

TITLE: DESALINATION DEVICE AND PROCESS FOR RECOVERY AND VALORISATION OF CHLORIDES IN DILUTE SOLUTIONS

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TECHNICAL FIELD

The present invention relates to a desalination device and process for the recovery and valorisation treatment of chlorine-containing solutions from industrial, mining or water treatment wastes, including marine brines, by way of non-limiting example, for the production of disinfectants and the sequestration of atmospheric CO₂, for example.

PRIOR ART

The reduction of chloride levels below the levels permitted for spillage into surface water (generally in the order of 1,000 ppm) is one of the main issues in the field of water treatment, since chlorides, unlike other elements or compounds such as calcium, magnesium, sulphates, and so forth, cannot be treated in physical-chemical plants by exploiting poorly soluble salts, oxides, hydroxides or flocculating agents.

However, chlorine salts, i.e. chlorides, are one of the most common pollutants of waste water from industrial processes (the food, textile, metal treatment and galvanic industries, etc.), mining, oil extraction (fracking) and, last but not least, from activities related to the desalination of marine water for the production of potable water for human consumption.

To date, the most commonly used methods for chloride abatement below the permitted limits for spillage into surface water depend strongly on their level of chloride concentration. In the case of levels close to the threshold (<5,000 ppm), generally the wastewater is mixed with other wastewater with a low chloride content and then undergoes chemical and physical treatment of the resulting mixture. For concentrations above 70,000 ppm, the only applicable technologies involve evaporation methods that make it possible to recover a volume of water by concentrating it until it (possibly) reaches saturation, with a subsequent solid recovery of chlorine salts. In the case of intermediate concentrations between 5,000 and 70,000 ppm, the

method normally consists in applying, in series, a purification by means of osmotic membrane and consequently an evaporative recovery of the concentrated osmotic rejection.

Needless to say, given the high plant and energy costs related to reverse osmosis and evaporation treatments, it is not uncommon to see fraudulent phenomena of environmental spillage or relocation, where possible, to countries with inadequate environmental regulations that permit spillage into surface water.

A further method developed in the early 2000s and marketed by the Applicant under the name SMIT is the subject matter of the European patent EP 3 250 516, and provides for the use of an electrochemical apparatus to extract the chlorine salts dissolved in an aqueous solution while simultaneously producing an aqueous solution depleted of chlorine salts and two chemical compounds, one of which is hydrochloric acid HCl and the other a base, by an inverse acid-base neutralisation process. The process disclosed in the aforementioned patent provides for the use of two electrodes enriched with a catalyst that, by supplying the cell with atmospheric oxygen and hydrogen, makes it possible to obtain two chemical reactions on the surfaces of the electrodes that result in the production on one side of H^+ ions and on the other of OH^- ions. Due to the principle of electro-neutrality of the aqueous solutions, the increase in the concentration of these ionic species in the chamber containing the two electrodes involves the displacement of the charged ionic species contained in the treated brine through dedicated anion and cation membranes with consequent sequestration thereof.

Despite the great advantage introduced by this technology given by the fact that it is possible to obtain a chemical valorisation of treated brines and a consequent production of electric energy from the electrochemical process involved, this technology has several problems, summarised here below:

The high cost of the catalysts used for the production of the electrodes (such as platinum oxides) implies a high initial outlay for the construction of a plant that makes its application possible only in the event that the treated wastewater entails very high disposal costs. The solutions produced, both acidic and basic, cannot be produced at a desired concentration since the pH of the two solutions must be kept above 1 in the case of the acidic solution and below 13 in the case of the basic solution.

The use of a spontaneous reaction does not make it possible to control the production rate of H^+ and OH^- ions, since this process is directly proportional to the electrical conductivity of the

treated brine. This phenomenon involves a decrease in the production rate of ions as the salinity of the treated brine decreases, thus making this type of technology economically uncompetitive in the case of brines containing less than 35,000 ppm of chlorides.

Finally, the need to supply the cell with hydrogen gas requires that a SMIT type plant be flanked by a plant for the *in situ* production of hydrogen. These plants can be built using water electrolysis technology or reforming of fossil and non-fossil hydrocarbons. This does not determine a limit in the case of applications in zones close to urbanised areas; however, it does represent a technical limit in the case in which the area involved for the realisation of the plants is not equipped for the management of constant supplies of hydrocarbons.

- 10 The desalination system described in WO 2016/120717 A1 works with diffusion electrodes and oxidises at H₂ the anode to form H⁺ and reduces O₂ at the cathode to form OH⁻ to turn brackish water into drinking water.

DISCLOSURE OF THE INVENTION

- 15 The object of the invention is to overcome the aforementioned drawbacks and to propose a device and a process for the recovery and valorisation of chlorides in dilute solutions, in particular brines with chloride concentrations that can be lower than 35,000 ppm and higher than 5,000 ppm.

- 20 The invention also has the object of proposing a device and a process for the recovery treatment of solutions containing chlorides with low management and investment costs and which can valorise the treated compounds chemically.

