membranes, 11(2), 152.

Acknowledgement of the above references herein is not to be inferred as meaning that these are in any way relevant to the patentability of the presently disclosed subject matter.

BACKGROUND

Hydrogen is emerging as a new energy vector outside of its traditional role and gaining more recognition internationally as a viable fuel route. In this connection, borohydrides are being considered as a low-cost hydrogen storage material with high

hydrogen generation capacity. The preparation of sodium borohydride from boric acid was originally described by Schlesinger et al. in 1953 in a process called Brown–Schlesinger process. The Brown–Schlesinger process comprises the preparation of trimethylborate $B(OCH_3)_3$ from a boric acid with a consecutive reaction of sodium hydride NaH, with $B(OCH_3)_3$, to make the product $NaBH_4$ and the by-product sodium methoxide $NaOCH_3$. Other borohydrides such as $LiBH_4$ and KBH_4 can be prepared by the same route by addition of LiOH and KOH to react with the $NaBH_4$ at the last step of the Brown–Schlesinger process.

The borohydrides have the potential to be used as hydrogen carriers thanks to the easy and efficient process of catalytic hydrogen release upon contacting these carriers with water in a dedicated reactor. The by-product of the hydrogen release process is metaborate salt of alkali metal dissolved in water. The metaborate salt of the alkali metal can be regenerated back to its borohydride salt via the Brown–Schlesinger process. The first step of this route is transforming the metaborate salt to the boric acid by its acidification as described by Pradyot Patnaik. Then, the Brown–Schlesinger process can be applied.

GENERAL DESCRIPTION

The presently disclosed subject matter provides, in accordance with a first of its aspects, a method for recovering alkali metal hydroxide (XOH) from waste comprising aqueous XBO_2 solution, X representing an alkali metal cation.

The method comprises, according to its broadest scope:

- subjecting a waste comprising aqueous XBO_2 solution, to a first electrodialysis process within a first electrodialysis unit that comprises at least one bipolar membrane, under conditions that provide a first XOH stream and a stream of dealkalized waste and discharging the first XOH stream; and optionally

- mixing the de-alkalized waste with an acid H_nY, n being an integer to form a slurry mixture of boric acid and X_nY;

- removing solids from said slurry mixture of boric acid and X_nY to form a solid-free aqueous mixture of boric acid and X_nY; and

- subjecting the solid-free aqueous mixture of boric acid and X_nY to a second electrodialysis process within a second electrodialysis unit comprising at least one bipolar membrane, the second electrodialysis unit being different from the first electrodialysis unit, under conditions that provides residual (desalinated) stream containing boric acid, a second XOH stream and a stream of H_nY;

- collecting the first XOH steam and the second XOH stream.

The present disclosure also provides, in accordance with a second of its aspects, a system comprising:

a first electrodialysis unit configured for receiving waste comprising aqueous XBO_2 solution, and for separately discharging XOH and dealkalized waste; and optionally;

a second electrodialysis unit, downstream to said first electrodialysis unit, configured for receiving saline boric acid comprising dissolved boric acid and X_nY, X representing an alkali metal cation, n representing an integer and Y representing an anion to said alkali metal cation, and for separately discharging at least a second XOH stream and a stream of aqueous solution of H_nY.

In some preferred examples, the presently disclosed method and system allow also for the recovery of H_nY from the same receiving waste comprising aqueous XBO_2 solution, as further detailed hereinbelow.

Further, in some preferred examples, the presently disclosed method and system allow also for the recovery of residual BA from the second electrodialysis unit to be further used in the recovery of BA.

BRIEF DESCRIPTION OF THE DRAWINGS

In order to better understand the subject matter that is disclosed herein and to exemplify how it may be carried out in practice, embodiments will now be described, by way of non-limiting example only, with reference to the accompanying drawings, in which:

Figures 1A-1B provides schematic illustrations of components of a first electrodialysis unit (Figure 1A) and its compartments during operation (Figure 1B), in accordance with a non-limiting example of the presently disclosed subject matter.

Figures 2A-2B provides schematic illustrations of components of a first electrodialysis unit (Figure 2A) and its compartments during operation (Figure 2B), in accordance with another non-limiting example of the presently disclosed subject matter.

Figures 3A-3B provides schematic illustrations of components of a second electrodialysis unit (Figure 3A) and its compartments during operation (Figure 3B), in accordance with a non-limiting example of the presently disclosed subject matter.

Figure 4 provides schematic flow chart illustrating the operation of a system according to a non-limiting example of the presently disclosed subject matter.

Figures 5A-5B are images of a lab scale system according to a non-limiting Example of the presently disclosed subject matter, including whole unit (Figure 5A) and the membrane assembly unit (stack) (Figure 5B).

DETAILED DESCRIPTION

The present disclosure is based on the development of a technology that allows the recovery of an alkali metal containing base, e.g. KOH, and preferably also acids, e.g. H_2SO_4, via electrodialysis processes that utilizes, *inter alia*, bipolar membranes.

Particularly, although not exclusively, the present technology is directed to the recovery of KOH or NaOH and H_2SO_4 from spent fuel.

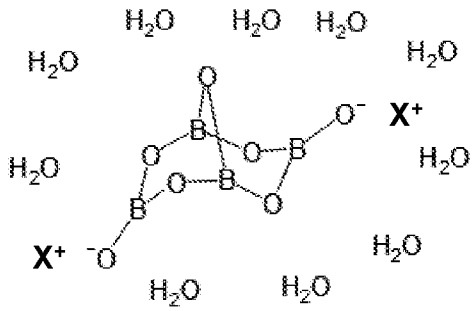
Spent fuel is an aqueous solution produced after completion of hydrogen release process from KBH_4, $LiBH_4$ or $NaBH_4$ (referred further as XBH_4) according to the following simplified reaction:

(Eq. 1) $$XBH_4 + 2\ H_2O \rightarrow XBO_2 + 4\ H_2\ (g)$$

This spent fuel needs to be recycled back to XBH_4 to complete the hydrogen release cycle. The first step of the recycling process is the acidification of the spent fuel (e.g. by H_2SO_4) to produce boric acid which is the starting point of the XBH_4 synthesis:

(Eq. 2) $$nXBO_2 + H_nY + nH_2O \rightarrow nB(OH)_3 + X_nY$$

The spent fuel is characterized by high pH due to the presence of XBO_2 in aqueous solutions, at high concentrations, near the solubility limit. Without being bound by theory, such high concentration creates a complex of tetraborate structure balanced by the X^+ cations, having the following general structure:



The formation of the tetraborate structure results in a high alkaline pH of the waste that results in the formation of also XOH.

(Eq. 3) $4\ XBO_2 + (n+1)H_2O \rightarrow X_2B_4O_7 \cdot nH_2O + 2\ XOH$

In the case of X=Na the and n=10 a well-known compound Borax is created ($Na_2B_4O_7 \cdot 10H_2O$).

Such a high pH generated by XOH liberated from XBO_2 in aqueous solution leads to excessive consumption of acid and results in excessive generation of *saline waste* (X_nY).

Generally, the presently disclosed subject matter thus provides methods and systems for recovery of XOH (which can then be used for production of XBH_4) and further of H_nY (which can then be used for production of boric acid and further XBH_4), from waste containing XBO_2, by the electrodialysis process aided by a series of membranes, including bi-polar membranes.

It has been found by the inventors that XOH and H_nY extracted from spent fuel according to the presently disclosed subject matter, drastically reduce the acid consumption in acidification process and the XOH consumption in XBH_4 production process.

It has also been found by the inventors that the presently disclosed methods and systems become especially attractive in the production of KBH_4 using H_2SO_4 as the acid H_nY. The following Table 1 compares specific consumption of H_2SO_4 and KOH in KBH_4 production process with and without electrodialysis according to the methods presently disclosed herein.

Table 1 – Base and Acid consumption during KBH_4 production

KBH_4 production process	**KOH consumption**	**H_2SO_4 consumption**
	kg_{KOH}/kg_{KBH4}	**kg_{H2SO4} /kg_{KBH4}**
Conventional Brown Schlesinger process	1.13	1.23
With bi-polar membrane electrodialysis	0.13	0.14

Table 1 shows that the presently disclosed methods and systems reduce the chemical consumption almost by an order of magnitude, thereby, significantly reducing the cost of the method and the carbon footprint of produced KBH_4.

Thus, based on the inventors' current findings, and in accordance with a first of its aspects, the presently disclosed subject matter broadly provides a method comprising:

- subjecting the waste comprising aqueous XBO_2 solution, to a first electrodialysis process within a first electrodialysis unit that comprises at least one bipolar membrane, under conditions that provide a first XOH stream and a stream of dealkalized waste and discharging the first XOH stream; and optionally,
- mixing the dealkalized aqueous waste with an acid H_nY, n being an integer to form a slurry mixture of boric acid and X_nY;
- removing solids from said slurry mixture of boric acid and X_nY to form a solid-free mixture of boric acid and X_nY; and
- subjecting the solid-free aqueous mixture of boric acid and X_nY to a second electrodialysis process within a second electrodialysis unit comprising at least one bipolar membrane, the second electrodialysis unit being different from the first electrodialysis unit, under conditions that provides a second XOH stream and a stream of H_nY and preferably also stream of residual BA (desalinated BA);
- collecting the first XOH steam and the second XOH stream.

In some preferred examples, the method also provides regeneration/recovery of H_nY as further described hereinbelow.

Further, based on the inventors' current findings, and in accordance with a second of its aspects, the presently disclosed subject matter broadly provides a system comprising

a first electrodialysis unit configured for receiving waste comprising aqueous XBO_2 solution, and for separately discharging a first XOH stream and de-alkalized waste; and optionally

a second electrodialysis unit, downstream to said first electrodialysis unit, configured for receiving saline boric acid comprising dissolved boric acid and X_nY, X representing an alkali metal cation, n representing an integer and Y representing an anion to said alkali metal cation, and for separately discharging, a second XOH stream and aqueous solution of H_nY and optionally or preferably also a stream of residual (desalinated) BA.

In the following, all examples and definitions apply to the methods according to the presently disclosed first aspect and to the systems according to the presently disclosed second aspect, *mutatis mutandis*.

In the context of the presently disclosed subject matter, when referring to "*aqueous XBO_2 waste* " or to "*waste comprising aqueous XBO_2 solution*" it is to be understood to refer to any aqueous based liquid that contains dissolved XBO_2, X representing any alkali metal cation.

In the context of the presently disclosed subject matter, when referring to "*de-alkalized waste* " it is to be understood to refer to any aqueous based liquid that contains dissolved XBO_2, X representing any alkali metal cation, yet, with a pH that is lower than the pH of the *aqueous XBO_2 waste* introduced into the first electrodialysis unit.

In some examples of the presently disclosed subject matter, the waste comprising aqueous XBO_2 solution is spent fuel having the meaning as described above, i.e. the aqueous solution produced during hydrogen release processes from KBH_4, $NaBH_4$ or $LiBH_4$ (referred further as XBH_4).

In some examples of the presently disclosed subject matter, X represents potassium, and the spent fuel is thus one comprising KBO_2.

In some examples of the presently disclosed subject matter, X represents sodium, and the spent fuel is thus one comprising $NaBO_2$.

In some examples of the presently disclosed subject matter, X represents lithium, and the spent fuel is thus one comprising $LiBO_2$.

In some examples of the presently disclosed subject matter, the waste comprises dissolved XBO_2 at a concentration close to *XBO_2 solubility limit*.

In the context of the present disclosure, the term "*solubility limit*" should be understood to refer to the maximum concentration at which XBO_2 can dissolve in water at the method temperature and pressure and represents the point at which no more XBO_2 can be dissolved in water under the given temperature/pressure conditions.

Thus, in the context of the present disclosure, the term "*close to XBO_2 solubility limit*" should be understood to refer a concentration that is about 1-2wt% below the maximum concentration (solubility limit) of *XBO_2* in water.

According to the presently disclosed method, the waste comprising aqueous XBO_2 solution is subjected to at least one, preferably two electrodialysis processes, each electrodialysis process involves the use of one or more bipolar membrane (*BPM*) in the respective electrodialysis cell.

Bi-polar membranes are well known in the art and in accordance with the presently disclosed subject matter, the first electrodialysis unit combines BPMs with cationic membranes (CMs) while the second electrodialysis unit combines BPMs with CMs and anionic membranes (AMs), each unit having a specifically selected arrangement of BPMs, CMs and, in case of the second unit, also AMs.

The presently disclosed subject matter can be executed using commercially available BPM, CM and AM.

For example, the BPM, CM and/or AM can be any commercially available heterogeneous CM, AM and BPM membranes such as RALEX membranes by Mega Group Ltd.

Further, for example, the BPM, CM and/or AM can be any commercially available homogeneous CM, AM and BPM membranes such as any one selected from NEOSEPTA, SELEMION, FUJIFILM® and Nafion membranes or other membranes having the same or similar functionality.

Any combination of heterogenous and homogenous membranes can also be used.

The electrodialysis units also include a cathode and an anode.

In some examples, the cathode can be selected from SS316 and Ni based materials. The cathode can be in a form of for example, a plate, foam, mesh structure.

With respect to the anode, since no corrosive gases, such as chlorine, are produced thereon, the anode can be of any type known in the art. In some examples, the anode is Graphite, or DSA© or Platinized Nickel, all being well known and commercially available anodes.

In some examples of the presently disclosed subject matter, the first electrodialysis unit comprises an electrodialysis cell including a membrane arrangement that receives the waste including at least aqueous dissolved XBO_2 and results in recovery of a first XOH stream that is collected, and a stream of a stream of dealkalized waste.

In some examples of the presently disclosed subject matter, the first electrodialysis unit comprises a first electrodialysis cell including a first membrane arrangement including a cathode-paired CM and from the anode end of the cell, a repeating set of CM-BPM or a repeating set of CM-BPM-CM.

In the context of the presently disclosed subject matter, when referring to "*a repeating set*" it is to be understood to refer to a set of membranes which are sequentially repeated in the membrane arrangement.

Thus, in the context of the presently disclosed subject matters when referring to a repeating set of CM-BPM it is to be understood that the membrane arrangement comprises more than one set of CM-BPM. Accordingly, when the repeating unit is CM-BPM the entire membrane arrangement can be defined as Anode-$(CM\text{-}BPM)_i$-CM-Cathode, where i represents and integer. Further accordingly, an electrodialysis cell comprising 3 repeating sets of CM-BPM, namely, i is equal to 3, the cell has the arrangement *Anode*-CM-BPM- CM-BPM- CM-BPM-CM-*Cathode*.

