

Description

Title of the invention: DEVICE AND METHOD FOR CAPTURING AND STORING ATMOSPHERIC CARBON DIOXIDE

The invention relates to a device and a method for capturing and storing atmospheric carbon dioxide.

Human activity has increased the concentration of carbon dioxide (CO₂) in the atmosphere. Causes of this rise in particular include the use of fossil fuels such as oil, gas or coal, as well as deforestation and cement production activities.

The accumulation of CO₂ resulting from human activities contributes to about two thirds of the increase in the greenhouse effect in the atmosphere. This is why the effect of other greenhouse gases is conventionally measured in CO₂ equivalent. It is therefore assumed that increasing the CO₂ concentration is equivalent to increasing greenhouse gas concentrations in the atmosphere in general. This increase is intensifying global warming.

In 2021, a carbon dioxide concentration of 421 ppm was measured in the atmosphere. This concentration is drastic, especially considering that in the mid-18th century it was only around 280 ppm. Thus, the current CO₂ concentration is causing concern for many scientists, who highlight the negative impacts on the climate, as well as on the environment.

Recently, new technologies have been explored to capture CO₂ from the atmosphere and store it, in order to mitigate the negative impacts on our planet. Among other things, the introduction of alkalinity into the oceans is a promising method for capturing and storing CO₂.

European patent document EP2024062 discloses a method for capturing atmospheric carbon dioxide using alkaline solutions of NaOH.

Other methods are considered such as mining trona, also known as tronite, or sodium sesquicarbonate dihydrate [Na₃(CO₃)(HCO₃)•2(H₂O)].

Nonetheless, prior art techniques are not satisfactory, in particular since the CO₂ balance is not effective when considering an application for mitigating global

warming on a large scale. Moreover, the provision of alkaline solutions is typically difficult, raw materials for mining methods are limited and these methods generate pollutants (particularly due to the need for transportation).

The present invention improves the situation.

The invention therefore relates to a method for capturing atmospheric carbon dioxide [CO₂]. The method of the invention comprises the following steps:

- i. Obtaining a saline stream (1) and calcium carbonate [CaCO₃] (7);
- ii. Producing an alkaline stream (5) comprising sodium hydroxide [NaOH]; and
- iii. Producing an acidic stream (6) comprising hydrochloric acid [HCl];

In this method, at least one of said steps ii. of producing the alkaline stream (5) and iii. of producing the acidic stream (6) comprises a step of electrochemically treating at least part of said saline stream (1).

The method of the invention further comprises the following steps:

- iv. Neutralising the hydrochloric acid [HCl] obtained in step iii. of producing an acidic stream (6) by bringing the calcium carbonate [CaCO₃] (7) from the obtaining step i. into contact, in an acid reactor (AR), with said hydrochloric acid [HCl], so as to obtain a liquid stream (8) of calcium chloride [CaCl₂] and a gaseous stream (9) of carbon dioxide [CO₂];
- v. Producing a stream (10) of sodium carbonate [Na₂CO₃] by bringing at least part of the carbon dioxide [CO₂] obtained in the neutralisation step iv. into contact, in a base reactor (BR), with the sodium hydroxide [NaOH] from the alkaline stream production step ii.; and
- vi. Discharging the stream (10) of sodium carbonate [Na₂CO₃] produced in the previous step v. into salt water chosen from either seawater or ocean water, so as to increase its alkalinity and thus cause atmospheric carbon dioxide [CO₂] to be captured.

In one embodiment, the saline stream of step i. is obtained by drawing in water chosen from either seawater or ocean water.

In a preferred embodiment, the electrochemical treatment is selected from the group consisting of electrodialysis and chlor-alkali electrolysis.

In another preferred embodiment, step **iv.** of neutralising the hydrochloric acid [HCl] further comprises collecting the liquid stream (8) of calcium chloride [CaCl₂].

In another preferred embodiment, the method further comprises, upstream of said steps **ii.** of producing an alkaline stream (5) and **iii.** of producing an acidic stream (6), the following steps:

i.1. Reverse osmosis (RO) to desalinate said saline stream (1) and thus obtain a stream of desalinated water (1') on the one hand, and a stream of water concentrated in salts (2) on the other hand; and

i.2. Purification (F), preferably chosen from filtration and precipitation, receiving at least part of said stream of water concentrated in salts (2) derived from reverse osmosis (RO), wherein Mg²⁺ and Ca²⁺ ions are removed from the stream of water concentrated in salts (2), thus obtaining a purified water stream essentially devoid of Mg²⁺ and Ca²⁺ ions (2').

In another preferred embodiment, the method further comprises, upstream of said steps **ii.** of producing an alkaline stream (5) and **iii.** of producing an acidic stream (6), the following steps:

i.3. Obtaining a stream of purified water essentially devoid of Mg²⁺ and Ca²⁺ ions (2'), and

i.4. An electrodialysis, wherein said purified water stream essentially devoid of Mg²⁺ and Ca²⁺ ions (2') is subjected to at least one electrical field so as to produce said alkaline stream (5) and said acidic stream (6) of steps **ii.** of producing an alkaline stream (5) and **iii.** of producing an acidic stream (6). In this embodiment, the method may further comprise, upstream of the electrodialysis step **i.4.**:

i.5. Obtaining a stream of desalinated water (1', 11), preferably a stream of filtered, desalinated water (1''), also subjected to said electrical field during electrodialysis so as to contribute to the production of said alkaline stream (5) and said acidic stream (6) of steps **ii.** of producing an alkaline stream (5) and **iii.** of producing an acidic stream (6).

Alternatively, the method of the invention can further comprise, upstream of said steps **ii.** of producing an alkaline stream (5) and **iii.** of producing an acidic stream:

i.6. Purification (F), preferably selected from filtration and precipitation, receiving said saline stream (1), wherein Mg^{2+} and Ca^{2+} ions are removed from said saline stream (1), thus obtaining a stream of purified water essentially devoid of Mg^{2+} and Ca^{2+} ions (2'); and

i.7. An electrodialysis, wherein said purified water stream essentially devoid of Mg^{2+} and Ca^{2+} ions (2'), and preferably a desalinated water stream (11), is/are subjected to at least one electrical field so as to produce said alkaline stream (5) and said acidic stream (6) of steps **ii.** of producing an alkaline stream (5) and **iii.** of producing an acidic stream (6).