Further purposes or advantages of the invention will be apparent from the following description. In a first aspect of the invention, the object is achieved by means of a desalination device comprising at least one electrochemical cell comprising:

- 25 (a) an anode suitable for permitting the electrochemical reaction of oxidation of the OH⁻ ion and consequent production of gaseous oxygen and release of H⁺ protons in a solution wherein said anode is contained in an anode chamber adapted to contain or else containing an acid solution as an anolyte;
- (b) a cathode connected through an electrical connection to said anode and adapted to make possible the electrochemical reaction of reduction of the proton H⁺ and consequent production of hydrogen gas and release in solution of OH⁻ ions wherein said cathode is contained in a
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cathode chamber adapted to contain or else containing a basic solution as a catholyte, in particular an aqueous solution of NaOH;

(c) a system for feeding said anode chamber with the anolyte;

(d) a system for feeding said cathode chamber with catholyte;

5 (e) an OH^- ion impermeable and cation permeable cation exchange membrane, in particular permeable for Na^+ ;

(f) an H^+ ion impermeable and anion permeable anion exchange membrane, in particular permeable for Cl^- ;

10 wherein said anode chamber and said cathode chamber are separated by said cation exchange membrane and by said anion exchange membrane which, in turn, are separated by a third chamber adapted to contain or else containing an aqueous solution of chloride salts, particularly NaCl,

where

15 (α) said cation exchange membrane is simultaneously a wall, or part thereof, of said cathode chamber and of said third chamber, so that a salt cation passage, in particular for Na^+ is possible from the third chamber to the cathode chamber;

(β) said anion exchange membrane is simultaneously a wall or a part thereof of said anode chamber and of said third chamber, such that from the third chamber to the anode chamber a passage of salt anions, in particular Cl^- , is possible.

20 In preferred variants, said electrodes are made of stainless steel or graphite. Advantageously, said membranes are made of reinforced polymeric material, in particular polyketones (PK). Materials for electrodes and membranes can be different; they must simply be suitable for the reactions and permeabilities specified above. The person skilled in the art can easily identify suitable electrodes and membranes.

25 In a preferred embodiment of the invention, the desalination device (i.e. the relative control unit adapted to manage its various components included in the device) is configured to perform the following algorithm:

(i) feeding the anode chamber (14; 114) via the system for feeding said anode chamber with anolyte, preferably water;

30 (ii) feeding the cathode chamber (16; 116) via the system for feeding said cathode chamber with the catholyte, preferably water, or the base produced therein at reduced concentration;

(iii) feeding the third chamber (12; 112) with a concentrated chloride salt solution;
(iv) oxidation of OH^- on the anode (18) with the formation of oxygen O_2 and H^+ protons;
(v) reduction of H^+ on the cathode (20) with the formation of H_2 hydrogen and OH^- hydroxide ions.

5 The anion membrane retains within the anode acidification chamber the protons H^+ , making possible, however, the transit of negative ions such as the chloride ion Cl^- from the central chamber. The central chamber is preferably made in such a way as to allow the transit of the treated saline solution and to maximise the residence time of the same within the chamber while minimising the active surface area used. The active surface is intended as the two walls of the
10 chamber delimited respectively by the anion membrane and the cation membrane.

Conversely, the cation membrane retains the OH^- ions within the basic production cathode chamber, while nevertheless allowing the transit of positive ions such as the sodium ion Na^+ from the central chamber.

In order to ensure continuity of electrochemical reactions and migration of salt ions from the
15 solution to be treated in the anode chamber and in the cathode chamber, in said desalination device according to the invention each of said chambers is preferably provided with an inlet and an outlet, specifically:

- (a) the anode chamber is provided with an inlet for the fresh anolyte and an outlet for the more acidic anolyte enriched with saline anions, in particular Cl^- or derivatives thereof, and oxygen;
- 20 (b) the cathode chamber is provided with an inlet for the fresh catholyte and an outlet for the more basic catholyte enriched with salt cations, in particular Na^+ and hydrogen; and
- (c) the third chamber is provided with an inlet for the initial salt solution and an outlet for the reduced concentration salt solution.

In a particularly advantageous embodiment of the invention, the desalination device further
25 comprises:

(g) a gas-liquid separation device, in particular a gas-liquid scrubber, adapted to recover the hydrogen produced which is connected to the outlet of the cathode chamber and which is preferably connected to a fuel cell.

A gas-liquid separation device makes it possible to recover the share of hydrogen produced
30 from the base production chamber, thus in the cathode chamber, in order to reuse it *in situ*, for example, for the production of electricity by means of a fuel cell. The electric energy produced

can be used immediately to power the electrochemical cell of the desalination device, resulting in a reduction of the power necessary to feed it by up to 15% from a direct source. Other gas-liquid separation systems are also known in the state of the art.

A particularly preferred embodiment of the invention provides that the desalination device further comprises:

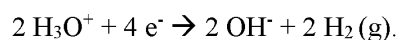
(h) a carbonation reactor with the cathode chamber comprising an inlet and an outlet which are connected to a circuit into which said carbonation reactor is inserted.

The carbonation reactor advantageously diffuses a gas containing carbon dioxide within the basic solution produced and circulates in a circuit between the cathode chamber and the carbonation reactor. This procedure allows the pH of the basic solution to remain buffered, advantageously between 8.5 and 9.5, ensuring optimal operation and durability of the membranes. By maintaining the buffered pH it is also possible to increase the concentration of reagent taken from the treatment solution, until a solution of saturated carbonates is obtained which can then be taken continuously from the solution by way of precipitation. When fed with atmospheric air, the reactor helps to reduce its CO₂ charge. The carbonation reactor therefore has the dual purpose of maintaining the pH of the basic solution in the cathode chamber buffered and of allowing the sequestration of atmospheric carbon dioxide through the production of solid carbonates and bicarbonates that can be extracted from the solution by crystallisation through supersaturation.