Further, in the context of the presently disclosed subject matters when referring to a repeating set of CM-BPM-CM it is to be understood that the membrane arrangement comprises more than one set of CM-BPM-CM. Accordingly, when the repeating unit is CM-BPM-CM the entire membrane arrangement can be defined as Anode-$(CM\text{-}BPM\text{-}CM)_i$-CM-Cathode, where i represents and integer. Further accordingly, an electrodialysis cell comprising 3 repeating sets of CM-BPM-CM, namely, i is equal to 3,

the cell has the arrangement *Anode*-CM-BPM-CM-CM-BPM-CM-CM-BPM-CM-CM-*Cathode*.

In some examples of the presently disclosed subject matter, a second electrodialysis unit is included and the second electrodialysis unit comprises a second electrodialysis cell including a second membrane arrangement that receives an aqueous mixture of boric acid (BA) and X_nY and provides a second XOH stream and a stream of H_nY, and optionally or preferably a stream of residual/ desalinated boric acid.

In some examples of the presently disclosed subject matter, the second electrodialysis unit comprises a second electrodialysis cell including a membrane arrangement including a cathode-paired CM and from the anode end of the cell, a repeating set of CM-BPM-AM.

Thus, in the context of the presently disclosed subject matters when referring to a repeating set of CM-BPM-AM it is to be understood that the membrane arrangement comprises more than one set of CM-BPM-AM. Accordingly, when the repeating unit is CM-BPM-AM the entire membrane arrangement can be defined as Anode-(CM-BPM-AM)$_i$-CM-Cathode, where i represents and integer. Further accordingly, an electrodialysis cell comprising 3 repeating sets of CM-BPM-AM has the arrangement *Anode*-CM-BPM-AM-CM-BPM-AM-CM-BPM-AM-CM-*Cathode*.

When a second electrodialysis unit is included, the first XOH stream and the second XOH stream are preferably combined.

In some preferred examples, when the second electrodialysis unit is included, also H_nY is recovered, which can be then utilized to produce boric acid, as further described hereinbelow.

More specifically, the presently disclosed method provides at least the recovery of XOH and the method comprises:

(a) providing a first electrodialysis unit comprising a first unit inlet end and a first unit outlet end, and extending therebetween a first electrodialysis cell comprising:

an anode

a cathode paired with a cathode-end CM,

a membrane arrangement stacked between the anode and the cathode-end CM, the membrane arrangement comprising, from the anode end, a repeating set of CM-BPM or a repeating set of CM-BPM-CM;

a power source configured for applying a voltage across said cell,

the anode, the cathode-end CM and the membrane arrangement providing an array of electrolyte flow compartments, each electrolyte flow compartment having a fluid inlet at the first unit inlet end and fluid outlet at the first unit outlet end, the array of electrolyte flow compartments including:

- an electrode wash compartment between the anode and an anode end-CM and between the cathode and the cathode-end CM,
- waste treatment compartment between two facing CM in the membrane arrangement comprising CM-BPM-CM repeating set or between BPM and cathode-side CM in the arrangement comprising CM-BPM repeating set;
- XOH compartment between a CM and a BPM within a repeating set; and
- when the arrangement comprises the CM-BPM-CM repeating set, a block loop compartment between BPM and its cathode-side CM;

(b) apply voltage between the anode and said cathode while introducing through the first unit inlet end the following liquids

- an electrode wash solution into an anode side electrode wash compartment and into a cathode-side electrode wash compartment;
- liquid waste comprising aqueous XBO_2 solution, into said waste treatment compartment; and
- lean XOH solution into said XOH compartment; and
- diluted acid solution H_nY, where n represents a number and Y represents an anion of said strong acid, into block loop compartment, if such compartment exists;

the voltage causing transfer of X^+ across each CMs and generation of OH^- by the BPM, to thereby form a XOH liquid in the XOH compartment and generation of H^+ by the BPM in the waste treatment compartment to balance the transfer of X^+ to the XOH compartment; and

(c) discharging the XOH liquid from the first unit outlet end, the XOH liquid having a concentration greater than XOH concentration in the lean XOH solution.

This high alkaline solution is fed into the first electrodialysis unit for dealkalization.

The operation of the first electrodialysis unit, in accordance with the presently disclosed method, involves the flow of different liquids into the different compartments of the first electrodialysis unit. The flow is from the first unit inlet end towards the first unit outlet end.

Through the electrode wash compartment flows an electrode wash solution. In the context of the presently disclosed subject matter, the electrode wash solution is a solution that contains dissolved X_kZ, X having the same meaning as above, namely, an alkali metal cation, k being an integer and Z being a counter anion.

In some examples of the presently disclosed subject matter, wherein the electrode wash solution comprises dissolved X_kZ salt, at least the cathode-end CM is has very low permeability (i.e. essentially impermeable) to the Z^{k-}. In the context of the present disclosure, the low permeability can be understood to mean that at least 99% of the Z^{k-} anions will be kept in the wash solution after a considerable period of operation of the system.

Without being bound thereto and in accordance with some examples, the wash solution has a concentration that provides sufficient conductivity to avoid energy losses and yet a minimal conductivity that will not add to the overall resistance of the system. Higher conductivities are less preferable to avoid excessive chemical loss upon replacement of the solution.

In some examples, the wash solution has a conductivity of > 10 mS/cm.

In some examples of the presently disclosed subject matter, the alkali metal cation of the wash solution is identical to the alkali metal cation in the waste, i.e. in the dissolved XBO_2 of the aqueous waste.

In some examples of the presently disclosed subject matter, the wash solution comprises XOH.

In some other examples of the presently disclosed subject matter, the wash solution comprises X_2SO_4.

Through the waste treatment compartment flows the liquid waste comprising aqueous XBO_2 solution.

Through the XOH compartment flows lean XOH solution.

In the context of the presently disclosed subject matter, the term "*lean XOH solution*" is to be understood to mean a solution of dissolved XOH having a concentration which is lower than final XOH concentration achieved at the end of the treatment process (concentrated XOH solution leaving the XOH compartment outlet). The concentration difference between the lean XOH solution and concentrated XOH solution depends on the overall system configuration. In the BPM systems operating in recycle mode with recycling tank, the concentration difference can be as low as 0.1%wt while in once through systems without recycling the concentration difference can reach 5-10%wt.

Through block loop compartment, if present in the first electrodialysis unit, diluted acid solution H_nY, where n represents a number and Y represents an anion of said strong acid.

In the context of the presently disclosed subject matter, the term "*diluted H_nY solution*" is to be understood to mean a solution of dissolved H_nY having a concentration that provides minimal conductivity such that it will note add to the overall resistance of the membranes and on the other hand provide sufficient conductivity to avoid energy losses.

In some examples, the diluted H_nY solution has a concentration that provides a conductivity of > 10 mS/cm.

As may be appreciated by those versed in the art, higher conductivities are less preferable in order to avoid excessive chemical loss upon replacement of the H_nY solution.

In some examples of the presently disclosed subject matter, the term "H_nY" refers to a strong acid.

In some examples of the presently disclosed subject matter, H_nY is H_2SO_4.

In some examples of the presently disclosed subject matter, H_nY is HCl.

According to the presently disclosed method, the different solutions are introduced into the first electrodialysis cell while voltage is applied between the anode and the cathode.

The applied voltage is selected to cause transfer of X^+ across the CMs and generate OH^- by the BPM, to thereby form a XOH liquid in the XOH compartment and to generate H^+ by the BPM in the waste treatment compartment to balance the transfer of X^+ to the XOH compartment.

As a result of operation of the first electrodialysis cell, a first stream of XOH is generated (being a *concentrated XOH solution*) and is discharged from the cell. The concentration of the XOH in the discharged XOH stream is greater than the concentration of XOH in the lean XOH solution.

In the context of the presently disclosed subject matter, the first unit stream discharged XOH (the *concentrated XOH* stream) comprises a concentration that is at least 5wt%; at times, at least 7wt%; at times, at least 9wt%; at times, at least 10wt%; at times, at least 12wt%; at times, at least 14wt%. It is to be appreciated that the concentration of XOH in this first stream of XOH discharged from the first electrodialysis unit can be higher, depending on the performance of the ion selective membranes used.

In some examples of the presently disclosed subject matter, the XOH concentration in the first stream of concentrated XOH discharged from the first electrodialysis unit is between about 10wt% and 30wt%; at times, between 10wt% and 25wt%; at times, between 15wt% and 25wt%; at times, between 10wt% and 20wt%; at times, between 10wt% and 15wt%.

Reference is now made to Figure 1A and to Figure 1B providing schematic illustrations of the different compartments and the different streams of solutions being introduced into each compartment in accordance with some examples of the presently disclosed subject matter.

Specifically, **Figure 1A** provides a schematic illustration of a first electrodialysis unit **100**, comprising a first unit inlet end **102** and a first unit outlet end **104**, and extending therebetween an electrolytic cell **106** including an anode **108**, a cathode **110** paired with

a cathode-end CM **112**, and a membrane arrangement stacked between the anode **108** and the cathode-end CM **112**. The membrane arrangement comprises in this non-limiting example, from the anode end, a plurality of *i* repeating sets (CM (**150**)-BPM (**152**)-CM (**150**))*i*, **114**$_{(1)}$, **114**$_{(2)}$... **114**$_{(i)}$.

Figure 1A also illustrates a power source **120** connected to anode **108** and cathode **110,** configured for applying a voltage across the electrolytic cell **102**, so as to cause the transfer of charged species as explained hereinabove and below and generation of H^+ and OH^- in BPM.

Figure 1A also illustrates the various array of electrolyte flow compartments as follows:

- an electrode wash compartment **122** between anode **108** and anode side (end) CM **124** and between cathode **110** and the cathode-end/paired CM **112**;
- waste treatment compartments **128** between two facing CM (between two repeating sets) in said membrane arrangement;
- XOH compartment **130** between a CM and a BPM within a repeating set; and
- a block loop compartment **132** between BPM and its cathode-side facing CM.

Reference is now made to **Figure 1B**, which schematically illustrates the electrodialysis unit of **Figure 1A**, in operation.

For simplicity, the same reference numerals used in Figure 1A, are used to identify components having a same function in Figure 1B. For example, anode **108** in Figure 1B is the same anode **108** in Figure 1A.

Figure 1B adds to **Figure 1A** in illustrating different liquid streams introduced into different compartments, upon activation of a voltage across the cell.

Specifically, **Figure 1B** illustrates the first electrodialysis unit **100** including the first unit inlet end **102**, the first unit outlet end **104**, and extending therebetween the electrolytic cell **106** including the anode **108**, the cathode **110** paired with the cathode-

end CM **112**, and the membrane arrangement stacked between the anode **108** and the cathode-end CM **112**.

In operation, power source (not illustrated in Figure 1B) applies voltage between the anode **108** and the cathode **110** and the following streams of liquids are introduced into the cell:

- a stream of an electrode wash solution **140** flow from the first unit inlet end **102**, into the anode side electrode wash compartment **122** and into a cathode-side electrode wash compartment **125** and is discharged from the first unit outlet end **104** via streamline **142** and can be circulated back into the electrode wash compartment;
- streams of the liquid waste **144** comprising aqueous XBO_2 solution flow from the first unit inlet end **102**, into the waste treatment compartments **128**, and are discharges as a stream of de-alkalized waste **146**;
- streams of lean XOH solution **148** flow from the first unit inlet end **102** into the XOH compartments **130**, and is discharged from the cell, via first unit outlet end, as the first stream of XOH **180**;
- streams of diluted acid solution H_nY **152** flow from the first unit inlet end **102** into the block loop compartments **132** and is discharged from the first unit outlet end **104** via streamline **154** and can be circulated back into the block loop compartment.

In some examples of the presently disclosed subject matter, the stream of waste comprising the aqueous XBO_2 solution has a pH of between 12 and 14 and as a result of treatment within the first electrodialysis unit, the pH of the de-alkalized steam of waste is reduced, at times, to a pH of between 9 and 12.

In some examples of the presently disclosed subject matter, the stream of waste comprising the aqueous dissolved XBO_2 has a pH of about 14 and as a result of treatment within the first electrodialysis unit, the pH of the de-alkalized steam of waste is reduced, at times, to a pH below 11.

In some examples, the recirculating of the wash solution comprises mixing the electrode wash solution discharged from the unit outlet ends, prior to being re-introduced into each electrode wash compartment.

Further illustrated in **Figure 1B**, by arrows, is the ions transfer that takes place in the electrodialysis cell upon application of the voltage, including:

- the transfer of X^+ across each CMs into the XOH compartment and the generation of OH^- by the BPM in the XOH compartment, which together provide a XOH solute in the XOH compartment; and

- the generation of H^+ by the BPM in each waste treatment compartment to balance said transfer of X^+ to the XOH compartment; and

- the prevention of boron compounds leakage from the liquid waste to the XOH compartment due to the presence of the block loop compartment.

With respect to the block loop compartment it is noted that such compartment may be relevant when using BPM that may be insufficient to prevent penetration of the tetraborate anions ($B_4O_7^{2-}$) to the XOH stream. This may cause loss of boron containing compounds and decrease yield of production of boric acid, which is processed as further described hereinbelow. When using a block loop as illustrated in **Figures 1A-1B**, the $B_4O_7^{2-}$ anions face a CM which is typically more selective than BPM and thus prevents any significant leak of the boron compounds to the XOH compartment (XOH stream).

Further, in accordance with some examples, such as those illustrated in **Figures 1A-1B**, when using a block loop compartment, the waste is fed to compartments that are bound by CM from both the anode side and the cathode side.

As illustrated in **Figure 1B**, when the electric potential is applied, the X^+ cations move towards cathode through the cathode side CM while the $B_4O_7^{2-}$ anions migration towards the anode is blocked by the anode-side CM, separating the liquid waste and block loop compartments.

As further illustrated in **Figure 1B**, the depletion of positively charged X^+ from the waste comprising the aqueous XBO_2 solution is balanced by H^+ ions transfer from the adjacent block loop. The X^+ ions are transferred to the XOH compartments which are bound by CM from the anode side and by BPM from the cathode side. The X^+ cations transferred from the liquid waste compartments are captured in XOH compartments since their further migration towards cathode is blocked by the anion part of the BPM. The captured X^+ cations are balanced by OH^- anions generated by BPM. In this way the

concentration of XOH is increased. The block loop is bound by BPM from the anode side and by the CM from the cathode side.

In some examples of the presently disclosed subject matter, the streams of diluted acid solution H_nY **152** comprise a diprotic or triprotic acid. In some examples of the presently disclosed subject matter, the acid in the diluted solution H_nY **152** comprise an anion Y^{n-} that is sufficiently large to prevent its penetration to the XOH compartments via the CM.