In another alternative embodiment of the method of the invention, the method can further comprise, upstream of said steps **ii.** of producing an alkaline stream (5) and **iii.** of producing an acidic stream:

i.8. Reverse osmosis (RO) to desalinate said saline stream (1) and thus obtain a stream of desalinated water (1') on the one hand, and a stream of water concentrated in salts (2) on the other hand; and

i.9. An electrodialysis, wherein said desalinated water stream (1') and said stream of water concentrated in salts (2) are subjected to at least one electrical field so as to produce said alkaline stream (5) and said acidic stream (6) of steps **ii.** of producing an alkaline stream (5) and **iii.** of producing an acidic stream (6).

In some embodiments, the electrodialysis further produces a partially desalinated stream (4) which is subjected to a second electrodialysis so as to contribute to the production of said alkaline stream (5) and of said acidic stream (6) of steps **ii.** of producing an alkaline stream (5) and **iii.** of producing an acidic stream (6).

In another alternative embodiment, the step **ii.** of producing an alkaline stream (5) of the method of the invention comprises:

- a chlor-alkali (C-A) electrolysis so as to produce the alkaline stream (5) comprising sodium hydroxide [NaOH], a gaseous stream (13) of dihydrogen [H_2], and a gaseous stream (14) of chlorine [Cl_2];

and wherein the step **iii.** of producing an acidic stream (6) comprises

- injecting, into a H_2/Cl_2 fuel cell (FC), said gaseous stream (13) of dihydrogen [H_2], and said gaseous stream (14) of chlorine [Cl_2] so as to obtain a

concentrated acid stream (15) comprising hydrochloric acid [HCl], and electricity and/or heat; and

- mixing, in a dilution tank (D), said concentrated acid stream (15) with a liquid, preferably a saline liquid (16), so as to obtain the acidic stream (6) comprising hydrochloric acid [HCl].

The present invention further relates to a device for capturing atmospheric carbon dioxide [CO₂], which device comprises a means for drawing a saline stream (1), preferably sea or ocean water, and a means for providing calcium carbonate [CaCO₃] (7). The device further comprises

- an electrochemical treatment unit (ED, U-CA) capable of producing, from at least a part of said saline stream (1),:
 - o an alkaline stream (5) comprising sodium hydroxide [NaOH]; and
 - o an acidic stream (6) comprising hydrochloric acid [HCl];
- an acid reactor (AR) in fluid communication with the electrochemical treatment unit (ED, U-CA) and connected to the means for supplying calcium carbonate [CaCO₃] (7) in order to respectively receive hydrochloric acid [HCl] and calcium carbonate [CaCO₃] (7) and bring them into contact with one another so as to neutralise the hydrochloric acid [HCl] and thus produce a liquid stream (8) of calcium chloride [CaCl₂] and a gaseous stream (9) of carbon dioxide [CO₂];
- a base reactor (BR) in fluid communication with the electrochemical treatment unit (ED, U-CA) and with the acid reactor (AR), to respectively receive the sodium hydroxide [NaOH] and the carbon dioxide [CO₂] and bring them into contact with one another so as to produce a sodium carbonate [Na₂CO₃] stream (10); and
- means for discharging said stream (10) of sodium carbonate [Na₂CO₃] produced by the base reactor (BR) into salt water chosen from either seawater or ocean water, so as to increase its alkalinity and thus cause atmospheric carbon dioxide [CO₂] to be captured.

In one embodiment, the electrochemical treatment unit (ED, U-CA) is selected from the group consisting of an electrodialyser and a chlor-alkali electrolysis plant.

The device of the invention can further comprise:

- a reverse osmosis unit (RO) arranged to receive the saline stream (1) so as to desalinate it and thus produce a stream of desalinated water (1') on the one hand, and a stream of water concentrated in salts (2) on the other; and
- a purification unit (F) in fluid communication with the reverse osmosis unit (RO) to receive at least part of said stream of water concentrated in salts (2) and arranged to remove Mg^{2+} and Ca^{2+} ions from said stream of water concentrated in salts (2), and thus obtain a purified water stream essentially devoid of Mg^{2+} and Ca^{2+} ions (2').

In another embodiment, the device further comprises:

- a means for supplying a stream of purified water essentially devoid of Mg^{2+} and Ca^{2+} ions (2'), and
- the electrochemical treatment unit is an electrodialyser (ED) arranged in fluid communication with the means for supplying the purified water stream essentially devoid of Mg^{2+} and Ca^{2+} ions (2') so as to subject this stream (2') to at least one electrical field and thus produce said alkaline stream (5) and said acidic stream (6).

In this embodiment, the device can comprise:

- a means for supplying a stream of desalinated water (1', 11), preferably a stream of filtered, desalinated water (1''), and wherein
- the electrodialyser (ED) is also arranged in fluid communication with the means for supplying a stream of desalinated water (1', 11, 1'') so as to subject this stream to said electrical field to produce the alkaline stream (5) and the acidic stream (6).

Alternatively, the device of the invention can further comprise:

- a reverse osmosis unit (RO) arranged to receive the saline stream (1) so as to desalinate it and thus produce a stream of desalinated water (1') on the one hand, and a stream of water concentrated in salts (2) on the other; and wherein

- the electrochemical treatment unit is an electrodialyser (ED) arranged in fluid communication with, on the one hand, at least a part of said desalinated water stream (1') and, on the other hand, at least a part of said water stream concentrated in salts (2), so as to subject them to at least one electrical field to produce said alkaline stream (5) and said acidic stream (6).