Advantageously, the fresh anolyte is simply water or a solution with a pH close to 7, while the fresh catholyte advantageously is a diluted basic solution, preferably coming from the NaOH recirculation produced in the cathode chamber and buffered during passage through a decarbonation reactor. The fresh salt solution is advantageously a concentrated NaCl solution. These fresh solutions then undergo chemical reactions, as in the anode chamber :



and in the cathode chamber:



An acid is then formed in the anode chamber and a base in the cathode chamber.

Another aspect of the invention relates to an electrochemical cell suitable for use in the desalination device according to the invention. It preferably comprises:

- (i) a first plate supporting in a first window applied to said first plate said anode chamber of meandering path having a thickness with respect to the plane of the meandering path extension preferably not exceeding 6 mm and having an inlet and an outlet for the anolyte at its ends;
- 5 (ii) a second plate supporting in a second window applied in said second plate said central chamber of meandering path with a thickness with respect to the plane of the extension of the meandering path which preferably does not exceed 6 mm and with an inlet and an outlet for the saline solution at its ends; and
- 10 (iii) a third plate supporting in a third window applied to said third plate said cathode chamber of meandering path with a thickness with respect to the plane of the extension of the meandering path that preferably does not exceed 6 mm and with an inlet and an outlet for the catholyte at its ends,
- (iv) said anion exchange membrane interposed between said first and said second plates;
- (v) said cation exchange membrane interposed between said second and said third plate;
- 15 (vi) a plate anode disposed next to said first plate on the side opposite the position of the anion exchange membrane; and
- (vii) a plate cathode disposed next to said third plate on the side opposite the position of the anion exchange membrane;
- wherein plates, membranes and electrodes are superimposed in the following order: anode,
- 20 anode chamber, anion exchange membrane, central chamber, cation exchange membrane, cathode,
- wherein each plate is optionally provided with a plurality of first holes arranged such that with the overlapping of the plates they are aligned so that they can be connected with relevant fixing means;
- 25 wherein each plate is provided with a plurality of second holes divided into three pairs of holes for conveying the flows of anolyte, catholyte and saline solution into separate channels, one hole of each pair provided for the entry of the respective flow into the system and the other hole for the exit from the system where the corresponding holes are arranged in such a way that with the overlapping of the plates they are aligned so that they can be connected to form separate
- 30 channels for the relative flows,

wherein each plate is preferably provided with a plurality of third holes for the collection of gases formed respectively in the anode and cathode chamber and arranged such that with the overlapping of the plates they are aligned so that they can be connected to form separate channels for the relative gas flows of the respective chambers,

5 wherein each flow passes through the entire system along the channel formed by the relative overlapping holes, but a communication with the inlet of the chamber is realised only in the plate which carries the chamber to which the relative channel flow is dedicated, in such a way as to allow the flow to pass through the chamber and enter through the outlet of the chamber into the corresponding outlet channel formed by the respective series of holes.

10 The realisation of the electrochemical cells in the form of three plates with meandering or serpentine chambers makes it possible to have a maximum surface, hence a maximum contact surface between each chamber and the relative ion exchange membrane, with a minimum of thickness or volume of the chambers themselves, a practically laminar extension of the chambers obtaining a uniform and homogeneous distribution of the corresponding solutions
15 contained therein and guaranteeing regular degassing. The meandering shape makes it possible to create a long path of solutions inside each chamber in a very small space.

In combination with an optimized contact surface, this space saving makes possible the reduction of the area of the membranes needed to separate the individual cells, a highly significant fact in view of the high costs for membranes.

20 In a preferred embodiment, the desalination device comprises as at least one electrochemical cell the electrochemical cell just described. However, it is understood that the electrochemical cell can be equipped with other types of electrodes and supplied with other types of solutions to carry out other electrochemical reactions and is not, therefore, strictly related to the desalination described.

25 Plate electrochemical cells can be supplemented with additional plates creating stacks of cells that can be applied in desalination devices according to the invention, but also in other contexts that require different solutions and types of electrodes, while still working with the three-chamber principle of the smallest unit of the stack.

In a variant of the invention, a plurality of three-chamber electrochemical cells are grouped in
30 a stack of cells according to:

variant (A) wherein the individual elements follow each other according to the following scheme:

$[+AZC-][+AZC-]_n$ with $n = 1, 2, \dots$;

OR according to:

- 5 the variant (B) in which the individual elements follow each other according to the following scheme:

$+AZC-CZA+AZC-CZA+\dots+AZC-$ with variable number of groups AZC and CZA wherein units with three adjacent chambers have the corresponding electrode in common,

- 10 wherein for both variants (A) and (B), A is a plate with anode chamber, Z is a plate with central chamber, C is a plate with cathode chamber, the sign "+" an anode and the sign "-" a cathode, between adjacent chambers A and Z an anion exchange membrane is placed and between adjacent chambers Z and C a cation exchange membrane; and

wherein for both variants (A) and (B) the chambers of the same kind are connected through the relative inlets and outlets of the chambers and corresponding holes in the plates.