In some examples of the presently disclosed subject matter, the streams of diluted acid solution H_nY **152** comprise H_2SO_4 acid.

In some examples of the presently disclosed subject matter, the streams of diluted acid solution H_nY **152** comprise an organic acid. In this respect, it is note that organic acids can be used given that the anion part has very low permeability through the cation part of the BPM.

The H^+ cations from the steam of diluted acid solution H_nY move towards the liquid waste compartments through the cathode-side CM. The depletion of H^+ ions in the block loop compartment is compensated by the H^+ cations generation by the BPM.

Reference is now made to Figures 2A and 2B providing a schematic illustration of a first electrodialysis unit in accordance with another non-limiting example of the presently disclosed subject matter.

For simplicity, like reference numerals to those used in **Figures 1A-1B**, shifted by 100 are used to identify components having a similar function in **Figures 2A-2B**. For example, anode **208** in **Figures 2A-2B** is an anode having the same function as anode **108** in **Figures 1A-1B**.

Similar to **Figure 1A**, **Figure 2A** illustrates a first electrodialysis unit **200**, comprising a first unit inlet end **202** and a first unit outlet end **204**, and extending therebetween an electrolytic cell **206** including an anode **208**, a cathode **210** paired with a cathode-end CM **212**, and a membrane arrangement stacked between the anode **208** and the cathode-end CM **212**. Membrane arrangement comprises in this non-limiting example, from the anode end, a plurality of repeating set of CM (**250**)-BPM (**252**), $\mathbf{214}_{(1)}$, $\mathbf{214}_{(2)}$... $\mathbf{214}_{(i)}$.

Figure 2A also illustrates a power source **220** connected to the anode **208** and the cathode **210,** configured for applying a voltage across the electrolytic cell **202**, so as to cause the transfer of charged species as described herein and generation of H^+ and OH^- in BPM.

Figure 2A also illustrates similar arrays of electrolyte flow compartments including an electrode (anode) wash compartment **222** between anode **208** and an anode-side CM **224** and a further electrode (cathode) wash compartment **225** between cathode **210** and cathode-end/paired CM **212**; waste treatment compartments **228** between the cation part of the BPM and a cathode-side CM (the CM of a next repeating set or of the cathode paired CM); and the XOH compartments **230** between a CM and anion part of BPM (i.e. of the BPM of the same repeating set).

As clearly observed, in the first electrodialysis unit of Figures 2A-2B, there is no block loop compartment.

Reference is now made to **Figure 2B**, which schematically illustrates the electrodialysis unit of **Figure 2A**, in operation.

For simplicity, the same reference numerals used in Figure 2A, are used to identify components having the same function in Figure 2B. For example, anode **208** in Figure 2B is the same anode **208** in Figure 2A.

Figure 2B adds to **Figure 2A** in illustrating the different liquid streams introduced into the different compartments, upon activation of a voltage across the cell by the power supply (not illustrated in Figure 2B).

Specifically, **Figure 2B** illustrates the first electrodialysis unit **200** including the first unit inlet end **202**, the first unit outlet end **204**, the and extending therebetween the electrolytic cell **206** including the anode **208**, the cathode **210** paired with the cathode-end CM **212**, and the membrane arrangement stacked between the anode **208** and the cathode-end CM **212**.

In operation, power source (not illustrated in Figure 2B) applies voltage between the anode **208** and the cathode **210** and the following streams of liquid are introduced into the cell:

- a stream of an electrode wash solution **240** flow from the first unit inlet end **202**, into the anode side electrode wash compartment **222** and into a cathode-side

electrode wash compartment **225** and is discharged from the first unit outlet end **204** via streamline **242** and can be circulated back into the electrode wash compartment as described above;

- streams of the liquid waste **244** comprising aqueous XBO_2 solution flow from the first unit inlet end **202**, into the waste treatment compartments **228**, and are discharges as a stream of de-alkalized waste **246**; and

- streams of lean XOH solution **248** flow from the first unit inlet end **202** into the XOH compartments **230**, and is discharged from the cell, via first unit outlet end, as the first stream of XOH **280.**

As noted above, the first electrodialysis unit of **Figure 2B** is lacking the block loop compartments.

Without being bound by theory, when the electric potential is applied, the X^+ cations move towards cathode through the CM while the $B_4O_7^{2-}$ anions migration towards anode is blocked by the cation part of the BPM. The depletion of positively charged X^+ from the solution is balanced by H^+ ions generated by BPM. The X^+ ions are transferred to the XOH compartments which are bound by CM from the anode side and by anion part of BPM from the cathode side. The X^+ cations transferred from the liquid waste compartments are captured in XOH compartments since their further migration towards cathode is blocked by the anion part of the BPM. The captured X^+ cations are balanced by OH^- anions generated by BPM. In this way the concentration of XOH is increased. As noted above, the anode and cathode are bound by CM and are washed (preferably by diluted XOH solution) to close the electrical circuit. The XOH washing solution is split and feed both anode and cathode compartments. The outlet XOH washing solution is mixed after exiting the compartments and is recycled back to the process.

Following electrodialysis within the first electrodialysis unit a first stream of XOH is recovered. In some examples of the presently disclosed subject matter, the first stream of XOH is subjected to a least one evaporating process to provide a first unit concentrated XOH that can be stored in a dedicated tank or communicated for further use, e.g. in XBH_4 production processes.

Further, the first electrodialysis unit discharges de-alkalized liquid waste.

In the context of the recently disclosed subject matter when referring to "*de-alkalized waste*" it is to be understood to refer to the aqueous waste solution comprising dissolved XBO_2 with a pH that is lower than the pH of the aqueous waste comprising the dissolved XBO_2 introduced into the first electrodialysis unit.

As noted above, the waste introduced into the first electrodialysis unit has high alkalinity.

In some examples of the presently disclosed subject matter, the stream of aqueous waste comprising the dissolved XBO_2 has a pH of between 12 and 14 and as a result of treatment within the first electrodialysis unit, the pH of the de-alkalized steam of waste is reduced, at times, to a pH of between 9 and 12.

In some examples of the presently disclosed subject matter, the stream of aqueous waste comprising the dissolved XBO_2 has a pH of about 14 and as a result of treatment within the first electrodialysis unit, the pH of the de-alkalized steam of waste is reduced, at times, to a pH of less than 11.

In some examples of the presently disclosed subject matter, the dealkalized liquid/aqueous waste is subjected to a process resulting in the regeneration of boric acid. In some examples, the generation comprises a reaction between the dealkalized liquid waste and a strong acid H_nY, n being an integer and Y representing an anion to form boric acid and X_nY slurry.

In some examples of the presently disclosed subject matter, the generation of boric acid can be represented by the following equation:

$$n\ XBO_2 + H_nY + n\ H_2O \rightarrow n\ B(OH)_3 + X_nY.$$

In some examples of the presently disclosed subject matter, the boric acid and X_nY salt are in a form of a slurry. This is due to the limited solubility of boric acid and X_nY, resulting in their partial precipitation. Yet, some of the boric acid and the X_nY salt remain dissolved and can be separated from the precipitated matter.

In some examples of the presently disclosed subject matter, the dissolved boric acid and X_nY (aqueous mixture thereof) are separated from the precipitated matter.

In some examples of the presently disclosed subject matter, the separation is by means of a solid-liquid separator.

Thus, in accordance with some examples of the presently disclosed subject matter, the slurry is introduced into a solid-liquid separator so as to separate between solids comprising solid boric acid and X_nY and dissolved aqueous boric acid and dissolved X_nY.

In some examples of the presently disclosed subject matter the dissolved aqueous boric acid/ X_nY comprises water saturated with dissolved boric acid and dissolved X_nY.

In some examples of the presently disclosed subject matter, the solids comprising the boric acid and X_nY are dried, i.e. the method further comprises drying the solids.

The solids can be dried by any means known in the art, including drying in an oven, exposing the solids to dry air, etc.

Separation between the boric acid and the X_nY can be achieved by the selective dissolution of boric acid.

In some examples, the selective dissolution may involve first dissolving the X_nY in a solvent that does not dissolve the boric acid.

In some examples of the presently disclosed subject matter, the dried boric acid is selectively dissolved in an organic solvent.

In some examples of the presently disclosed subject matter, the boric acid organic solvent is selected from the group consisting of short chain alcohols, such as methanol, ethanol, 1-propanol.

In some examples of the presently disclosed subject matter, boric acid organic solvent is methanol.

The dissolving of the dried boric acid in methanol, results in the selective dissolution of boric acid while leaving most of the X_nY salt in solid form. This allows for the collection of dissolved boric acid and further utilization of the residual solid X_nY salt for the purpose of e.g. generating the acid H_nY.

In some examples of the solid X_nY salt is dissolved in water.

In some examples, the water dissolved boric acid / X_nY obtained from the solid-liquid separator is combined with the water dissolved X_nY, in a boric acid tank. The boric acid tank thus comprises a mixture of dissolved boric acid and dissolved X_nY, at times, referred to herein by the term "*saline boric acid*" or "*saline BA*". This mixture (saline BA) can be further processed to recover further XOH and acid H_nY.

In some examples of the presently disclosed subject matter, the saline BA is subjected to a second electrodialysis process utilizing a second electrodialysis unit that is different in the membrane arrangement from that used in the first electrodialysis unit.

In some examples of the presently disclosed subject matter, the method thus further comprises subjecting the saline BA to an electrodialysis reaction within a second electrodialysis unit.

The second electrodialysis unit forming part of the presently disclosed method and system comprises a second unit inlet end and a second unit outlet end, and extending therebetween a second electrodialysis cell comprising:

an anode,

a cathode paired with a cathode-end CM,

a second unit membrane arrangement stacked between the anode and the cathode-end CM, the second unit membrane arrangement comprising, from the anode, a repeating set of CM-BPM-AM;

a power source configured for applying a voltage across the second cell,

the cathode end CM and the second unit membrane arrangement providing an array of electrolyte flow compartments, each electrolyte flow compartment having a fluid inlet at the second unit inlet end and fluid outlet at the second unit outlet end, the array of electrolyte flow compartments providing:

an electrode wash compartment between the anode and an anode side/end CM and between the cathode and the cathode-end CM;

XOH compartment between CM and BPM of a repeating set (CM-BPM-AM);

X_nY compartment between BPM and AM of a repeating set (CM-BPM-AM); and

a saline boric acid compartment between an AM and a CM.

In accordance with the presently disclosed method, the subjecting of the saline BA to an electrodialysis reaction within a second electrodialysis unit comprises

(a) introducing through the second unit inlet end:

- a wash solution into each of said electrode wash compartment;

- lean XOH solution into the XOH compartment;
- lean H_nY solution into the H_nY compartment; and
- saline BA into the saline boric acid compartment; and

(b) apply voltage between the anode and the cathode, the voltage causing transfer of X^+ across each CM, and Y^{n-} across each AM, and causing generation of OH^- in the XOH compartment and H^+ in the H_nY compartment by the BPM; to thereby increase XOH concentration in the XOH compartment and H_nY concentration in H_nY compartment; and

(c) discharging at least the XOH liquid from the second unit outlet end, the XOH liquid having a concentration greater than XOH concentration in the lean XOH solution.

The wash solution of the passing through the electrode compartment of the second electrodialysis unit can be the same or different from the wash solution employed in the first electrodialysis unit, as long as the alkali metal cation is the same as that present in the waste to be treated (i.e. of the XBO_2).

In the context of the presently disclosed subject matter, the term "*lean H_nY solution*" that is being introduced into the H_nY compartment of the second electrodialysis unit is to be understood to mean the solution having low H_nY concentration. The concentration difference between the lean H_nY and the discharged final H_nY solution depends on the actual process configuration of the industrial scale electrodialysis unit. In once through operation regime the concentration of lean H_nY can be lower than 1%wt. In systems having H_nY stream recirculated through circulation tank, the concentration difference between lean H_nY stream and final H_nY stream can be lower than 1%wt.

In the context of the presently disclosed subject matter, the term "*saline BA*" that is being introduced into the Saline BA compartment of the second electrodialysis unit is to be understood to mean a solution comprising dissolved boric acid and dissolved acid X_nY, the X_nY having the meaning as described herein.

In some preferred examples of the presently disclosed subject matter, the second electrodialysis unit also provides, in addition to the second stream of XOH, discharging of H_nY from the H_nY compartment, to be re-used in the presently disclosed method and system.

Reference is now made to **Figures 3A-3B** providing a schematic illustration of a second electrodialysis unit in accordance with a non-limiting example of the presently disclosed subject matter.

For simplicity, like reference numerals to those used in **Figures 1A-1B**, shifted by 200 are used to identify components having a similar function in **Figures 3A-3B**. For example, anode **308** in **Figures 3A-3B** is an anode having the same function as anode **108** in **Figures 1A-1B**.

Figure 3A illustrates a second electrodialysis unit **320**, comprising a first unit inlet end **302** and a first unit outlet end **304**, and extending therebetween an electrolytic cell **306** including an anode **308**, a cathode **310** paired with a cathode-end CM **312**, and a membrane arrangement stacked between the anode **308** and the cathode-end CM **312**. Membrane arrangement comprises in this non-limiting example, from the anode end, a plurality of repeating set of CM (**350**)-BPM (**352**)-AM (**354**), $\mathbf{314}_{(1)}$, $\mathbf{314}_{(2)}$... $\mathbf{314}_{(i)}$.

Figure 3A also illustrates a power source **320** connected to the anode **308** and the cathode **310,** configured for applying a voltage across the electrolytic cell **302**, so as to cause the transfer of charged species as described herein and generation of H^+ and OH^- in BPM.

Figure 3A also illustrates an array of electrolyte flow compartments including an electrode (anode) wash compartment **322** between anode **308** and an anode-end CM **325** and a further electrode (cathode) wash compartment **325** between cathode **310** and cathode-paired CM **312;** XOH compartments **330** between CM and BPM; acid compartments **360** between the BPM and AM; and saline boric acid compartments **362** between AM and CM.

Reference is now made to **Figure 3B**, which schematically illustrates the electrodialysis unit of **Figure 3A**, in operation.

For simplicity, the same reference numerals used in Figure 3A, are used to identify components having a same function in Figure 3B. For example, anode **308** in Figure 3B is the same anode **308** in Figure 3A.

Figure 3B illustrates the different liquid streams introduced into the different compartments illustrated in **Figure 3A**, upon activation of a voltage across the cell by the source of power supply (not illustrated in Figure 3B).