In another alternative embodiment of the invention, the device can further comprise:

- a reverse osmosis unit (RO) arranged to receive the saline stream (1) so as to desalinate it and thus produce a stream of desalinated water (1') on the one hand, and a stream of water concentrated in salts (2) on the other; and
- a purification unit (F) in fluid communication with the reverse osmosis unit (RO) to receive at least part of said stream of water concentrated in salts (2) and arranged to remove Mg^{2+} and Ca^{2+} ions from said stream of water concentrated in salts (2), and thus obtain a purified water stream essentially devoid of Mg^{2+} and Ca^{2+} ions (2'),

and wherein the electrochemical treatment unit is a chlor-alkali electrolysis plant comprising:

- a chlor-alkali reactor (C-A) in fluid communication, on the one hand, with the reverse osmosis unit (RO) to receive at least part of said desalinated water stream (1'), and, on the other hand, with the purification unit (F) to receive at least part of said purified water stream essentially devoid of Mg^{2+} and Ca^{2+} ions (2') so as to subject these streams (1', 2') to at least one electrical field and thus produce said alkaline stream (5) comprising sodium hydroxide [NaOH] (5), a gaseous stream (13) of dihydrogen [H_2], and a gaseous stream (14) of chlorine [Cl_2];
- a H_2/Cl_2 fuel cell (FC) in fluid communication with the chlor-alkali reactor (C-A) to receive said gaseous stream (13) of dihydrogen [H_2] and said gaseous stream (14) of chlorine [Cl_2] and thus produce a concentrated acid stream (15) comprising hydrochloric acid [HCl], and electricity and/or heat; and

a dilution tank (D) arranged to receive a liquid stream (1, 16), preferably a saline stream, and in fluid communication with the H_2/Cl_2 fuel cell (FC) so as to mix said

liquid stream (1, 16) with said concentrated acid stream (15) and thus produce the acidic stream (6) comprising hydrochloric acid [HCl].

Other advantages and features of the invention will appear upon reading the detailed description below, and upon analysing the appended drawings, wherein:

[Fig. 1] shows a flowchart of the method of the invention according to a preferred embodiment;

[Fig. 2] shows a flowchart of a method according to a second embodiment of the invention;

[Fig. 3] shows a flowchart of a method according to a third embodiment of the invention;

[Fig. 4] shows a flowchart of a method according to a fourth embodiment of the invention;

[Fig. 5] shows a flowchart of a method according to a fifth embodiment of the invention;

[Fig. 6] shows a flowchart of a method according to a sixth embodiment of the invention;

[Fig. 7] shows a flowchart of a method according to a seventh embodiment of the invention;

[Fig. 8] shows a flowchart of a method according to an alternative embodiment of the invention; and

[Fig. 9] shows a flowchart of a method according to another alternative embodiment of the invention.

The drawings, tables and description below contain, for the most part, elements of a certain nature. The figures and tables are an integral part of the description, and may therefore not only be used to help with the understanding of the present invention, but also to contribute to its definition, where relevant.

In general, the invention makes it possible to increase the alkalinity of inland seawater and/or ocean water. By increasing the alkalinity of waters, these waters are able to better capture and improve the permanent storage of atmospheric CO₂.

Thus, the present invention relates to a device arranged to increase the alkalinity of the seas and oceans. More particularly, the invention includes discharging an alkaline stream into sea or ocean water, hereinafter referred to as seawater. This discharge helps restore seawater chemistry, including its acidity (pH), to pre-industrial levels. This increases the capacity of the seas and oceans to capture, store and sustainably retain CO₂.

The present invention further relates to a method involving sea and/or ocean water, electricity and minerals (e.g., calcium carbonate) to obtain a sodium carbonate solution of an alkaline nature, as well as a neutralised solution. Both of the alkaline and neutralised solutions can be discharged into seas and/or oceans to increase their alkalinity and thus capture CO₂. Although the method of the invention is accompanied by the intermediate formation of CO₂, the method controls this formation and reuses this gas at least partially during the method. One advantage of the invention is thus that the overall equation of the method does not lead to the production of any CO₂ that is harmful to the environment, nor to the production of polluting waste.

Another advantage is that the raw materials used in the method of the invention are naturally abundant. These are in particular seawater, or more generally brine, and CaCO₃. Consequently, the logistics involved for implementing the method of the invention are made easier.

The seawater particularly concerned by the invention is that of the Baltic Sea, the Antarctic Ocean, the Indian Ocean, the Atlantic Ocean, the Pacific Ocean, the Mediterranean Sea and/or the Red Sea. Just for indication, typically 1 kg of seawater contains about 964.8 g of water (H₂O) and 35.2 g of ionic compounds (mainly salts). In general, these 35.2 g of ionic compounds include approximately: 19.352 g of chloride ion (Cl⁻); 10.784 g of sodium ion (Na⁺); 2.712 g of sulphate ion (SO₄²⁻); 1.284 g of magnesium ion (Mg²⁺); 0.108 g of bicarbonate ion (HCO₃⁻); 0.412 g of calcium ion (Ca²⁺); 0.399 g of potassium ion (K⁺); and the remainder being composed of other ions; cf. Zeebe and Wolf-Gladrow, 2001, *CO₂ in Seawater: Equilibrium, Kinetics, Isotopes*, Gulf Professional Publishing.

Recently, the addition of sodium carbonate Na₂CO₃ has been considered in order to increase the alkalinity of seawater, cf. Hartmann *et al.*, *Stability of alkalinity in Ocean*

Alkalinity Enhancement (OAE) approaches - consequences for durability of CO₂ storage, Biogeosciences Discuss., 2022 - DOI: 10.5194/bg-2022-126. However, implementing a large-scale method with Na₂CO₃ presents many challenges that must first be overcome. In particular, Na₂CO₃ synthesis remains difficult. For this reason, the prior art is more focused on methods using alkaline solutions, such as sodium hydroxide (NaOH) solutions.

Despite the known difficulties, the Applicant focused on research involving Na₂CO₃. One reason is that Na₂CO₃ does not seem to present any safety risks since it is routinely used in industry for environmental sanitation; see Brockmann and Janse, 2008, *Calcium and carbonate in closed marine aquarium systems*, Advances in coral husbandry in public aquariums, pages 133-142, chapter 14, Burgers' Zoo, Arnhem, The Netherlands.