- 15 The principle of plate electrochemical cells is illustrated later with reference to Figure 2, wherein the configurations (number and arrangement) of the holes for connecting the inputs and outputs of the individual chambers may vary.

In an embodiment according to the invention for exploiting the technology on a large scale, the desalination device comprises not only at least one electrochemical cell but a plurality thereof,

- 20 for example 50, in a multipolar configuration in a stack containing the alternating polarity cells.

Advantageously, the active surface of the membranes and electrodes is approximately 1600 cm². The cell can be fed through a direct current generator at a voltage comprised between 0 and 9 Volts. In a preferred version of the invention, the cell is supplied with a constant voltage between 2.5 and 3.5 V and a current between 4.5 and 6.5 mA/cm² for each cell, for example
25 through a photovoltaic system and a voltage stabiliser or through a direct current generator supplied by the mains voltage. Alternatively or in a supplementary form, it may be powered by the energy produced by the above-mentioned fuel cell. The amperage depends on the conductivity of the brine treated. For the same voltage, a brine less rich in salts produces a lower current and the above range can thus be extended to 0.5 - 6.5 mA/cm².

- 30 The flow of the saline solution to be treated is preferably kept stable within the central chamber of each cell, this in exemplary form through the use of peristaltic metering pumps that can be

controlled using a Programmable Logic Controller (PLC) by monitoring the conductivity of the solution analysed at the point where it leaves the cell. Also inside the anode and cathode chamber, advantageously, a flow of anolyte/catholyte, such as a water flow, is kept stable, for example through the use of peristaltic metering pumps managed via PLC by monitoring the pH
5 of the same solutions analysed at the point where they exit the cell.

In this regard, the desalination device according to the invention comprises adjustable speed pumping systems for feeding said chambers.

By controlling the pumping speed of the solution to be treated and the voltage applied to the cell, it is possible to carry out a continuous dynamic control of its desalination capacity,
10 ensuring that a solution containing a level of chlorides consistent with the required values is available at the exit from the central chamber.

In an alternative embodiment of the invention, the desalination device further comprises a reverse osmosis system for dividing the solution exiting the central chamber into a fresh water fraction and a fraction of a concentrated saline solution which feeds in a circuit the central
15 chamber of the electrochemical cell and wherein, preferably, the reverse osmosis plant is fed not just from the saline solution exiting the central chamber but also by brackish water. The brackish water has a salinity equal to or at least similar to that of the solution leaving the central chamber to withdraw an additional portion of potable water.

In the treatment of marine water, for example, this configuration makes possible the recovery
20 of 100% of the water withdrawn as drinking water with zero discharge. This configuration is not the only one applicable. For example, in the case of industrial water treatment the electrochemical cells are used to lower the chloride levels below the one allowed for spillage into surface water.

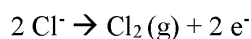
A further aspect of the invention relates to a process for desalination comprising the following
25 steps:

- (a) providing a desalination device according to the invention;
- (b1) feeding of the anode chamber with an anolyte, preferably water;
- (b2) feeding the cathode chamber with a catholyte, preferably water or the base produced therein at reduced concentration;
- 30 (b3) feeding of the third chamber with a concentrated chloride salt solution;
- (c1) oxidation of OH^- on the anode with the formation of oxygen O_2 and H^+ ;

(c2) reduction of H^+ on the cathode with formation of hydrogen H_2 and OH^- hydroxide ions;
 (d1) in response to the increase in the concentration of H^+ ions in the anode chamber, passage of salt anions, particularly chlorides, from the third chamber into the anode chamber ;
 (d2) in response to the increased concentration of OH^- ions in the cathode chamber, passage of
 5 salt cations, particularly Na^+ , from the third chamber into the cathode chamber.

The process uses an electrochemical cell or a stack of electrochemical cells according to the invention to lower the salt content of a concentrated saline solution and simultaneously to produce oxygen and hydrogen. As regards hydrogen, which cannot be contaminated by other gases, it can be used for energy production. Conversely, the oxygen in the anode chamber can
 10 be contaminated with chlorine by the anodic oxidation of Cl^- . The base produced in the cathode chamber can be used to capture CO_2 from the atmosphere and produce carbonates and bicarbonates. The carbonation simultaneously transforms the concentrated base into a dilute base solution to be reintroduced into the cathode chamber, thus avoiding the need to introduce fresh catholyte.

15 In a preferred embodiment of the invention said at least one electrochemical cell is configured to work at a constant voltage comprised between 2.5 and 3.5 V and a current comprised between 4.5 and 6.5 mA/cm² (in the case of brines with a low concentration of salts a range between 0.5 and 6.5 mA/cm² is conceivable) for each cell causing the oxidation of the chloride inside the anode chamber forming gaseous chlorine which in turn spontaneously undergoes a dismutation
 20 reaction with consequent production of hydrochloric acid (HCl) and hypochlorous acid (HClO) in equal proportion. The following reactions are then added to the anode chamber:



A supply voltage of at least 3 Volts makes it possible to obtain the oxidation reaction of the
 25 chloride inside the acid chamber with the consequent generation of gaseous chlorine. The gaseous chlorine diffused in aqueous solution spontaneously undergoes a dismutation or disproportionation reaction with consequent production of hydrochloric acid and hypochlorous acid in equal proportion. Control of the pumping rate of the feed water of the acid chamber enables control of the ratio between hydrochloric acid and hypochlorous acid at the exit of the
 30 chamber making it possible to obtain a solution containing active chlorine in the desired amount, for example to be used for the production of disinfectants. In order to ensure the further

increase of concentrations of active chlorine obtainable, advantageously, it is possible to buffer the acid solution produced by the use of an appropriate base. This procedure makes it possible to increase further the residence time of the solution inside the acidification chamber.