Specifically, **Figure 3B** illustrates, inter alia, the second electrodialysis unit **300** including the second unit inlet end **302**, the second unit outlet end **304**, and extending therebetween the electrolytic cell **306** including the anode **308**, the cathode **310** paired with the cathode-end CM **312**, and the membrane arrangement stacked between the anode **308** and the cathode-end CM **312**.

In operation, voltage is applied between the anode **308** and the cathode **310** and the following streams of liquids are introduced into the cell's compartments:

- a stream of an electrode wash solution **340** flowing from the second unit inlet end **302**, into the anode side electrode wash compartment **322** and into a cathode-side electrode wash compartment **325**, the stream of electrode wash solution being discharged from the second unit outlet end **304** via streamline **342** and can be circulated back into the electrode wash compartment as described above;

- streams of lean XOH solution **348** flowing from the second unit inlet end **302** into the XOH compartments **330**, which is then discharged from the cell, via second unit outlet end **304**, as a second stream of XOH **380;**

- streams of lean acid, H_nY **364**, flowing from the second unit inlet end **302** into the H_nY compartments **360**, which are then discharged from the cell, via second unit outlet end **304**, as a stream of concentrated H_nY **366**; and

- streams of saline BA **368**, flowing from the second unit inlet end **302** into the saline BA compartments **362**, which are then discharged from the cell, via second unit outlet end **304**, as a stream of residual BA **370.**

Without being bound by theory, H_nY compartments receive H^+ generated from the BPM and Y^{n-} anion transferred through the AM from the saline BA compartment **362** thus resulting in an increase in the acid H_nY concentration in the H_nY compartment **360**.

Further, without being bound by theory, the saline BA compartments receive the mixture of dissolve boric acid and dissolved X_nY and as a result of the applied potential, the cation X^+ is transferred, via CM, to the XOH compartments **330** and the anion Y^{n-} is transferred, via the AM, to the H_nY compartments **360**, such that in the stream passing through the saline BA compartments loose most of X_nY while maintaining BA . The latter can be explained by the fact that the weekly charged boric acid, $B(OH)_3$, is almost not

attracted to the electrodes and most of it remains in the compartment's outlet stream which is then directed for further boric acid recovery.

With respect to the wash solution, as also explained above, passing through the electrode compartment it is to be noted that it can be the same or different from the wash solution employed in the first electrodialysis unit, as long as the alkali metal cation is the same.

Thus, for example, while the wash solution in the first electrodialysis unit can be XOH, e.g. KOH, the wash solution in the second electrodialysis unit can be X_2SO_4, e.g. K_2SO_4.

As a result of operation of the second electrodialysis cell, the concentration of the second unit XOH being discharged is greater than the concentration of XOH in the lean XOH solution.

In the context of the presently disclosed subject matter, the XOH discharged from the second electrodialysis unit comprises a concentration that is at least 5wt%; at times, at least 7 wt%; at times, at least 9wt%; at times, at least 10wt%; at times, at least 12wt%; at times, at least 14wt%. It is to be appreciated that the concentration of XOH in this second unit discharged XOH can be higher than 12wt%, depending on the performance of the ion selective membranes used.

In some examples of the presently disclosed subject matter, the XOH concentration discharged from the second electrodialysis unit is between about 5wt% and 20wt%; at times, between 5wt% and 15wt%; at times, between 10wt% and 20wt%; at times, between 5wt% and 10wt%; at times, between 8wt% and 15wt%.

In accordance with some examples of the presently disclosed subject matter, the XOH discharged from the second electrodialysis unit is concentrated. Accordingly, the disclosed method also comprises subjecting the second unit XOH from the second unit outlet end to at least one evaporating process to provide second unit concentrated XOH.

In some examples of the presently disclosed subject matter, the second unit XOH from the second unit outlet end is combined with the first unit XOH (from the first electrodialysis unit) prior to being introduced into an evaporator, i.e. the combined XOH is subjected to at least one evaporating process to provide a combined concentrated XOH.

In some examples of the presently disclosed subject matter, the concentrated XOH is collected in a XOH tank.

In some examples of the presently disclosed subject matter, the method also comprises collecting the concentrated H_nY generated in the second electrodialysis unit. This allows for the recovery of H_nY which can then be reused in for the boric acid production. Thus, in the context of the presently disclosed subject matter, the method also provides recovery of H_nY from the H_nY compartment of the second electrodialysis unit.

In some examples of the presently disclosed subject matter, H_nY represents H_2SO_4 and thus, the method provides recovery of H_2SO_4.

The chemical reactions occurring on the electrodes of the electrodialysis unit (the first and second) are as follows:

Neutral pH conditions (Z^{n-} and W^{j-} are anions of salts):

Anode:

$$2H_2O \rightarrow O_{2(g)} + 4H^+ + 4e^- (E^0 = -1.23\ V)$$

Cathode:

$$4H_2O_{(l)} + 4e^- \rightarrow 4OH^- + 2H_{2(g)}\ (E^0 = -0.83\ V)$$

Overall reaction in electrode wash stream:

$$2H_2O_{(l)} \rightarrow O_{2(g)} + 2H_{2(g)}\ (E^0 = -2.06\ V)$$

Basic pH conditions (Z^{n-} and W^{j-} are OH^-):

Anode:

$$4OH^- \rightarrow 2H_2O_{(l)} + O_{2(g)} + 4e^-\ (E^0 = -0.4\ V)$$

Cathode:

$$4H_2O_{(l)} + 4e^- \rightarrow 4OH^- + 2H_{2(g)}\ (E^0 = -0.83\ V)$$

Overall reaction in electrode wash stream:

$$2H_2O_{(l)} \rightarrow O_{2(g)} + 2H_{2(g)}\ (E^0 = -1.23\ V)$$

As can be seen, in both cases the closing of the electrical circuit is achieved by the decomposition of water molecules to O_2 and H_2 gases. The water loss in electrode wash stream in both the first electrodialysis unit and second electrodialysis unit can be compensated by periodic water makeup, when required. The makeup can be achieved by automatic control of the conductivity of the recycling stream by periodic water addition.

The presently disclosed subject matter, according to a second aspect thereof, also provides a system for regeneration of at least XOH.

In its broadest scope, the system comprises:

a first electrodialysis unit configured for receiving waste comprising aqueous XBO_2 solution, and for separately discharging a first XOH stream and dealkalized waste; and optionally,

a second electrodialysis unit, downstream to said first electrodialysis unit, configured for receiving saline boric acid comprising dissolved boric acid and X_nY, X representing an alkali metal cation, n representing an integer and Y representing an anion to said alkali metal cation, and for separately discharging a second XOH stream and aqueous solution of H_nY.

Without being bound by theory, in operation, the presently disclosed method and system, provide the following:

In the first electrodialysis unit as defined hereinabove, the applied voltage between the anode and the cathode provide for:

- transfer of X^+ across each CMs;
- generation of OH^- by the BPM, to thereby form a XOH liquid in the XOH compartment
- generation of H^+ by the BPM in the waste treatment compartment to balance the transfer of X^+ to the XOH compartment; and
- separate discharge of a first steam of XOH and a stream of de-alkalized waste.

In some examples of the presently disclosed subject matter, the system comprises a step of subjecting the dealkalized liquid/aqueous waste to a process resulting in the regeneration of boric acid.

In some examples of the presently disclosed subject matter, the system comprises a first mixing chamber configured for mixing the stream of de-alkalized waste with H_nY acid (e.g. H_2SO_4), prior to introducing the aqueous boric acid into the solid-liquid separator.

In some examples, the generation of boric acid comprises a reaction between the dealkalized liquid waste and a strong acid H_nY, n being an integer and Y representing an anion to form boric acid and X_nY slurry.

In some examples of the presently disclosed subject matter, the system comprises a solid-liquid separator (as described hereinabove) configured to receive the boric acid and X_nY slurry and to separate between solution saline boric acid and X_nY salt (liquid part) and solid boric acid and X_nY containing matter (solid part).

In some examples, the solid boric acid and X_nY containing matter is subjected to drying. Thus, in some examples of the presently disclosed subject matter, the system comprises a drying unit configured to dry the solid boric acid-containing matter received from the (boric acid and X_nY slurry) solid-liquid separator and second electrodialysis unit.

In some examples of the presently disclosed subject matter, the system comprises boric acid separation unit downstream to the drying unit, the separation unit being configured to selectively dissolve the dried solid boric acid containing matter in an organic solvent and discharge/recover dissolved boric acid, and discharge solid X_nY.

In some examples of the presently disclosed subject matter, the system comprises a X_nY dissolution unit configured to dissolve solid X_nY received from the boric acid separation unit.

In some examples of the presently disclosed subject matter, the system comprises a second mixing chamber configured to mix saline boric acid discharged from the solid-liquid separator with the dissolved X_nY received from the X_nY dissolution unit, the second mixing chamber being upstream to said second electrodialysis unit and is configured to communicate the mixed dissolved boric acid and X_nY into the second electrodialysis unit. In some examples of the presently disclosed subject matter, the liquid saline boric acid containing dissolved X_nY salt is collected for further treatment by the second electrodialysis unit, as further described hereinabove and below.

In the second electrodialysis unit as defined hereinabove, the applied voltage between the anode and the cathode provides for:

- transfer of X^+ across each CM,
- transfer of Y^{n-} across each AM,
- generation of OH^- by said BPM in the XOH compartment
- generation of H^+ by said BPM in the H_nY compartment; and
- separate discharge of a second stream of concentrated XOH and a stream of H_nY.

In some cases, the second electrodialysis unit as defined hereinabove, the applied voltage between the anode and the cathode also allows to keep a weakly charged boric acid in residual boric acid waste stream for further utilization.

Further in accordance with the presently disclosed subject matter, in some examples, the system also comprises a first evaporator (as described hereinabove), which is configured to evaporate water from the aqueous solution of XOH discharged from the first electrodialysis unit and to discharge first unit concentrated XOH.

In some examples of the presently disclosed subject matter, the system comprises a second evaporator configured to evaporate water from the aqueous solution of H_nY received from the second electrodialysis unit and to discharge concentrated H_nY.

In some examples of the presently disclosed subject matter, the system comprises a third evaporator between said second electrodialysis unit and said drying unit, said third evaporator being configured to evaporate water from said residual boric acid.

Reference is now made to **Figure 4** providing a schematic illustration of a system comprising all the above-described optional system elements and is configured for recovery of XOH and preferably also H_nY from aqueous XBO_2 waste solution, such as spent fuel, according to some examples of the presently disclosed subject matter.

Specifically, **Figure 4** shows a schematic illustration of a system according to some examples of the presently disclosed subject matter, constructed to allow the recovery of XOH from waste containing the aqueous dissolved XBO_2 and preferably also recovery of H_nY utilized in the process of XOH recovery.

According to the non-limiting illustration of **Figure 4**, waste comprising the aqueous dissolved XBO_2 ("***XBO_2 Waste***") is fed to the first electrodialysis unit for dealkalization ("***1st ED Unit***"). As noted hereinbefore, the XBO_2 containing waste is an aqueous solution of XBO_2 at high concentration near the solubility limit. Such a solution creates a complex tetraborate structure balanced by X^+ cations. This process results in a highly alkaline pH of the XBO_2 waste due to consecutive liberation of XOH according to the following route:

$$4\ XBO_2 + (1+n)\cdot H_2O \rightarrow X_2B_4O_7\cdot nH_2O + 2\ XOH$$

This solution is fed to the 1st ED Unit composed of the power source, cathode and anode and ion selective membranes arranged in a stack between the cathode and anode.

The membrane arrangement in the 1st ED Unit can have a repeating sequence of *CM-BPM-CM* as schematically illustrated in Figure 1A (in case of working with a block loop) or a sequence of *CM-BPM* as schematically illustrated in Figure 2A (in case of working without a block loop).

The 1st ED Unit generates two main process streams. The first stream is a first XOH stream. The first XOH stream is sent to a ***1st Evaporator*** to increase the XOH concentration to a desired level (e.g. 40wt%-45wt%) and stored in dedicated tank ("***XOH Tank***"), e.g. for later use in XBH_4 production process.

The second stream discharged from the 1st ED Unit is de-alkalized waste which is sent to a boric acid production stage in a BA reactor ("***BA Reactor***"). In the BA reactor, concentrated acid H_nY is added to the dealkalized waste to produce boric acid slurry. As explained above, boric acid has limited solubility and it is precipitated together with the generated salt X_nY. Part of the boric acid and X_nY salt remain in dissolved form.

The resulting slurry is separated in solid/liquid separator ("***Solid-Liquid Separator***") to solid BA + X_nY which is sent for drying ("***Boric Acid Drying***") and liquid boric acid production waste which is sent to "***Waste Collection Tank***".

Dry boric acid and X_nY are contacted by methanol in boric acid dissolution ("***Boric Acid Dissolution***"). As noted above, methanol selectively dissolves the boric acid leaving most of the X_nY salt in solid form. The methanol dissolved BA is sent to further use, e.g. in XBH_4 production processes, while the solid X_nY is sent to water dissolution step ("***X_nY Dissolution***"). The dissolved X_nY salt is transferred to the same Waste

Collection Tank into which the liquid BA waste is sent ("***Waste Collection Tank***") and is thus mixed with waste from boric acid production step. The total waste stream from the ***Waste Collection Tank*** is sent to a 2nd electrodialysis unit ("***2nd ED Unit***") to recover a second XOH stream, the boric acid and also H_nY.

The 2nd ED unit operational principle is detailed hereinabove. The 2nd ED Unit is generally composed of the power source, cathode and anode and ion selective membranes arranged in a stack between the cathode and anode. The membrane arrangement in the 2nd ED Unit has a repeating sequence of *CM-BPM-AM* as schematically illustrated in Figure 3A.

The 2nd ED unit generates three main process streams.

A first stream discharged from the 2nd ED Unit is a second XOH stream which is sent to a ***1st Evaporator*** to increase the XOH concentration to the desired level and stored together with the first XOH stream, in the XOH Tank.

A second stream discharged from the 2nd ED Unit is H_nY stream, which is sent to a ***2nd Evaporator*** to increase the H_nY acid concentration to the desired level, which can then be stored in a H_nY Tank and from the H_nY Tank, communicated to the BA Reactor for reused in the BA production stage.

A third stream comprising desalinated solution containing residual boric acid. This stream is sent to a ***3rd Evaporator*** to produce solid boric acid which can be then dried in the ***Boric Acid Drying*** unit together with the boric acid discharged from the ***Solid-Liquid Separator***.

As used herein, the forms "***a***", "***an***" and "***the***" include singular as well as plural references unless the context clearly dictates otherwise. For example, the term "***a membrane"*** includes one or more membranes.