The Applicant has therefore developed a method for capturing atmospheric carbon dioxide [CO₂], comprising several operations. The method of the invention begins in particular with first operations comprising obtaining products essential for the technical effect of the invention. Thus, an operation is provided for obtaining a saline stream on the one hand, and for obtaining calcium carbonate [CaCO₃] on the other hand. Obtaining the saline stream can comprise, for example, the drawing of salt water or the manufacture of a saline solution by adding salts to water. Preferably, the drawing of salt water is intended to take place directly from seawater, for example by means of a pump. The saline stream can also come from a mine or plant brine (industrial brine stream), in particular in the context of colocalisation of the device of the invention in an already installed plant structure. Obtaining CaCO₃ is facilitated by the fact that CaCO₃ is one of the most abundant minerals on our planet. More specifically, it accounts for around 4% of the Earth's crust. CaCO₃ is in particular found in rock, mainly in chalk, limestone and marble.

The method further comprises an operation comprising producing an alkaline stream. In this operation, the alkaline stream that is produced comprises sodium hydroxide [NaOH]. Moreover, the method further comprises an operation comprising producing an acidic stream. In this operation, the acidic stream comprises hydrochloric acid [HCl]. According to the invention, these production steps can be carried out by electrochemical treatment. For this purpose, the electrochemical

treatment is carried out for at least part of the saline stream previously supplied in the obtaining operation.

The method of the invention further comprises an operation for neutralising the hydrochloric acid [HCl] produced during the operation comprising producing the acidic stream. The neutralisation of hydrochloric acid [HCl] is carried out by bringing it into contact, in an acid reactor (AR), with the calcium carbonate [CaCO₃] obtained during the first operations of the method. In this way, a liquid stream of calcium chloride [CaCl₂] and a gaseous stream of carbon dioxide [CO₂] are obtained in the method of the invention according to the present embodiment.

In another embodiment, step **iv.** of neutralising the hydrochloric acid [HCl] provides for not giving priority to the formation of CO₂ over the simple dilution, in an acid medium, of calcium carbonate [CaCO₃] into Ca²⁺ and CO₃⁻ ions.

The method then comprises an operation comprising the production of a sodium carbonate [Na₂CO₃] stream. For this purpose, the method according to the invention provides for bringing the carbon dioxide [CO₂] obtained during neutralisation (or, where applicable, another gas containing CO₂ from elsewhere, see below) into contact, in a base reactor (BR), with the sodium hydroxide [NaOH] produced during the operation comprising producing an alkaline stream. The sodium carbonate [Na₂CO₃] stream is thus obtained.

Finally, the method of the invention comprises discharging this sodium carbonate [Na₂CO₃] stream into salt water. Salt water is seawater and ocean water. This increases the alkalinity of the water. This results in the increased capture of atmospheric carbon dioxide [CO₂].

Discharging can take place either directly or indirectly into seawater. An indirect discharge is in particular a discharge into a stream of a plant that is then conveyed to the sea to be discharged there.

Fig. 1 shows a flowchart of a method according to one embodiment of the invention.

In this embodiment, the method begins when a stream of seawater, ocean water, or more typically a brine 1 enters reverse osmosis equipment RO. A stream of desalinated water 1' and a stream of water concentrated in salts 2 are thus obtained. This stream concentrated in salts 2 is sometimes referred to as a "rejected" stream

comprising concentrated brine. A reverse osmosis device from the FilmTec product range available from DuPont can be used.

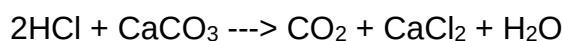
Part of the rejected stream 2 is sent to a filter F which removes most of the Ca^{2+} and Mg^{2+} ions. The filter can, for example, be a PRO-XS2 nanofiltration membrane filter available from Hydranautics, or a FilmTec NF270 available from Dupont. Thus, a filtered stream 2' and a residual stream 3 substantially comprising the remainder of the Ca^{2+} and Mg^{2+} ions are obtained. This residual stream 3 is rejected and the Ca^{2+} and Mg^{2+} ions are thus eliminated.

In another embodiment, the filter can be replaced with a precipitation device that removes most of the Ca^{2+} and Mg^{2+} ions.

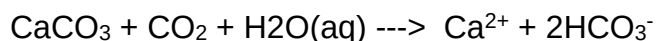
The filtered stream 2' enters an electrodialysis device ED, as well as optionally a portion of the desalinated water when required by the specifications of the electrodialysis device ED, like in the case of the present embodiment. In particular, a three-circuit electrodialysis device EDBM available from the PCCell GmbH or Eurodia company may be used.

Three streams exit the electrodialysis device ED: (i) a partially desalinated stream 4, (ii) an alkaline stream 5 containing NaOH, and (iii) an acidic stream 6 containing HCl. The partially desalinated stream 4 can be eliminated or optionally transformed in various applications, for example in steam generation. Where necessary, in one embodiment, part of the partially desalinated stream 4 originating from the electrodialysis device ED may be partially or totally recirculated in the electrodialysis device ED.

The acidic stream 6 enters a reactor AR referred to as an "acid reactor". CaCO_3 is added to the acid reactor via a supply path 7 to neutralise the HCl contained in the acidic stream 6. Neutralisation is performed according to the following equation:



In addition to this reaction, the calcium carbonate can be dissolved (and the acid neutralised) without the formation of CO_2 or with the consumption of CO_2 , according to the following equation:



The acid reactor and other neutralisation equipment are in particular described in Maree and Plessis, 1993 (Kinetics of Calcium Carbonate Neutralization First-Order Case of the Cube-Root Law).

A liquid stream 8 of calcium chloride [CaCl_2] and a gaseous stream 9 of carbon dioxide [CO_2] are thus obtained. The CO_2 stream 9 is conveyed towards a reactor BR, referred to as the “base reactor”. The alkaline stream 5 originating from the electrodialysis device enters the base reactor BR and reacts with the CO_2 stream 9. A stream 10 of sodium carbonate [Na_2CO_3] is obtained. The main reaction occurring in the reactor is essentially represented by the following equation:

$2\text{NaOH} + \text{CO}_2 \rightarrow \text{Na}_2\text{CO}_3 + \text{H}_2\text{O}$ (partial neutralisation of NaOH); and as well as potential dilution.