In an embodiment of the process according to the invention,

- 5 (i) the anode chamber is fed at a controlled flow rate (with an acidic solution) and acidic solutions containing oxygen and preferably HCl and HClO are extracted from it;
- (ii) the cathode chamber is fed at a controlled flow rate with a basic solution (NaOH) and concentrated basic solutions and hydrogen are extracted from it; and
- (iii) the central chamber is fed at a controlled rate by concentrated saline solutions and diluted
10 salt solutions are extracted. The control of speed makes it possible to monitor the concentrations of the components of the aqueous solutions contained in the relative chambers.

In an embodiment of the method according to the invention, the feeding of the cathode chamber and the extraction of its contents take place in a circuit from which the hydrogen is diverted, preferably by feeding a fuel cell, and comprising a carbonation reactor from which carbonates
15 and/or bicarbonates are diverted with the effect of buffering the pH of the basic solution returning to the cathode chamber, preferably at values between 8.5 and 9.5. The energy produced in the fuel cell may be used to power the desalination device.

Further aspects of the invention relate to the use of the device and desalination process, in particular for reducing the concentration of chlorides in brackish water, industrial, mining or
20 water treatment waste, in marine water according to the invention, and further for one or more purposes selected from the group consisting of:

- production of carbonates and/or bicarbonates;
- elimination of CO₂ from the atmosphere;
- production of hydrogen to produce energy;
- 25 - production of HCl and HClO for the manufacture of disinfectants.

The features and advantages disclosed for one aspect of the invention may be transferred *mutatis mutandis* to other aspects of the invention.

The industrial applicability is obvious from the moment when it becomes possible to reduce the concentration of chlorides from brackish water, marine water, industrial waste etc., even for
30 chloride concentrations below 35,000 ppm in an economical way while being able at the same

time to use the by-products such as hydrogen, HCl/HClO and NaOH to produce energy and carbonates/bicarbonates, and to reduce the carbon footprint in the environment.

Said purposes and advantages will be further highlighted during the description of preferred embodiment examples of the invention provided by way of non-limiting example only.

- 5 Variant and further features of the invention are the subject matter of the dependent claims. The description of preferred embodiments of the device, process, electrochemical cell and uses relating to desalination and recovery and valorisation of chlorides contained in dilute solutions according to the invention is given by way of non-limiting example only with reference to the accompanying drawings. In particular, unless specified otherwise, the number, shape,
10 dimensions and materials of the system and of the individual components may vary, and equivalent elements may be applied without deviating from the inventive concept.

DESCRIPTION OF PREFERRED EMBODIMENT EXAMPLES

- Fig. 1 illustrates a schematic diagram of a desalination device according to the
15 invention.
- Fig. 2 illustrates individual elements of an electrochemical cell usable in the device according to Figure 1.

- Figure 1 illustrates a schematic diagram a desalination device according to the invention. The
20 plant contains as a central element an electrochemical cell **10** comprising a central chamber **12**, an anode chamber **14** and a cathode chamber **16**. The anode chamber **14** contains an electrode, i.e. the anode **18**. The corresponding electrode, the cathode **20**, is located in the cathode chamber **16**. The electrodes **18**, **20** are connected by a circuit **22** powered by a photovoltaic cell **24**. The electrons move from the negative electrode **18** to the positive electrode **20**. The anode chamber
25 **14** is separated by an anion exchange membrane **26** from the central chamber **12**, while the cathode chamber **16** is separated from the central chamber **12** by a cation exchange membrane **28**. Each of the three chambers **12**, **14** and **16** is provided with an inlet and an outlet, the central chamber **12** of the inlet **30** and the outlet **32**, the anode chamber **14** of the inlet **34** and the outlet **36** and the cathode chamber **16** of the inlet **38** and the outlet **40**. Water (arrow **a**) is pumped by
30 a pump **42** through the inlet **34** into the anode chamber **14**. The central chamber **12** is fed through the inlet **30** with a concentrated NaCl solution (arrow **b**), for example 70 g NaCl/l. With

a pump **44** a diluted basic aqueous solution, here NaOH with a concentration of 0.1 M, is pumped (arrow **c**) through the inlet **38** into the cathode chamber **16**. At cathode **20**, H_3O^+ cations are reduced to form hydrogen H_2 according to reaction $2 \text{H}_3\text{O}^+ + 4 \text{e}^- \rightarrow 2 \text{OH}^- + 2 \text{H}_2 (\text{g})$. The basicity of the solution in the cathode chamber **16** is then increased. The NaOH solution, which leaves (arrow **d**) the cathode chamber **16** via the outlet **40**, is thus more concentrated (here 1M). At the same time, the hydrogen formed exits (arrow **e**) via the outlet **46** separating it from the aqueous NaOH flow which is managed in a circuit **48** connecting the inlet **38** and the outlet **40** of the cathode chamber **16**. A carbonation reactor **50** is installed in circuit **48**, the concentrated NaOH solution leaving the cathode chamber **16** enters the reactor **50** which is fed (arrow **f**) through a line **52** with the help of a pump **54** with a gas (i.e. air) containing carbon dioxide CO_2 that bubbles in the reactor **50**. From the reaction between NaOH and CO_2 in water respectively, sodium carbonate and/or bicarbonate are formed and can be discharged via an outlet **56** from the reactor **50**. The reactor **50** has a separator wall **58** for separating the formation of the solid carbonate/bicarbonate salts from the circuit **48**.