Further, as used herein, the term "***comprising***" is intended to mean that the composition include the recited components, e.g. 1st elecrodialysis unit, but not excluding other elements or components than may form part of the presently disclosed subject matter. The term "***consisting essentially of***" is used to define methods and systems which include the recited components or elements but exclude other components or elements that may have an essential significance on the performance of the disclsoed methods and systems.

"***Consisting of***" shall thus mean excluding components or elements that are not specifically recited. Embodiments defined by each of these transition terms are within the scope of this invention.

Further, all numerical values, e.g. when referring the amounts or ranges of the elements constituting the recited compositions, e.g. the streams of XOH are approximations which are varied (+) or (-) by up to 20%, at times by up to 10% of from the stated values. It is to be understood, even if not always explicitly stated that all numerical designations are preceded by the term "***about***".

The invention will now be exemplified in the following description of experiments that were carried out in accordance with the invention. It is to be understood that these examples are intended to be in the nature of illustration rather than of limitation. Obviously, many modifications and variations of these examples are possible in light of the above teaching. It is therefore, to be understood that within the scope of the appended claims, the invention may be practiced otherwise, in a myriad of possible ways, than as specifically described hereinbelow.

DESCRIPTION OF NON-LIMITING EXAMPLES

Ion selective membranes: Heterogeneous CM, AM and BPM membranes: RALEX membranes by Mega Group Ltd.

Cathode: SS316 cathode

Anode: Graphite anode

Experimental system

The proof-of-concept experiments were conducted in laboratory scale electrodialysis system provided by Mega Group Ltd. and shown in **Figure 5A**.

The system consisted of 5 independent circulating loops (the "compartments") marked as D1, D2, E, C1 (not in use in the current example) and C2. Each circulating loop includes a respective dedicated circulating vessel, piping, flowmeter and circulating pump (pump and flowmeter are not shown in Figure 5A). The circulating vessels were submerged in a thermal bath to enable constant temperature conditions during the experiment.

The system also included a dedicated power source (Power supply) with its Power supply Voltmeter and Power supply Amperemeter. The pumps and the power source were operated from a control panel, also shown in Figure 5A.

The system was designed to operate with a single replaceable membrane unit (stack) including a stack of membranes' arrangement that allows the switching between an operation with a block loop circulating stream (D2) and without a block loop circulating stream (where D2 is "not in use"). The system of Figure 5A can also simulate the operation of the 2nd electrodialysis unit, as evident from Table 2 below.

Figure 5B shows that the shown stack of membranes' arrangements also includes an anode plate and a cathode plate with electrical connections to the power source (the power source not shown).

Circulation piping lines were connected to the relevant membrane arrangement port located in electrode plates. The membranes were arranged between the anode and cathode and held by tightening rods.

For lab scale production, sensing electrodes were used and were located between the electrodes and the membrane adjacent thereto. The purpose of the sensing electrodes is to measure the potential drop on the membranes without the interference of the potential drop related to the reaction occurring on the electrodes and electrical system resistance. The potential difference measured by sensing electrodes serves for determination of process energy consumption used for system scale up.

The system shown in Figures 5A-5B was used to test the performance in different configurations of the electrodialysis units. The membrane type and arrangement inside the stack (e.g. with or without the block loop) and accordingly circulating streams were selected to adapt the system for different operating conditions.

Table 2 summarizes the circulating streams' designation for different system configurations (e.g. with or without the circulation of a block loop stream).

Table 2: Streams designation for different BPM systems configuration

	D1	D2	E	C1	C2
1st electrodialysis unit block loop	XOH	Block Loop	Electrode wash	Not in use	Aqueous XBO_2 solution
1st electrodialysis unit without block loop	XOH	Not in use	Electrode wash	Not in use	Aqueous XBO_2 solution
2nd electrodialysis unit	XOH	H_nY	Electrode wash	Not in use	Saline BA waste

Experimental conditions

The experimental conditions for the different system configurations include the following:

Voltage	20 – 30 V (measured parameter)
Amperage	1.9 – 2 A (controlled parameter)
Current density	30 mA/cm^2
AM, CM and BPM membranes	RALEX membranes by Mega Group Ltd.
No. of repeating membrane sets	10
Effective membrane area	640 cm^2
Temperature	30°C
Solution mass	1 kg for all streams
Circulation flowrates	500 ml/min for all streams
Experiment duration	2-4 hours

Results

Operation of 1st electrodialysis unit with block loop

Experiments conducted with spent fuel solutions containing 40%wt KBO_2 showed that more than 30% of K^+ ions can be recovered out of the solution as KOH. The KOH recovery led to pH decrease from pH ~ 14 to pH below 13.

Experiments conducted with spent fuel solutions containing 30%wt KBO_2 showed that more than 40% of K^+ ions can be recovered out of the solution as KOH. The KOH recovery led to pH decrease from pH > 13.8 to pH below 12.

Experiments conducted with spent fuel solutions containing 30%wt KBO_2 showed that more than 50% of K^+ ions can be recovered out of the solution as KOH. The KOH recovery led to pH decrease from pH ~ 13 to pH below 10.

The KOH solution recovered reached concentration of up to 7.5%wt at the end of the experiment. Less than 1% of $B_4O_7^{2-}$ anions were lost from the treated waste stream. The process energy consumption was estimated as ~ 1.5 kWh per 1 kg of recovered KOH.

Operation of 1st electrodialysis unit without block loop

The results obtained without block loop circulation were similar to the results obtained with block loop circulation, except the loss of the $B_4O_7^{2-}$ anions in the former configuration. The $B_4O_7^{2-}$ anions loss from the treated waste stream to the KOH stream increased without the block loop circulation, from ~1% to ~ 5%.

Operation of 2nd electrodialysis unit

The treated saline Boric Acid waste obtained from operating the 1st electrodialysis unit (with or without the operation of a block loop) contained ~ 60 gr of Boric Acid and ~ 120 gr of K_2SO_4 in one liter of the solution.

The expected level of K^+ ions recovery as KOH and SO_4^{2-} ions recovery as H_2SO_4 is more than 90%. The expected loss of weakly charged Boric Acid to the KOH and H_2SO_4 streams is < 5% in total.

CLAIMS:

1. A method for recovery of alkali metal hydroxide (XOH) from waste comprising aqueous XBO_2 solution, the method comprising:

subjecting the waste to a first electrodialysis process within a first electrodialysis unit that comprises at least one bipolar membrane, under conditions that provide a first XOH stream and a stream of de-alkalized waste and discharging the first XOH stream; and optionally

mixing the de-alkalized waste with an acid H_nY, n being an integer and Y a counter anion to the alkali metal cation to form a slurry of boric acid and X_nY;

removing solids from said slurry of boric acid and X_nY to form a solid-free aqueous mixture of boric acid and X_nY; and

subjecting the solid-free aqueous mixture of boric acid and X_nY to a second electrodialysis process within a second electrodialysis unit comprising at least one bipolar membrane, the second electrodialysis unit being different from the first electrodialysis unit, under conditions that provides a second XOH stream and a stream of H_nY;

collecting the first XOH steam and the second XOH stream.

2. The method of claim 1, wherein said

first electrodialysis unit comprises a first unit inlet end and a first unit outlet end, and extending therebetween a first electrodialysis cell comprising:

an anode

a cathode paired with a cathode-end CM,

a membrane arrangement stacked between said anode and said cathode-end CM, the membrane arrangement comprising, from the anode end, a repeating set of CM-BPM or a repeating set of CM-BPM-CM;

a power source configured for applying a voltage across said cell,

said anode, said cathode-end CM and said membrane arrangement providing an array of electrolyte flow compartments, each electrolyte flow

compartment having a fluid inlet at said first unit inlet end and fluid outlet at said first unit outlet end, the array of electrolyte flow compartments including

an electrode wash compartment between said anode and said anode paired-CM and between said cathode and said cathode-paired CM,

waste treatment compartment between two facing CM in the membrane arrangement comprising CM-BPM-CM repeating set or between BPM and cathode-side CM in the arrangement comprising CM-BPM repeating set;

XOH compartment between a CM and a BPM within a repeating set; and

when said arrangement comprises said CM-BPM-CM repeating set, a block loop compartment between BPM and its cathode-side CM.

3. The method of claim 2, comprising

(a) apply voltage between said anode and said cathode while introducing through said first unit inlet end

an electrode wash solution into an anode side electrode wash compartment and into a cathode-side electrode wash compartment;

liquid waste comprising aqueous XBO_2 solution, into said waste treatment compartment; and

lean XOH solution into said XOH compartment; and

diluted acid solution H_nY, where n represents a number and Y represents an anion of said strong acid, into block loop compartment, if such compartment exists;

said voltage causing transfer of X^+ across each CMs and generation of OH^- by said BPM, to thereby form a XOH liquid in said XOH compartment and generation of H^+ by said BPM in said waste treatment compartment to balance said transfer of X^+ to said XOH compartment; and

(b) discharging at least said first XOH stream from said first unit outlet end, said first XOH stream having a concentration greater than XOH concentration in said lean XOH solution.

4. The method of any one of claims 1 to 3, wherein said alkali metal in said waste is selected from the group consisting of sodium, potassium and lithium.

5. The method of any one of claims 1 to 4, wherein said XBO_2 is at a concentration close to its solubility limit.

6. The method of any one of claims 1 to 5, wherein said liquid waste is spent fuel obtained during hydrogen release from XBH_4 based on the following equation (1):

$$XBH_4 + 2\ H_2O \rightarrow \mathbf{XBO_2} + 4\ H_2\ (g).$$

7. The method of any one of claims 2 to 6, whenever dependent on claim 2, wherein said electrode wash solution comprises dissolved X_kZ salt, X being said alkali metal cation, k being an integer, Z^{k-} being an anion and at least said cathode-end CM is essentially impermeable to said Z^{k-}.

8. The method of claim 7, wherein said X_kZ salt is selected from the group consisting of XOH and X_2SO_4.

9. The method claim 8, wherein concentration of said XOH in said electrode wash solution dissolved XOH lower than the XOH concentration in said waste.

10. The method of any one of claims 2 to 7, whenever dependent on claim 2, comprising recirculating electrode wash solution discharged from first unit outlet ends of each said electrode wash compartment.

11. The method of claim 10, wherein said recirculating comprises mixing the electrode wash solution discharged from said first unit outlet ends, prior to being re-introduced into each electrode wash compartment.

12. The method of any one of claims 1 to 11, comprising subjecting said first XOH stream to at least one evaporating process to provide first unit concentrated XOH.

13. The method of claim 12, comprising collecting said first unit concentrated XOH in a XOH tank.

14. The method of any one of claims 1 to 11, wherein said dealkalized waste has a pH of less than 11.

15. The method of any one of claims 1 to 14, wherein said mixing said dealkalized waste with acid H_nY results in regenerating boric acid from said dealkalized waste, said regenerating reaction being represented by the following equation (2):

$$n\ XBO_2 + H_nY + n\ H_2O \rightarrow n\ B(OH)_3 + X_nY.$$

16. The method of claim 15, comprising introducing said slurry into a solid-liquid separator and separating between solids comprising solid boric acid and solid X_nY and saline boric acid comprising aqueous solution saturated with dissolved boric acid and X_nY.

17. The method of claim 16, comprising drying said solids comprising the solid boric acid and solid X_nY.

18. The method of claim 17, comprising separating solid boric acid from solid X_nY, said separating comprises dissolving said solids in methanol, and collecting solid X_nY separated from methanol dissolved boric acid.

19. The method of claim 18, comprising dissolving the collected solid X_nY in water.

20. The method of claim 16, comprising collecting said saline boric acid into a boric acid tank.

21. The method of claim 19 and 20, further comprising

(a) subjecting the saline boric acid to an electrodialysis reaction within a second electrodialysis unit, said second electrodialysis unit comprises a second unit inlet end and a second unit outlet end, and extending therebetween a second electrodialysis cell comprising:

an anode,

a cathode paired with a cathode-end CM,

a second unit membrane arrangement stacked between said anode and said cathode-end CM, the second unit membrane arrangement comprising, from the anode, a repeating set of CM-BPM-AM;

a power source configured for applying a voltage across said second cell,

said cathode-end CM and said second unit membrane arrangement providing an array of electrolyte flow compartments, each electrolyte flow compartment having a fluid inlet at said second unit inlet end and fluid outlet at said second unit outlet end, the array of electrolyte flow compartments including:

an electrode wash compartment between said anode and an anode-end CM and between said cathode and its cathode-end CM;

XOH compartment between CM and BPM in a repeating set;

X_nY compartment between BPM and AM in a repeating set; and

a saline boric acid compartment between an AM and a cathode side CM in a repeating set;

said subjecting comprises introducing through said second unit inlet end

a wash solution into each of said electrode wash compartment;

lean XOH solution into said XOH compartment;

lean H_nY solution into said H_nY compartment;

aqueous boric acid comprising dissolved boric acid and H_nY into said saline BA compartment.

22. The method of claim 21, wherein said electrodialysis reaction within the second electrodialysis unit comprises:

(a) apply voltage between said anode and said cathode, said voltage causing transfer of X^+ across each CM, and Y^{n-} across each AM, to thereby form a second XOH stream in said XOH compartment; and to cause generation of OH^- in said XOH compartment and H^+ in said H_nY compartment by said BPM; and

(b) discharging at least said second XOH stream from said second unit outlet end, said second XOH stream having a concentration greater than XOH concentration in said lean XOH solution.

23. The method of claim 22, comprising subjecting said second XOH stream from said second unit outlet end to at least one evaporating process to provide second unit concentrated XOH.

24. The method of claim 23, comprising collecting said second unit concentrated XOH in said XOH tank.

25. The method of any one of claims 1 to 24, comprising recovery of H_nY.

26. The method of claim 25, whenever dependent on any one of claims 21 to 25, wherein said recovery of H_nY is from said H_nY compartment.

27. A system comprising

a first electrodialysis unit configured for receiving waste comprising aqueous XBO_2 solution, and for separately discharging a first XOH stream and dealkalized waste; and optionally

a second electrodialysis unit, downstream to said first electrodialysis unit, configured for receiving saline boric acid comprising dissolved boric acid and X_nY, X representing an alkali metal cation, n representing an integer and Y representing an anion to said alkali metal cation, and for separately discharging a second XOH stream and aqueous solution of H_nY.