Partial neutralisation of NaOH can be carried out in a CO_2 injector available from Air Liquide. Dilution can be carried out in a conventional retention tank. In this way, the base reactor BR allows the alkaline stream 5 to be diluted, obtaining a stream 10 with a high concentration of NaOH rather than Na_2CO_3 .

The following operation comprises discharging this stream 10 of sodium carbonate [Na_2CO_3] into seawater, or more generally, discharging is carried out into salt water, either directly or indirectly.

This method may be carried out continuously or in batches, depending on what is most appropriate for the given resources (e.g. seawater or brine, electricity, CaCO_3).

Furthermore, alternatively, the conditions of the operations to set a residence time in the acid reactor AR can be controlled in order to regulate CO_2 production. The residence time is thus chosen according to the concentration of the acidic stream 6 and the size of the calcium carbonate (CaCO_3) particles 7.

The Applicant has considered several alternative embodiments of the preferred embodiment described above. These alternative embodiments are described below. Structural elements (equipment, device(s), etc.), as well as equations and/or chemical formulas and/or elements and/or streams bearing the same numerical, alphabetical or alphanumeric reference identify identical or similar elements.

Fig. 2 shows a flowchart of a method according to a second embodiment of the invention.

This second embodiment of the method of the invention does not provide for reverse osmosis. In this case, the electrodialysis device ED is arranged so as to carry out the electrodialysis with the initial NaCl concentration of the saline stream (1) obtained at the beginning of the method. In this embodiment, the electrodialysis device ED does not require a stream of desalinated water (1'). Alternatively, an external stream of desalinated water (11) from another source can be obtained. After the operation comprising the electrolysis, the method of this second embodiment is comparable to that described with reference to Fig. 1.

Fig. 3 shows a flowchart of a method according to a third embodiment of the invention.

This third embodiment of the method of the invention does not provide for filtration. In this case, the rejected stream 2 concentrated in salts, or at least part thereof, is directly subjected to electrodialysis, i.e. it directly enters the electrodialysis device ED. This implies that the electrodialysis device ED is arranged to operate with increased Ca^{2+} and Mg^{2+} salt concentrations. In all other aspects, the method of this third embodiment is comparable to that described with reference to Fig. 1.

Fig. 4 shows a flowchart of a method according to a fourth embodiment of the invention.

This fourth embodiment of the method of the invention provides for filtering the desalinated water 1' exiting the reverse osmosis equipment RO using additional filtration equipment F'. This additional filtration equipment F' is arranged to remove all, or almost all, of the traces of the remaining Ca^{2+} and Mg^{2+} ions after reverse osmosis. The desalinated water 1' after reverse osmosis is thus conveyed into the additional filtration equipment F'. Thus, a filtered, desalinated stream 1'' is obtained, which is conveyed to the electrodialysis device ED. The additional filtration equipment F' generates a rejected desalinated stream 12 which is typically disposed of. Alternatively, the rejected, desalinated stream 12 can be recirculated to the base reactor BR, as shown in Fig. 4, with a view to diluting the base stream 10. In all other aspects, the method of this third embodiment is comparable to that described with reference to Fig. 1.

Fig. 5 shows a flowchart of a method according to a fifth embodiment of the invention.

This fifth embodiment of the method of the invention provides for an electrochemical treatment operation to carry out a chlor-alkali (C-A) type treatment. For this purpose, an electrochemical device is used outputting an alkaline stream 5 containing NaOH, a first gaseous stream 13 of dihydrogen (H_2), and a second gaseous stream 14 of chlorine (Cl_2). The alkaline stream 5 is conveyed to the base reactor BR in a manner similar to that of the embodiment described with reference to Fig. 1. The first gaseous stream 13 and second gaseous stream 14, of H_2 and of Cl_2 respectively, are injected into a H_2/Cl_2 fuel cell FC to obtain: a concentrated acid stream 15 comprising HCl and electricity and/or heat (optionally used for the method). Alternatively, the H_2/Cl_2 fuel cell FC can be replaced by a reactor to produce HCl without generating electricity.

In particular, for this embodiment, it is possible to use an electrochemical device of the Chlor-pack type available from the 3V-tech company; electrodes for Chlor-Alkali available from the De Nora company and Chlor-Alkali membranes available from the Nafion company.

The concentrated acid HCl stream 15 is conveyed into a dilution tank D, where it is mixed with a liquid stream 16 (e.g. seawater or brine) to obtain an acid stream 6 that can be diluted with seawater. The dilution tank is a conventional tank arranged to receive and dilute one or more liquids.

More generally, the dilution tank (D) is arranged to receive a liquid stream (1, 16), preferably a saline stream, and more preferably a seawater stream. In another embodiment, the liquid stream can comprise fresh water, for example from a channel, a river, or even a tap.

Fig. 6 shows a flowchart of a method according to a sixth embodiment of the invention.

This sixth embodiment of the method of the invention provides for electrodialysis with a two-compartment bipolar membrane device. In particular, a two-circuit EDBM device available from MEGA or Eurodia can be used. Furthermore, it is possible to use CPM-CEM cell pairs available from the REDstack B.V. company and “spacers” available from the Aqua Battery B.V. company.

The electrodialysis device produces an alkaline stream 5 containing NaOH, and an acidic stream 6 containing HCl.

Unlike other embodiments described hereinabove with other electrodialysis devices, in the present embodiment, no partially desalinated stream 4 is generated.

Fig. 7 shows a flowchart of a method according to a seventh embodiment of the invention.

This seventh embodiment of the method of the invention provides for an operation comprising introducing a stream of liquid 17 (e.g., seawater, brine, that is partially desalinated) into the base reactor BR and the acid reactor AR. This provides additional control over these two reactors (BR and AR).

In the embodiment described above, each filter can be replaced with a precipitation device that removes most, if not all, of the targeted ions.