In the anode chamber **14** OH^- ions are oxidised to form oxygen O_2 according to reaction $4 \text{OH}^- \rightarrow 4 \text{e}^- + 2 \text{H}_2\text{O} + \text{O}_2 (\text{g})$. The aqueous solution results in a lower pH as the H_3O^+ ion concentration increases.

The concentrated NaCl solution introduced into the central chamber **12** is diluted as reactions occur at the electrodes **18**, **20** because the Na^+ cations cross (arrows **g**) the cation exchange membrane **28** reacting to the increase in the concentration of OH^- , while Cl^- anions cross (arrows **h**) the anion exchange membrane **26** reacting to the increase in the concentration of H_3O^+ . At the outlet **32** of the central chamber **12**, a dilute NaCl solution of about 35 g/l exits. The Cl^- ions entering the anode chamber **14** are oxidised at anode **18** forming Cl_2 chlorine. Chlorine reacts with water to form HCl and HClO, here about 1 molar, and exits (arrow **i**) from outlet **36**.

The diluted saline solution exiting the central chamber **12** is admixed with brine of similar concentration (arrow **j**) and pumped with a pump **60** into a reverse osmosis plant **62** from which a fresh water fraction (arrow **k**) and a concentrated NaCl solution fraction (70 g/L) are obtained and pumped with a pump **64** into the central chamber **12** forming the NaCl flow (arrow **b**).

Figure 2 illustrates individual elements of an electrochemical cell usable in the plant according to Figure 1. From left to right can be observed a first plate **166** with an anode chamber **114**, a

second plate **168** with a central chamber **112**, and a third plate **170** with a cathode chamber **116**. Each chamber follows a meandering or serpentine path.

In a three-chamber base cell which stands alone or in an isolated form according to the above variants (A) or (B) in a succession of a plurality of three-chamber units, an anion exchange
5 membrane **127** is at all times interposed between the anode chamber **114** and central chamber **112** and between the central chamber **112** and cathode chamber **116** a cation exchange membrane **128**. In the left-hand plate **166** the reference number **127** indicates the anion exchange membrane placed above the anode chamber **114**; in the plate **170** on the right the reference number **128** indicates the cation exchange membrane placed above the cathode
10 chamber **116**, while in the plate **168** in the centre the reference number **126** indicates the set of the anion and cation exchange membranes (also represented individually in the drawings on the side) that include the central chamber **112** as in a sandwich.

By placing the second plate **168** above the first plate **166** and the third plate **170** above the second plate **168** with the anion exchange membrane **127** between the first **166** and second **168**
15 plate, and the cation exchange membrane **128** between the second **168** and third **170** plate, a base electrochemical cell is obtained. To connect one plate to the other, a plurality of holes **172** is provided along the edge of each plate that serve to pass relative fixing means. By repeating the construction of electrochemical cells several times and placing one cell on top of the other, according to the sequences illustrated above, a stack of electrochemical cells is obtained that
20 can be connected to work together. In this regard, each plate is provided with two three-hole assemblies, one for the outlets of the relative chambers **114**, **112** and **116**, and one for the inlets of the relative chambers. The anode chamber **114** of the first plate **166** connects at its ends to the outlet hole **136** and to the inlet hole **134**; the central chamber **112** connects at its ends to the outlet hole **132** and to the inlet hole **130**; and the cathode chamber **116** connects at its ends to
25 the outlet hole **140** and to the inlet hole **138**. Thus, in a stack of electrochemical cells, the outlets and inlets of the individual chambers are connected together, creating a unique flow of anodic solution, saline solution and cathodic solution between the chambers of the same category (anodic, central or cathodic).

Furthermore, there are holes **146**, **147** on each plate that can be aligned in the stack that serve
30 for the degassing of the anode and cathode chambers where gases are produced, in particular in

the case of the connected cathode chambers **116**, the relative holes **146** serve to create channels to convey the hydrogen formed.

The plates are made in the form of chips and have, by way of example, a thickness of approximately 6 mm.