28. The system of claim 27, wherein said first electrodialysis unit comprises a first electrodialysis cell comprising a first unit inlet end and a first unit outlet end, and extending therebetween:

an anode

a cathode paired with a cathode-end CM,

a membrane arrangement stacked between said anode and said cathode-end CM, the membrane arrangement comprising, from the anode end, a repeating set of CM-BPM or a repeating set of CM-BPM-CM;

a power source configured for applying a voltage across said cell,

said anode, said cathode-end CM and said membrane arrangement providing an array of electrolyte flow compartments, each electrolyte flow compartment having a fluid inlet at said first unit inlet end and fluid outlet at said first unit outlet end, the array of electrolyte flow compartments including

an electrode wash compartment between said anode and anode-side CM and between said cathode and cathode paired CM,

waste treatment compartment between two facing CM in the membrane arrangement comprising CM-BPM-CM repeating set or between BPM and cathode-side CM in the arrangement comprising CM-BPM repeating set, configured to receive waste comprising an aqueous mixture of boric acid and X_nY;

XOH compartment between a CM and a BPM within a repeating set; and

when said arrangement comprises said CM-BPM-CM repeating set, a block loop compartment between BPM and its cathode-side CM.

29. The system of claim 27 or 28, wherein said first electrodialysis unit is configured for

applying on said cell voltage causing transfer of X^+ across each CMs and generate OH^- by said BPM, to thereby form a XOH liquid in said XOH compartment and generate H^+ by said BPM in said waste treatment compartment to balance said transfer of X^+ to said XOH compartment; and for

separately discharging XOH and a stream of said de-alkalized waste .

30. The system of any one of claims 27 to 29, wherein said second electrodialysis unit comprises a second electrodialysis cell comprising a second unit inlet end and a second unit outlet end, and extending therebetween a second electrodialysis cell comprising:

an anode,

a cathode paired with a cathode-end CM,

a second unit membrane arrangement stacked between said anode and said cathode-end CM, the second unit membrane arrangement comprising, from the anode, a repeating set of CM-BPM-AM;

a power source configured for applying a voltage across said second cell,

said cathode-end CM and said second unit membrane arrangement providing an array of electrolyte flow compartments, each electrolyte flow compartment having a fluid inlet at said second unit inlet end and fluid outlet at said second unit outlet end, the array of electrolyte flow compartments including:

an electrode wash compartment between said anode and an anode-end CM and between said cathode and a cathode-end CM, configured to allow flow

therethrough of a wash solution, from said second unit inlet end to said second unit outlet end;

XOH compartment between CM and BPM in a repeating set configured to allow flow therethrough of lean XOH solution, from said second unit inlet end to said second unit outlet end;

X_nY compartment between BPM and AM in a repeating set configured to allow flow therethrough of lean H_nY solution, from said second unit inlet end to said second unit outlet end; and

a saline boric acid compartment between an AM and a CM; configured to allow flow therethrough of said aqueous boric acid, from said second unit inlet end to said second unit outlet end.

31. The system of any one of claims 27 to 30, wherein said second electrodialysis unit is configured for

applying voltage between said anode and said cathode, said voltage being configured to cause transfer of X^+ across each CM, and Y^{n-} across each AM, to thereby form a XOH liquid in said XOH compartment; and to cause generation of OH^- in said XOH compartment and H^+ in said H_nY compartment by said BPM; and

separately discharging said second XOH stream and H_nY.

32. The system of any one of claims 27 to 31, comprising a first evaporator configured to evaporate water from said aqueous solution of said first XOH stream received from said first electrodialysis unit and to discharge concentrated XOH.

33. The system of any one of claim 27 to 32, comprising a solid-liquid separator configured to receive boric acid slurry and to separate between saline boric acid and solid boric acid containing matter.

34. The system of claim 33, comprising a drying unit, configured to dry solid boric acid containing matter received from any one of said solid-liquid separator and second electrodialysis unit.

35. The system of claim 34, comprising boric acid separation unit downstream to said drying unit, said separation unit configured to selectively dissolve the dried solid boric

acid containing matter in an organic solvent and separately discharge dissolve boric acid and solid X_nY.

36. The system of claim 35, wherein said boric acid organic solvent is a short chain alcohol.

37. The system of claim 36, wherein said organic solvent is methanol.

38. The system of any one of claims 27 to 37, comprising a second evaporator configured to evaporate water from said aqueous solution of H_nY and recover concentrated H_nY.

39. The system of claim 33 and 38, comprising a first mixing chamber configured for mixing said de-alkalized waste with H_nY recovered from said second evaporator, prior to introducing said aqueous boric acid into said solid-liquid separator.

40. The system of any one of claims 27 to 39, comprising a third evaporator configured to concentrate residual boric acid discharged from said second electrodialysis unit.

41. The system of any one of claims 27 to 40, whenever dependent on claim 35, comprising a X_nY dissolution unit configured to dissolve said solid X_nY.

42. The system of claim 33 and 41, comprising a second mixing chamber configured to mixed saline boric acid discharged from the solid-liquid separator with the dissolved X_nY.

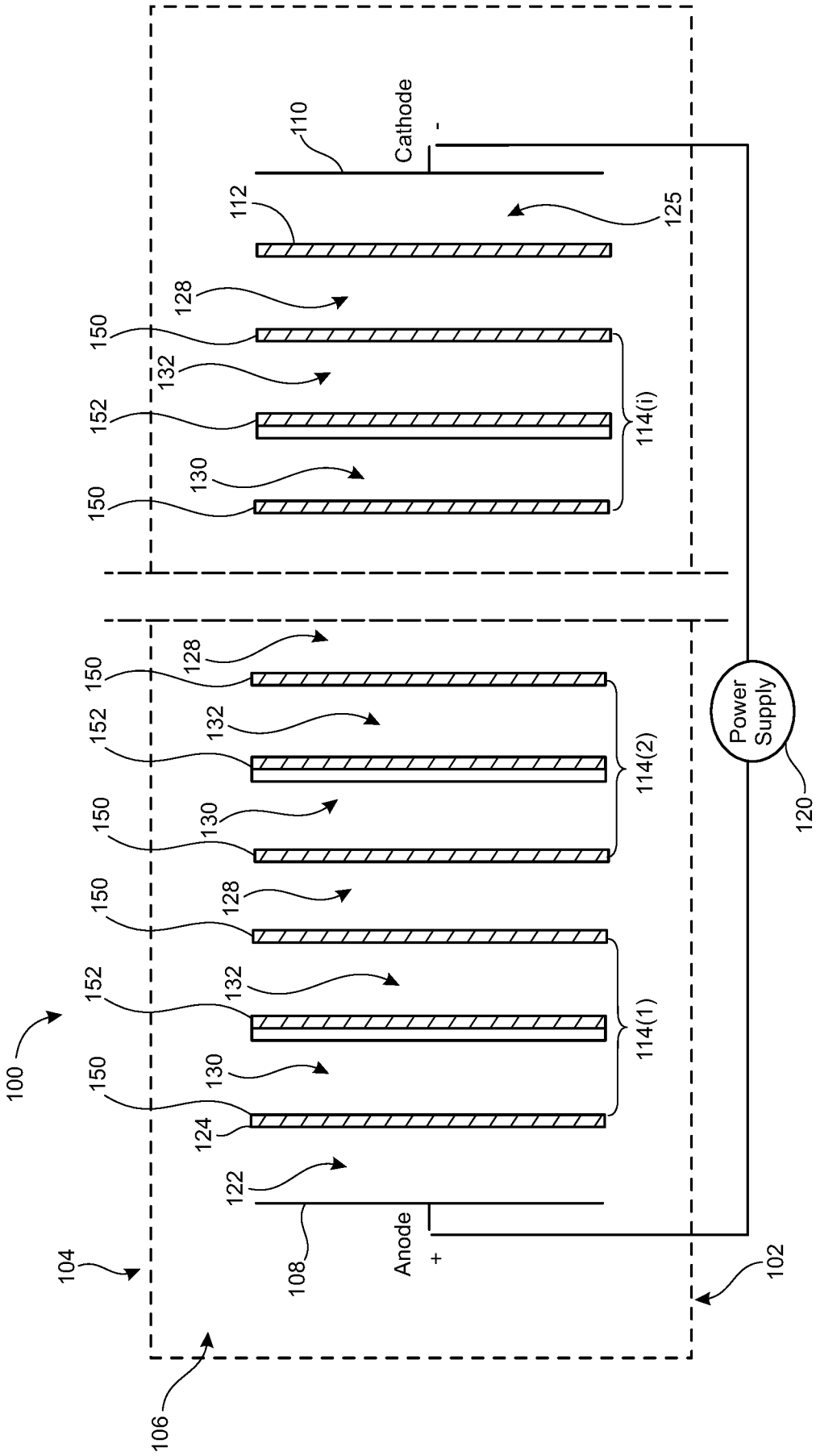

Cathode
-
110
112
125
128
150
132
152
130
114(i)
114(2)
114(1)
Power Supply
120
100
124
122
108
Anode
+
104
102
106

FIG. 1A

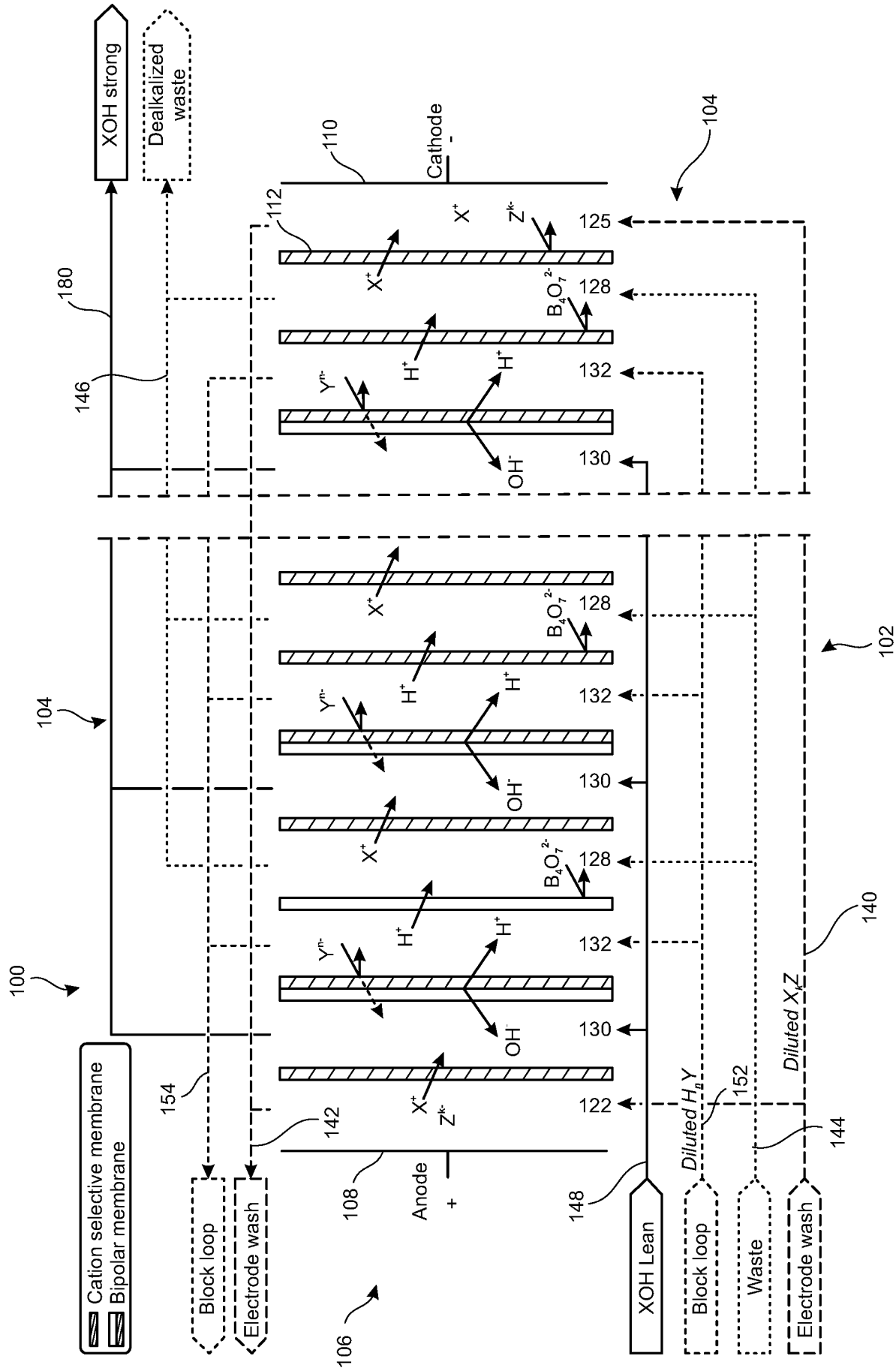
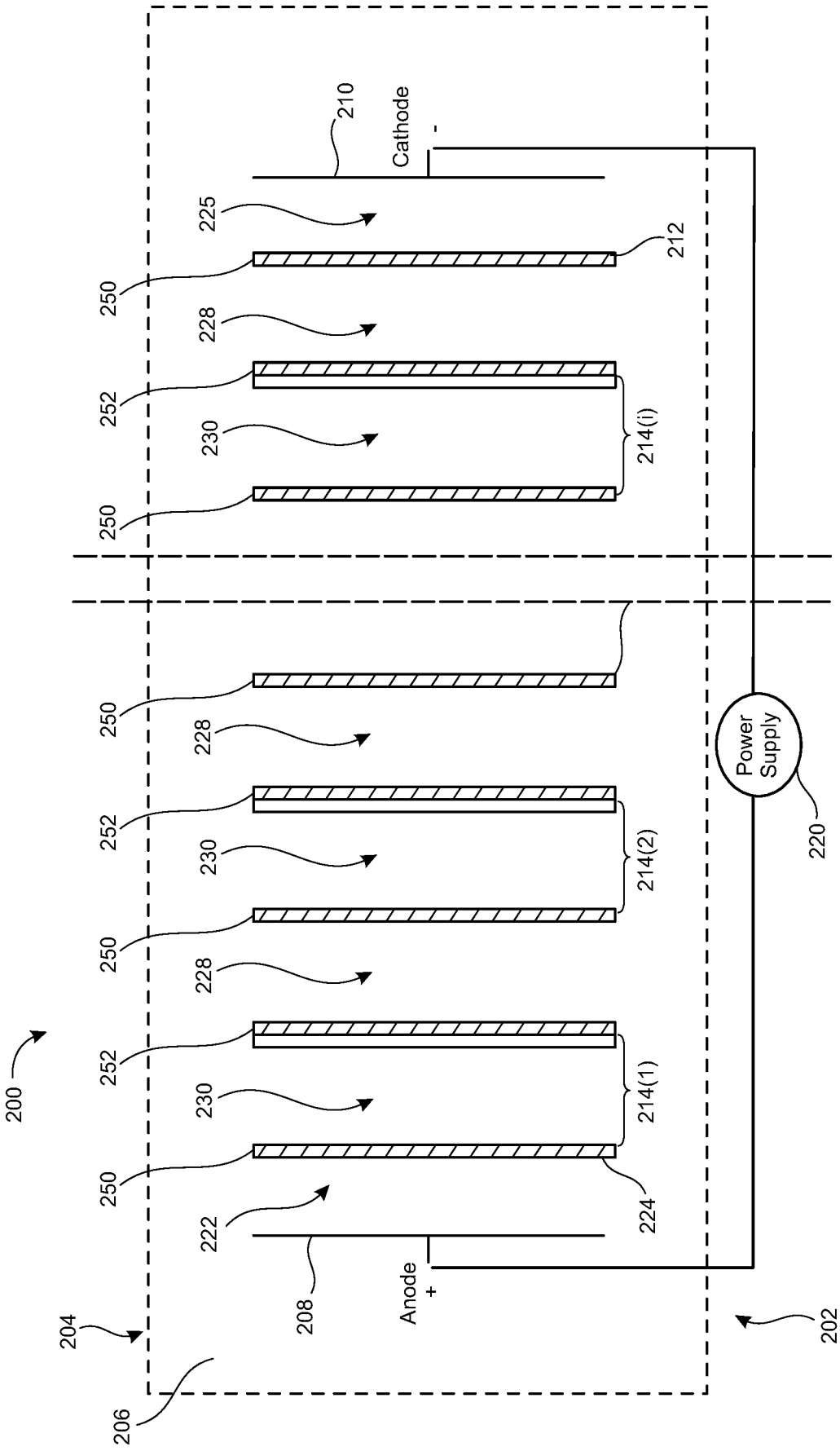