Moreover, it should be noted that the calcium chloride $[\text{CaCl}_2]$ generated in the method of the invention (stream 8) can be transformed, in particular in the agri-food industry.

It should also be noted that the neutralisation of the acidic stream (HCl) from the electrochemical treatment step allows the method to be scaled up. This is because, without this neutralisation of the acid according to the invention, significant amounts of acid would be generated, which is not sustainable when implementing the method at high capacity and/or in many geographies. If the acidic stream is not neutralised, it must be recovered or disposed of, which limits the implementation of the method depending on the availability of HCl or the possibilities of its disposal. It should be noted that the transport of HCl may require a prior concentration step to reduce transport costs. Such a concentration step, on the other hand, increases the energy requirements of the method, as well as the CO_2 emissions (those particularly associated with the transport of HCl). This affects the efficiency of the method. Moreover, the transportation of acids is a typically hazardous activity, and is limited by safety standards.

One additional advantageous effect of the method and device of the invention is that they can be used in various industrial sectors (e.g. the chemical, food, or pharmaceutical sectors) for the production of sodium carbonate, or even of sodium bicarbonate.

In a particular embodiment, the Applicant has arranged the method and the device so as to recover, at least in part, the carbon dioxide from the acid reactor AR.

Fig. 8 shows a flowchart of a method according to one alternative embodiment of the invention. In this embodiment, the CO₂ stream 9 is conveyed to its final destination for transformation. This embodiment is of particular interest due to the purity of the CO₂ generated by the acid reactor AR. As a result, in this embodiment, the base reactor BR is supplied with CO₂ via another gaseous stream 12. The gaseous stream 12 comprising the CO₂ can be a pure stream comprising 100% CO₂ or a less pure stream (air or industrial smoke for example). The base reactor BR then generates the sodium carbonate [Na₂CO₃] stream 10, which is accompanied in parallel by a stream 13 corresponding to the exhaust of the remaining elements of the gaseous stream 12.

Fig. 9 shows a flowchart of a method according to another alternative embodiment of the invention, wherein the CO₂ stream 9 from the acid reactor is divided so as to be partially conveyed to the base reactor (BR) and partially to its final destination for transformation. Optionally, the part of the stream 9 conveyed to the base reactor (BR) can join a less pure gaseous CO₂ stream 12 (air). The base reactor BR then generates the sodium carbonate [Na₂CO₃] stream 10, which is accompanied in parallel by a stream 13 corresponding to the exhaust of the remaining elements of the gaseous stream 12.

Thus, this alternative embodiment of the invention can be defined as follows:

A method for capturing atmospheric carbon dioxide [CO₂], characterised in that it comprises the following steps:

- a)** Obtaining a saline stream (1) and calcium carbonate [CaCO₃] (7);
- b)** Producing an alkaline stream (5) comprising sodium hydroxide [NaOH];
and

- c)** Producing an acidic stream (6) comprising hydrochloric acid [HCl];

and wherein, at least one of said steps **b)** of producing the alkaline stream (5) and **c)** of producing the acidic stream (6) comprises a step of electrochemically treating at least part of said saline stream (1), and in that the method further comprises the following steps:

- d)** Neutralising the hydrochloric acid [HCl] obtained in step **c)** of producing an acidic stream (6) by bringing the calcium carbonate [CaCO₃] (7) from the obtaining step **a)** into contact, in an acid reactor (AR), with said hydrochloric acid [HCl], so as to obtain a liquid stream (8) of calcium chloride [CaCl₂] and a gaseous stream (9) of carbon dioxide [CO₂];
- e)** Producing a stream (10) of sodium carbonate [Na₂CO₃] by bringing carbon dioxide [CO₂], optionally obtained in the neutralisation step **d)**, into contact, in a base reactor (BR), with the sodium hydroxide [NaOH] from the alkaline stream production step **b)**; and
- f)** Discharging the stream (10) of sodium carbonate [Na₂CO₃] produced in the previous step **e)** into salt water chosen from either seawater or ocean water, so as to increase its alkalinity and thus cause atmospheric carbon dioxide [CO₂] to be captured.

The present description generally discloses that the sodium carbonate [Na₂CO₃] stream (10) can be discharged in salt water chosen from seawater and ocean water. Of course, in each embodiment described, the sodium carbonate [Na₂CO₃] stream (10) can be discharged either directly or indirectly in salt water. The discharge can thus also be carried out in salt water contained in a tank provided for this purpose. Any salt water can capture atmospheric carbon dioxide [CO₂] when it is modified by means of a device and/or the method of the invention. The invention can be implemented on land or in territorial waters (in particular on a stationary or moving platform).

The invention uses calcium carbonate [CaCO₃]. More particularly, and within the scope of the invention, CaCO₃ comes from a source that is, in itself, independent of the atmospheric carbon dioxide [CO₂] capture method. This is a so-called “third-party source”. The third-party source of CaCO₃ can be rock, chalk, limestone and marble as mentioned above. As CaCO₃ is one of the most abundant minerals on earth, it is easier to supply. The external origin of this component of the method is advantageous, in particular in terms of energy balance. This is because the method of the invention harvests CaCO₃ from a natural source. It therefore does not need to be synthesised by conversion or chemical synthesis, for example, which typically

generates CO₂, which further degrades the atmosphere and is detrimental to the energy balance.

In particular, the method of the present invention allows for the use of limestone, without the need for a storage solution and/or the use of CO₂. In particular, the physical link existing between the acid reactor (AR) and the base reactor (BR) allows conveying the gaseous stream (9) of carbon dioxide and enables the direct use of limestone.

The use of limestone minerals has an additional advantage. This is because limestone minerals have a high purity level. They are typically free from heavy metals - especially nickel, which is typical of silicate minerals or rocks containing reduced iron (Fe, Fe⁺, Fe²⁺) - which have negative impacts on ecosystems.

Compared to existing approaches, the energy balance of the invention is improved, inter alia, by the fact that the method increases the alkalinity of seawater (referred to as "*Ocean Alkalinity Enhancement*"). The prior art mainly relates to methods for direct CO₂ capture in seawater (referred to as "*Direct Ocean Capture*"). Direct CO₂ capture methods represent a radically different approach to the present invention, in particular in that they release CO₂ from seawater rather than treating CO₂ *in situ*, directly in these waters. Thus, direct capture methods pose problems with the storage of the captured CO₂ and/or its conversion treatment. The invention overcomes these issues.