CLAIMS

- 1) Desalination device comprising at least one electrochemical cell (10) comprising:
- (a) an anode (18) suitable for allowing the electrochemical reaction of oxidation of the OH^- ion and consequent production of oxygen gas and release in solution of protons H^+ wherein said anode (18) is contained in an anode chamber (14; 114) suitable for containing or containing as an anolyte an acidic solution;
 - (b) a cathode (20) connected through an electrical connection (22) to said anode (18) and suitable to allow the electrochemical reaction of reduction of proton H^+ and consequent production of hydrogen gas and release in solution of OH^- ions wherein said cathode (20) is contained in a cathode chamber (16; 116) suitable to contain or containing as a catholyte a basic solution, in particular an aqueous solution of NaOH ;
 - (c) a system for feeding said anode chamber with said acidic solution;
 - (d) a system for feeding said cathode chamber with said basic solution;
 - (e) a cation exchange membrane (28; 128) impermeable for OH^- ions and permeable for cations, in particular Na^+ ;
 - (f) an anion exchange membrane (26; 126) impermeable for H^+ ions and permeable for anions, particularly Cl^- ;
- wherein said anodic chamber (14; 114) and said cathodic chamber (16; 116) are separated by said cation exchange membrane (28; 128) and said anion exchange membrane (26; 126) which in turn are separated by a third chamber (12; 112) suitable for containing or containing an aqueous solution of chloride salt, in particular NaCl ,
- where
- (α) said cation exchange membrane (28; 128) is simultaneously a wall or a portion thereof of said cathode chamber (16; 116) and of said third chamber (12; 112) such that from the third chamber (12; 112) to the cathode chamber (16; 116) a passage of salt cations, in particular Na^+ , is possible;
 - (β) said anion exchange membrane (26; 126) is simultaneously a wall or a portion thereof of said anode chamber (14; 114) and of said third chamber (12; 112) such that from the third chamber (12; 112) to the anode chamber (14; 114) a passage of salt anions, in particular Cl^- , is possible.

2) Desalination device according to claim 1, **characterized in that** said electrodes (18, 20) are made of stainless steel or graphite.

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3) Desalination device according to claim 1 or 2, **characterized in that** it is configured to perform the following algorithm:

(i) feeding the anode chamber (14; 114) with an anolyte, preferably water;

(ii) feeding the cathode chamber (16; 116) with a catholyte, preferably water or the base produced therein at reduced concentration;

(iii) feeding the third chamber (12; 112) with a concentrated chloride salt solution;

(iv) oxidation of OH^- on the anode (18) with the formation of oxygen O_2 and H^+ protons;

(v) reduction of H^+ on the cathode (20) with the formation of H_2 hydrogen and OH^- hydroxide ions.

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4) Desalination device according to anyone of the preceding claims, **characterized in that** each of said chambers (12, 14, 16; 112, 114, 116) is provided with an inlet (30, 34, 38; 130, 134, 138) and an outlet (32, 36, 40; 132, 136, 140), namely:

(a) that the anode chamber (14; 114) is provided with an inlet (34; 134) for fresh anolyte and an outlet (36; 136) for anolyte enriched with salt anions, particularly Cl^- , or their derivatives, and oxygen;

(b) that the cathode chamber (16; 116) is provided with an inlet (38; 138) for the fresh catholyte and an outlet (40; 140) for the catholyte enriched in salt cations, particularly Na^+ , and hydrogen; and

(c) that the third chamber (12; 112) has an inlet (30; 130) for the aqueous starting salt solution and an outlet (32; 132) for the reduced concentration salt solution.

5) Desalination device according to any one of the preceding claims, **characterized in that** it further comprises

(g) a gas-liquid separation device, in particular a gas-liquid scrubber, suitable for recovering the hydrogen produced which is connected to the outlet of the cathode chamber (16; 116) and which preferably is connected to a fuel cell.

- 5 6) Desalination device according to any one of the preceding claims, **characterized in that** it further comprises

(h) a carbonation reactor (50)

and in that the cathode chamber (16) comprises an inlet (38) and an outlet (40) which are connected in a circuit in which said carbonation reactor (50) is inserted.

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- 7) Desalination device according to any one of the preceding claims, **characterized in that** said at least one electrochemical cell comprises

(i) a first plate (166) supporting in a first window applied in said first plate said anode chamber (114) of meandering path having a thickness with respect to the plane of the meandering path extension preferably not exceeding 6 mm and having an inlet and an outlet for the anolyte at its ends;

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(ii) a second plate (168) supporting in a second window applied to said second plate said central chamber (112) of meandering path having a thickness relative to the plane of the meandering path extension that preferably does not exceed 6 mm and having an inlet and outlet for saline solution at its ends; and

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(iii) a third plate (170) supporting in a third window applied in said third plate said cathode chamber (116) of meandering path having a thickness with respect to the plane of the meandering path extension that preferably does not exceed 6 mm and having an inlet and outlet for the catholyte at its ends,

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(iv) said anion exchange membrane (127) interposed between said first (166) and said second (168) plate;

(v) said cation exchange membrane (128) interposed between said second (168) and said third (170) plate;

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(vi) a plate anode disposed alongside said first plate (168) on the opposite side from the position of said anion exchange membrane (127); and

(vii) a plate cathode disposed alongside said third plate (170) on the opposite side with respect to the position of the cation exchange membrane (128);

wherein plates, membranes and electrodes are superimposed in the following order: anode, anode chamber, anion exchange membrane, central chamber, cation exchange membrane, cathode,

wherein each plate is optionally provided with a plurality of first holes (172) arranged so that as the plates are overlapped, they are aligned so that they can be connected with relative fastening means;

wherein each plate is provided with a plurality of second holes divided into three pairs of holes (134, 136; 130, 132; 138, 140) for conveying in separate channels the flows of anolyte, catholyte and saline solution, one hole (134; 130; 138) of each pair provided for inlet of the respective flow into the system and the other hole (136; 132; 140) for exit from the system wherein the corresponding holes are arranged so that with the overlapping of the plates they result aligned to be able to connect them to form separate channels for the respective flows,

wherein each plate is preferably provided with a plurality of third holes (146, 147) for collecting gases formed in the anode and cathode chambers respectively (114, 116) and arranged in such a way that with the overlapping of the plates they result aligned to be able to connect them to form separate channels for the relative gas flows of the respective chambers,

in which each flow traverses along the channel formed by the relative overlapping holes the whole system, but only in the plate carrying the chamber to which the relative channel flow is dedicated a communication with the chamber inlet is realized in such a way as to allow the flow to pass through the chamber and enter through the chamber outlet into the corresponding outlet channel formed by the respective set of holes.