XOH strong
Dealkalized waste
Cathode
-
110
104
112
125
128
132
130
180
146
Cation selective membrane
Bipolar membrane
Block loop
Electrode wash
154
142
108
Anode
+
106
148
XOH Lean
Block loop
Waste
Electrode wash
Diluted H_nY
152
144
Diluted X_kZ
140
102
100
122

FIG. 1B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Cathode
-
225
212
250
228
252
230
214(i)
250
250
228
252
230
214(2)
250
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250
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208
Anode
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206
202
Power Supply
220

FIG. 2A

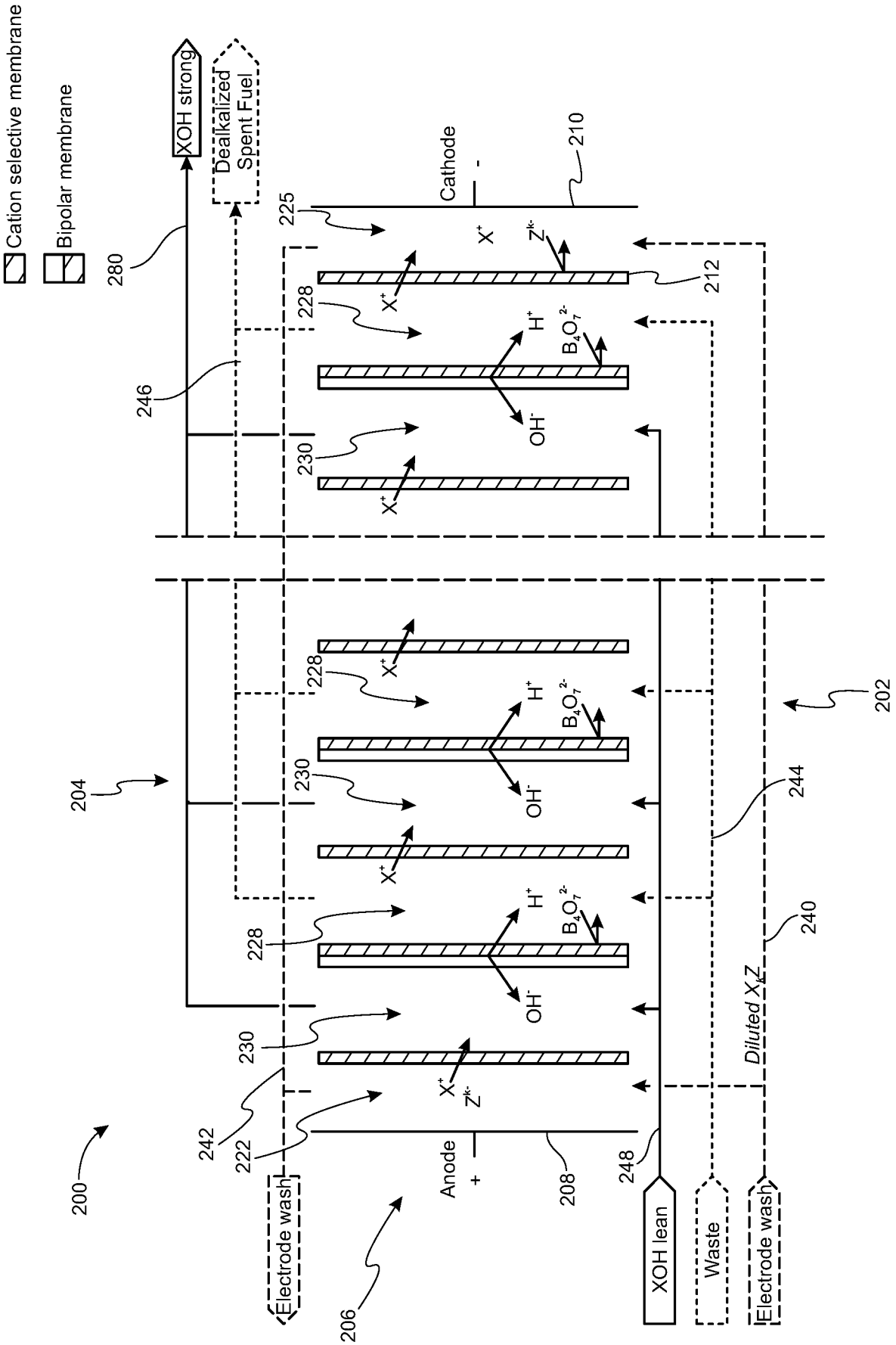
Cation selective membrane
Bipolar membrane
XOH strong
Dealkalized Spent Fuel
Cathode
-
210
225
280
212
228
246
230
204
202
244
240
Diluted X_kZ
242
222
Anode
+
208
248
200
206
Electrode wash
XOH lean
Waste
Electrode wash

FIG. 2B

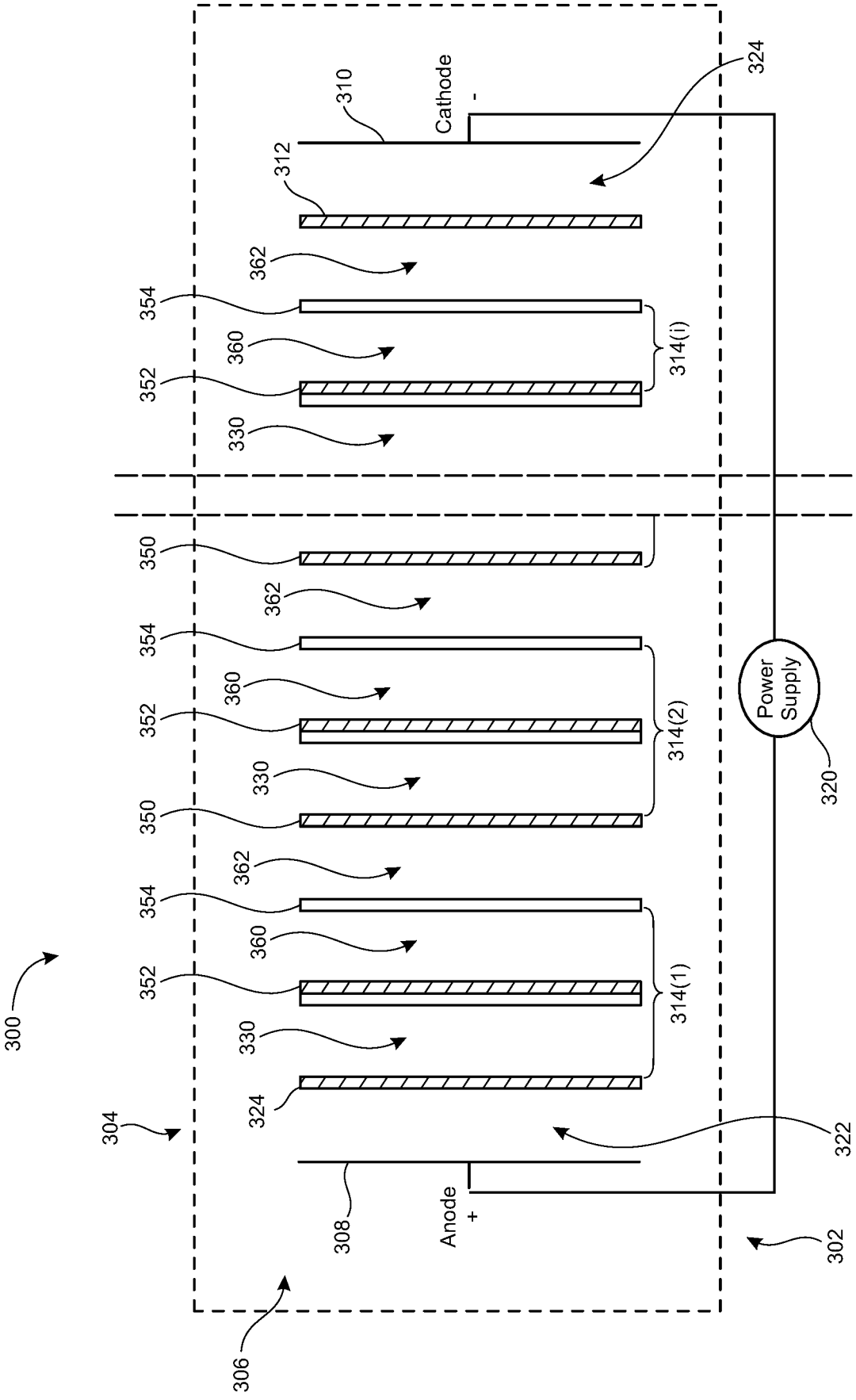
300
302
304
306
308
310
312
314(1)
314(2)
314(i)
320
322
324
330
350
352
354
360
362
Cathode
-
Anode
+
Power Supply

FIG. 3A

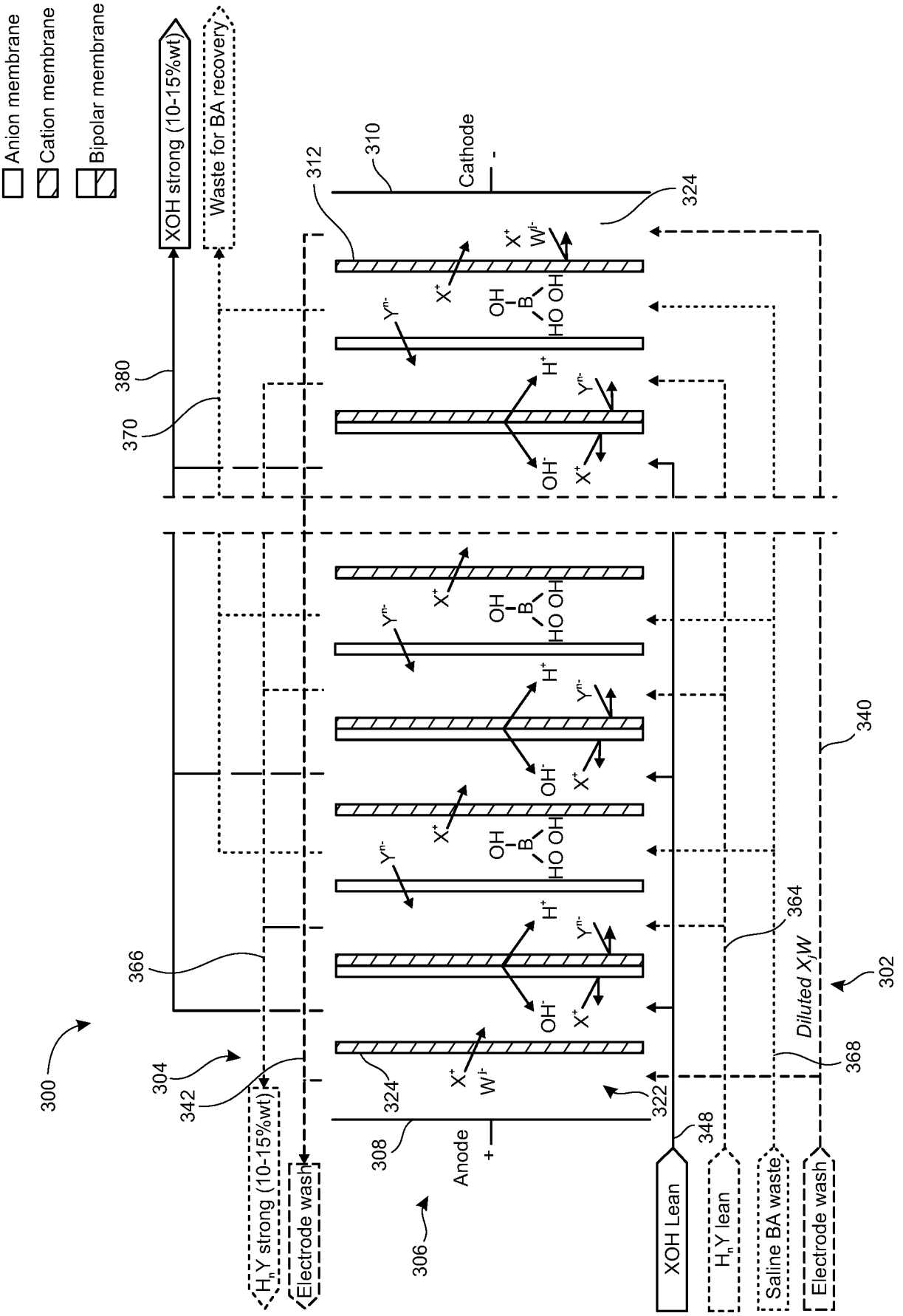
Anion membrane
Cation membrane
Bipolar membrane
XOH strong (10-15%wt)
Waste for BA recovery
310
Cathode
-
312
324
380
370
366
304
342
H_nY strong (10-15%wt)
Electrode wash
300
308
Anode
+
306
322
348
XOH Lean
H_nY lean
Saline BA waste
Electrode wash
340
364
Diluted X_jW
368
302
X^+
W^{j-}
Y^{n-}
H^+
OH^-
OH
B
HO OH