Claims

[Claim 1] A method for capturing atmospheric carbon dioxide [CO₂], characterised in that it comprises the following steps:

- i. Obtaining a saline stream (1) and calcium carbonate [CaCO₃] (7);
- ii. Producing an alkaline stream (5) comprising sodium hydroxide [NaOH]; and
- iii. Producing an acidic stream (6) comprising hydrochloric acid [HCl];

and wherein, at least one of said steps ii. of producing the alkaline stream (5) and iii. of producing the acidic stream (6) comprises a step of electrochemically treating at least part of said saline stream (1), and in that the method further comprises the following steps:

- iv. Neutralising the hydrochloric acid [HCl] obtained in step iii. of producing an acidic stream (6) by bringing the calcium carbonate [CaCO₃] (7) from the obtaining step i. into contact, in an acid reactor (AR), with said hydrochloric acid [HCl], so as to obtain a liquid stream (8) of calcium chloride [CaCl₂] and a gaseous stream (9) of carbon dioxide [CO₂];
- v. Producing a stream (10) of sodium carbonate [Na₂CO₃] by bringing at least part of the carbon dioxide [CO₂] obtained in the neutralisation step iv. into contact, in a base reactor (BR), with the sodium hydroxide [NaOH] from the alkaline stream production step ii.; and
- vi. Discharging the stream (10) of sodium carbonate [Na₂CO₃] produced in the previous step v. into salt water chosen from either seawater or ocean water, so as to increase its alkalinity and thus cause atmospheric carbon dioxide [CO₂] to be captured.

[Claim 2] Method according to **claim 1**, wherein the saline stream of step i. is obtained by drawing in water chosen from either seawater, ocean water or industrial brine.

[Claim 3] Method according to one of the **preceding claims**, wherein the electrochemical treatment is selected from the group consisting of electrodialysis and chlor-alkali electrolysis.

[Claim 4] Method according to one of the **preceding claims**, wherein step **iv.** of neutralising the hydrochloric acid [HCl] further comprises collecting the liquid stream (8) of calcium chloride [CaCl₂].

[Claim 5] Method according to one of the **preceding claims**, further comprising, upstream of said steps **ii.** of producing an alkaline stream (5) and **iii.** of producing an acidic stream, the following steps:

i.1. Reverse osmosis (RO) to desalinate said saline stream (1) and thus obtain a stream of desalinated water (1') on the one hand, and a stream of water concentrated in salts (2) on the other hand; and

i.2. Purification (F), preferably chosen from filtration and precipitation, receiving at least part of said stream of water concentrated in salts (2) derived from reverse osmosis (RO), wherein Mg²⁺ and Ca²⁺ ions are removed from the stream of water concentrated in salts (2), thus obtaining a purified water stream essentially devoid of Mg²⁺ and Ca²⁺ ions (2').

[Claim 6] Method according to one of the **preceding claims**, further comprising, upstream of said steps **ii.** of producing an alkaline stream (5) and **iii.** of producing an acidic stream, the following steps:

i.3. Obtaining a stream of purified water essentially devoid of Mg²⁺ and Ca²⁺ ions (2'), and

i.4. An electrodialysis, wherein said purified water stream essentially devoid of Mg²⁺ and Ca²⁺ ions (2') is subjected to at least one electrical field so as to produce said alkaline stream (5) and said acidic stream (6) of steps **ii.** of producing an alkaline stream (5) and **iii.** of producing an acidic stream (6).

[Claim 7] Method according to **claim 6**, further comprising, upstream of the electrodialysis step **i.4.**:

i.5. Obtaining a stream of desalinated water (1', 11), preferably a stream of filtered, desalinated water (1''), also subjected to said electrical field during electrodialysis so as to contribute to the production of said alkaline stream (5) and said acidic stream (6) of steps **ii.** of producing an alkaline stream (5) and **iii.** of producing an acidic stream (6).

[Claim 8] Method according to one of **claims 1 to 4**, further comprising, upstream of said steps **ii.** of producing an alkaline stream (5) and **iii.** of producing an acidic stream:

i.6. Purification (F), preferably selected from filtration and precipitation, receiving said saline stream (1), wherein Mg^{2+} and Ca^{2+} ions are removed from said saline stream (1), thus obtaining a stream of purified water essentially devoid of Mg^{2+} and Ca^{2+} ions (2');

i.7. An electrodialysis, wherein said purified water stream essentially devoid of Mg^{2+} and Ca^{2+} ions (2'), and optionally a desalinated water stream (11), is/are subjected to at least one electrical field so as to produce said alkaline stream (5) and said acidic stream (6) of steps **ii.** of producing an alkaline stream (5) and **iii.** of producing an acidic stream (6).

[Claim 9] Method according to one of **claims 1 to 4**, further comprising, upstream of said steps **ii.** of producing an alkaline stream (5) and **iii.** of producing an acidic stream:

i.8. Reverse osmosis (RO) to desalinate said saline stream (1) and thus obtain a stream of desalinated water (1') on the one hand, and a stream of water concentrated in salts (2) on the other hand; and

i.9. An electrodialysis, wherein said desalinated water stream (1') and said stream of water concentrated in salts (2) are subjected to at least one electrical field so as to produce said alkaline stream (5) and said acidic stream (6) of steps **ii.** of producing an alkaline stream (5) and **iii.** of producing an acidic stream (6).

[Claim 10] Method according to one of **claims 5 to 9**, wherein the electrodialysis further produces a partially desalinated stream (4) which is subjected to a second electrodialysis so as to contribute to the production of said alkaline stream (5) and of said acidic stream (6) of steps **ii.** of producing an alkaline stream (5) and **iii.** of producing an acidic stream (6).