8) Desalination device according to claim 7, **characterized in that** it comprises a plurality of three-chamber electrochemical cells which is grouped into a cell stack according to variant (A) wherein the individual elements follow each other according to the following scheme: [+AZC-][+AZC-]_n with n = 1, 2, ...;

OR according to

variant (B) in which the individual elements follow each other according to the following scheme: +AZC-CZA+AZC-CZA+....+AZC- with varying number of AZC- and CZA-groups in which units with three adjacent chambers have the corresponding electrode in common, wherein for both variants (A) and (B) A is a plate (166) with an anode chamber (114), Z is a plate (168) with a central chamber (112), C is a plate (170) with a cathode chamber (116), the "+" sign an anode and the "-" sign a cathode, an anion exchange membrane (127) is placed between adjacent chambers A and Z, and a cation exchange membrane (128) is placed between adjacent chambers Z and C; and wherein for both variants (A) and (B) the chambers of the same type are connected through the relative inlets and outlets of the chambers and corresponding holes in the plates.

9) Desalination device according to any one of the preceding claims, **characterized in that** it comprises a plurality of electrochemical cells in a multipolar configuration in a stack containing the cells with alternating polarity.

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10) Desalination device according to any one of the preceding claims, **characterized in that** it comprises pumping systems (42, 44, 64) with adjustable speed for feeding said chambers.

11) Desalination device according to any one of the preceding claims, **characterized in that** said electrochemical cell (10) is configured to operate at a voltage between 2.5 and 3.5 V and a current between 0.5 and 6.5 mA/cm², preferably between 4.5 and 6.5 mA/cm².

12) A desalination process comprising the following steps:

- (a) providing a desalination device according to any one of the preceding claims;
- (b1) feeding the anode chamber (14; 114) with an anolyte, preferably water;
- (b2) feeding the cathode chamber (16; 116) with a catholyte, preferably water or the base produced therein at reduced concentration;
- (b3) feeding of the third chamber (12; 112) with a concentrated chloride salt solution;
- (c1) oxidation of OH⁻ on the anode (18) with the formation of oxygen O₂ and protons H⁺;
- (c2) reduction of H⁺ on the cathode (20) with the formation of hydrogen H₂ and hydroxide ions OH⁻;

(d1) in reaction to increased concentration of H^+ ions in the anode chamber (14; 114) passage of salt anions, particularly chlorides, from the third chamber (12; 112) into the anode chamber (14; 114);

(d2) in reaction to the increased concentration of OH^- ions in the cathode chamber (16; 116)
5 passage of salt cations, particularly Na^+ , from the third chamber (12; 112) into the cathode chamber (16; 116).

13) Process according to claim 12 **characterized in that** said at least one electrochemical cell (10) is supplied with a voltage between 2.5 and 3.5 V and a current between 0.5 and 6.5
10 mA/cm^2 , preferably between 4.5 and 6.5 mA/cm^2 causing the oxidation of chloride within the anode chamber (14; 114) forming chlorine gas which in turn spontaneously undergoes a dismutation reaction resulting in the production of hydrochloric acid (HCl) and hypochlorous acid (HClO) in equal proportions.

14) Process according to claim 12 or 13, **characterized in that**

(i) the anode chamber (14; 114) is fed with controlled flow, in particular with an acid solution or water, and that acid solutions containing oxygen and preferably HCl and HClO are extracted therefrom;

(ii) the cathode chamber (16; 116) is fed with controlled flow with a basic solution, particularly
20 NaOH, or with water and that concentrated basic solutions and hydrogen are extracted therefrom;

(iii) the central chamber (12; 112) is fed at a controlled rate by concentrated salt solutions and that dilute salt solutions are extracted therefrom allowing control of the concentrations of the components of the aqueous solutions contained in the relevant chambers (12, 14, 16; 112, 114,
25 116).

15) Process according to any one of claims 12 to 14, **characterized in that** the feeding of the cathode chamber (16) and the extraction of its contents take place in a circuit from which hydrogen (46) is diverted, preferably feeding a fuel cell, and comprising a carbonation reactor
30 (50) from which carbonates and bicarbonates (56) are diverted with the effect of buffering the pH of the basic solution which returns to the cathode chamber (16), preferably at values between

8.5 and 9.5, in which the energy produced in the fuel cell can be used to power the desalination device.

- 16) Use of the desalination device and process according to any one of the preceding claims for
- 5 reducing the concentration of chlorides in brackish water, industrial waste, mining, water treatment, or marine waters for one or more purposes selected from the group consisting of:
- production of carbonates and/or bicarbonates;
 - removal of CO₂ from the atmosphere;
 - production of hydrogen for the purpose of producing energy;
 - 10 - production of HCl and HClO for the production of disinfectants.