FIG. 3B

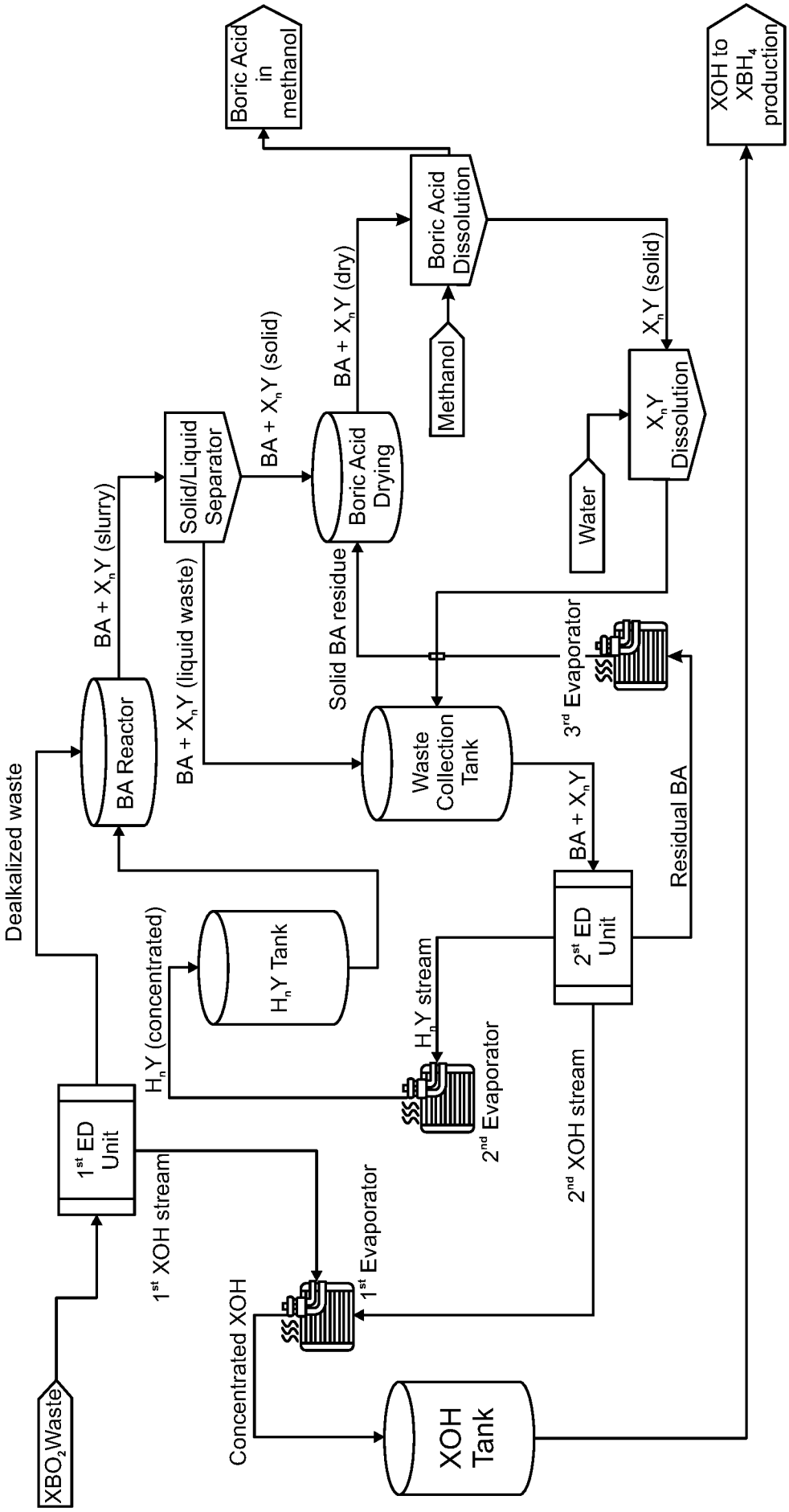
XBO2Waste
1st ED Unit
1st XOH stream
1st Evaporator
Concentrated XOH
XOH Tank
XOH to XBH4 production
Dealkalized waste
BA Reactor
BA + XnY (slurry)
Solid/Liquid Separator
BA + XnY (solid)
BA + XnY (liquid waste)
Boric Acid Drying
BA + XnY (dry)
Solid BA residue
Boric Acid Dissolution
Boric Acid in methanol
Methanol
Water
XnY Dissolution
XnY (solid)
Waste Collection Tank
3rd Evaporator
BA + XnY
2nd ED Unit
Residual BA
HnY (concentrated)
HnY Tank
HnY stream
2nd Evaporator
2nd XOH stream

FIG. 4

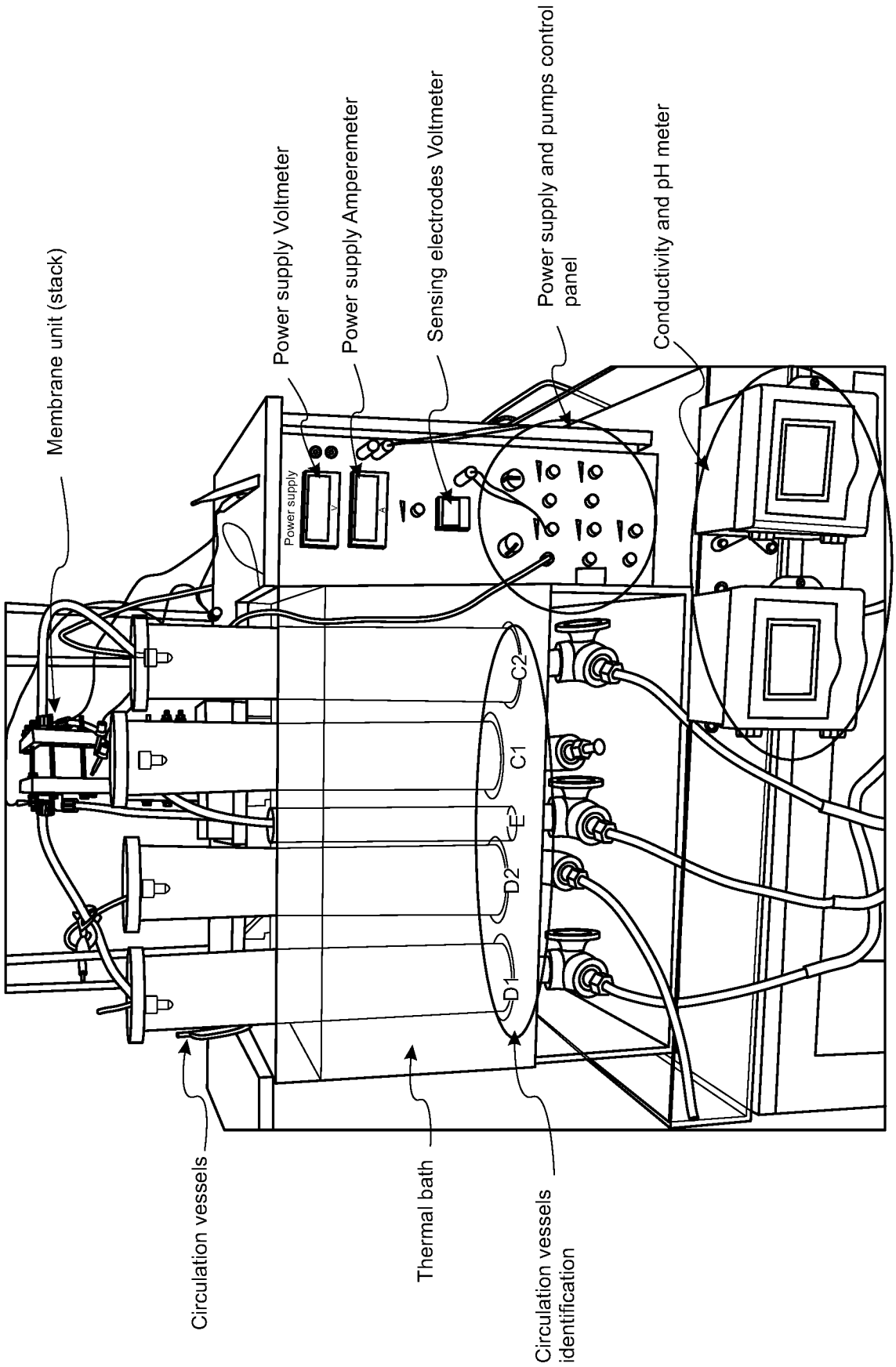
Membrane unit (stack)
Power supply Voltmeter
Power supply Amperemeter
Sensing electrodes Voltmeter
Power supply and pumps control panel
Conductivity and pH meter
Power supply
V
A
C2
C1
E
D2
D1
Circulation vessels
Thermal bath
Circulation vessels identification

FIG. 5A

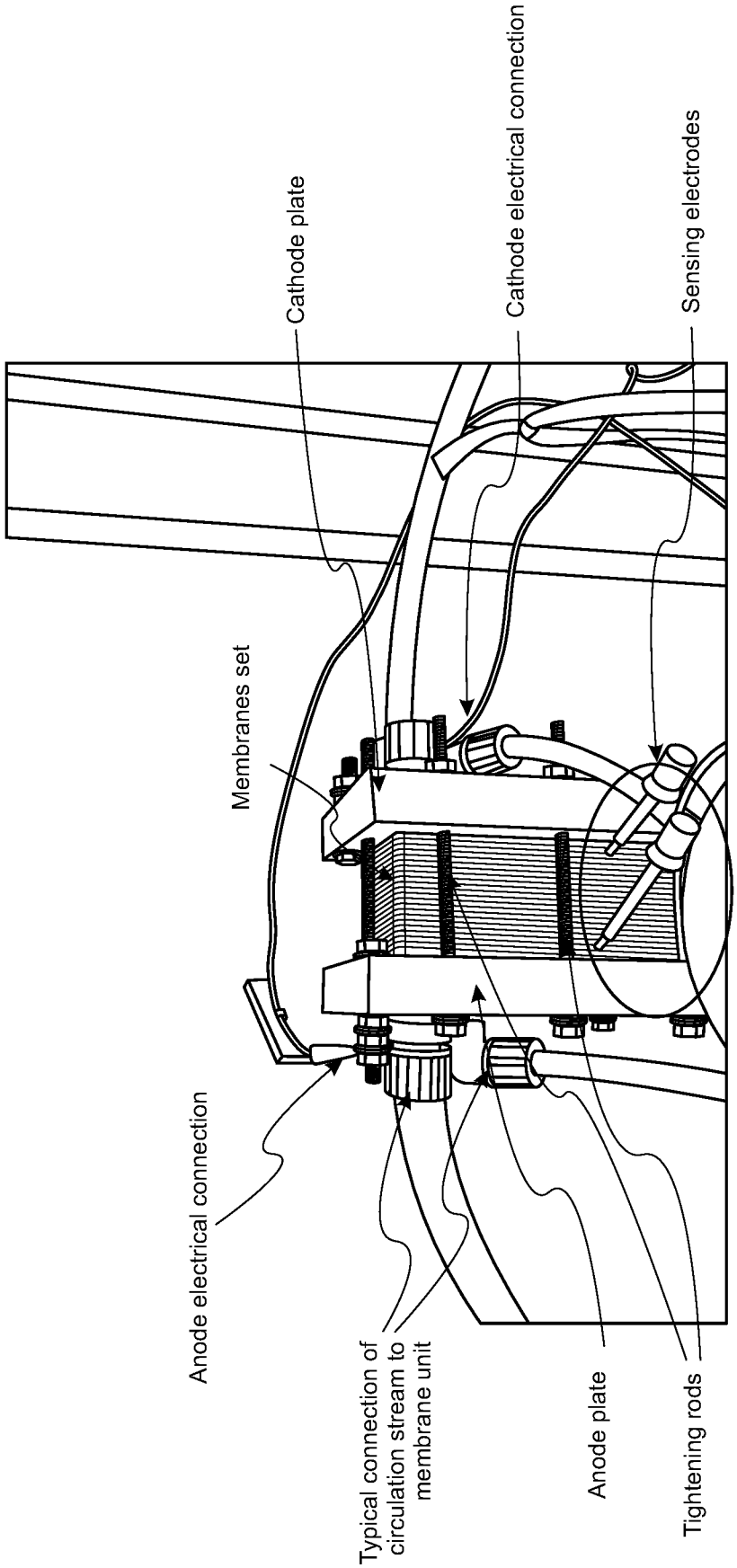
Cathode plate
Cathode electrical connection
Sensing electrodes
Membranes set
Anode electrical connection
Typical connection of circulation stream to membrane unit
Anode plate
Tightening rods

FIG. 5B

INTERNATIONAL SEARCH REPORT

International application No
PCT/IL2024/050561

A. CLASSIFICATION OF SUBJECT MATTER

INV. B01D61/42 B01D61/44 B01D61/46 C25B1/16 C01B3/06
C25B1/22 C25B9/21
ADD.

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)
B01D C25B

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)
EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6 294 066 B1 (MANI K N [US]) 25 September 2001 (2001-09-25) abstract figure 6 column 13, line 52 - column 14, line 21	27-29
X	US 2020/024757 A1 (MANI K N [US]) 23 January 2020 (2020-01-23)	27,29
A	paragraphs [0001], [0005]	1-26
X	US 2021/308347 A1 (DING YUANPANG SAMUEL [US] ET AL) 7 October 2021 (2021-10-07) abstract figure 13 paragraph [0293]	27,29

-/--

[X] Further documents are listed in the continuation of Box C.

[X] 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

"E" earlier application or patent but published on or after the international filing date

"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)

"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

"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

"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

"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

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
23 September 2024	04/10/2024

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Lançon, Eveline

2

Form PCT/ISA/210 (second sheet) (April 2005)

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2020/385280 A1 (DAI YIHUA [CN] ET AL) 10 December 2020 (2020-12-10)	27-42
A	abstract paragraphs [0094] - [0103] figure 6 paragraphs [0105] - [0107], [0110], [0111]	1-26

X	US 4 504 373 A (MANI KRISHNAMURTHY N [US] ET AL) 12 March 1985 (1985-03-12) abstract claim 28	27,29

A	GAO WENJIE ET AL: "Recovery of Acid and Base from Sodium Sulfate Containing Lithium Carbonate Using Bipolar Membrane Electrodialysis", MEMBRANES, vol. 11, no. 2, 22 February 2021 (2021-02-22), page 152, XP093205012, CH ISSN: 2077-0375, DOI: 10.3390/membranes11020152 cited in the application abstract	1-26, 28-42

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/IL2024/050561

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		CL 2022000827 A1	10-03-2023
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