[Claim 11] Method according to one of **claims 1 to 4**, wherein step **ii.** of producing an alkaline stream (5) comprises:

- a chlor-alkali (C-A) electrolysis so as to produce the alkaline stream (5) comprising sodium hydroxide [NaOH], a gaseous stream (13) of dihydrogen [H₂], and a gaseous stream (14) of chlorine [Cl₂];

and wherein the step **iii.** of producing an acidic stream (6) comprises

- injecting, into a H₂/Cl₂ fuel cell (FC), said gaseous stream (13) of dihydrogen [H₂], and said gaseous stream (14) of chlorine [Cl₂] so as to obtain a concentrated acid stream (15) comprising hydrochloric acid [HCl], and electricity and/or heat; and
- mixing, in a dilution tank (D), said concentrated acid stream (15) with a liquid, preferably a saline liquid (16), so as to obtain the acidic stream (6) comprising hydrochloric acid [HCl].

[Claim 12] Device for capturing atmospheric carbon dioxide [CO₂], which device comprises:

- a means for drawing a saline stream (1), preferably sea or ocean water, and a means for providing calcium carbonate [CaCO₃] (7);

characterised in that the device comprises

- an electrochemical treatment unit (ED, U-CA) capable of producing, from at least a part of said saline stream (1),:
 - o an alkaline stream (5) comprising sodium hydroxide [NaOH]; and
 - o an acidic stream (6) comprising hydrochloric acid [HCl];
- an acid reactor (AR) in fluid communication with the electrochemical treatment unit (ED, U-CA) and connected to the means for supplying calcium carbonate [CaCO₃] (7) in order to respectively receive hydrochloric acid [HCl] and calcium carbonate [CaCO₃] (7) and bring them into contact with one another so as to neutralise the hydrochloric acid [HCl] and thus produce a liquid stream (8) of calcium chloride [CaCl₂] and a gaseous stream (9) of carbon dioxide [CO₂];
- a base reactor (BR) in fluid communication with the electrochemical treatment unit (ED, U-CA) and with the acid reactor (AR), to respectively receive the sodium hydroxide [NaOH] and the carbon dioxide [CO₂] and bring them into

contact with one another so as to produce a sodium carbonate [Na_2CO_3] stream (10); and

- means for discharging said stream (10) of sodium carbonate [Na_2CO_3] produced by the base reactor (BR) into salt water chosen from either seawater or ocean water, so as to increase its alkalinity and thus cause atmospheric carbon dioxide [CO_2] to be captured.

[Claim 13] Device according to **claim 12**, wherein the electrochemical treatment unit (ED, U-CA) is selected from the group consisting of an electrodialyser and a chlor-alkali electrolysis plant.

[Claim 14] Device according to one of **claims 12 and 13**, further comprising:

- a reverse osmosis unit (RO) arranged to receive the saline stream (1) so as to desalinate it and thus produce a stream of desalinated water (1') on the one hand, and a stream of water concentrated in salts (2) on the other; and
- a purification unit (F) in fluid communication with the reverse osmosis unit (RO) to receive at least part of said stream of water concentrated in salts (2) and arranged to remove Mg^{2+} and Ca^{2+} ions from said stream of water concentrated in salts (2), and thus obtain a purified water stream essentially devoid of Mg^{2+} and Ca^{2+} ions (2').

[Claim 15] Device according to one of **claims 12 to 14**, further comprising:

- a means for supplying a stream of purified water essentially devoid of Mg^{2+} and Ca^{2+} ions (2'), and wherein
- the electrochemical treatment unit is an electrodialyser (ED) arranged in fluid communication with the means for supplying the purified water stream essentially devoid of Mg^{2+} and Ca^{2+} ions (2') so as to subject this stream (2') to at least one electrical field and thus produce said alkaline stream (5) and said acidic stream (6).

[Claim 16] Device according to **claim 15**, further comprising:

- a means for supplying a stream of desalinated water (1', 11), preferably a stream of filtered, desalinated water (1''), and wherein

- the electrodialyser (ED) is also arranged in fluid communication with the means for supplying a stream of desalinated water (1', 11, 1'') so as to subject this stream to said electrical field to produce the alkaline stream (5) and the acidic stream (6).

[Claim 17] Device according to **claim 12**, further comprising:

- a reverse osmosis unit (RO) arranged to receive the saline stream (1) so as to desalinate it and thus produce a stream of desalinated water (1') on the one hand, and a stream of water concentrated in salts (2) on the other; and wherein
- the electrochemical treatment unit is an electrodialyser (ED) arranged in fluid communication with, on the one hand, at least a part of said desalinated water stream (1') and, on the other hand, at least a part of said water stream concentrated in salts (2), so as to subject them to at least one electrical field to produce said alkaline stream (5) and said acidic stream (6).

[Claim 18] Device according to **claim 12**, further comprising:

- a reverse osmosis unit (RO) arranged to receive the saline stream (1) so as to desalinate it and thus produce a stream of desalinated water (1') on the one hand, and a stream of water concentrated in salts (2) on the other; and
- a purification unit (F) in fluid communication with the reverse osmosis unit (RO) to receive at least part of said stream of water concentrated in salts (2) and arranged to remove Mg^{2+} and Ca^{2+} ions from said stream of water concentrated in salts (2), and thus obtain a purified water stream essentially devoid of Mg^{2+} and Ca^{2+} ions (2'),

and wherein the electrochemical treatment unit is a chlor-alkali electrolysis plant comprising:

- a chlor-alkali reactor (C-A) in fluid communication, on the one hand, with the reverse osmosis unit (RO) to receive at least part of said desalinated water stream (1'), and, on the other hand, with the purification unit (F) to receive at least part of said purified water stream essentially devoid of Mg^{2+} and Ca^{2+} ions (2') so as to subject these streams (1', 2') to at least one electrical field and thus produce said alkaline stream (5) comprising sodium hydroxide

[NaOH] (5), a gaseous stream (13) of dihydrogen [H_2], and a gaseous stream (14) of chlorine [Cl_2];

- a H_2/Cl_2 fuel cell (FC) in fluid communication with the chlor-alkali reactor (C-A) to receive said gaseous stream (13) of dihydrogen [H_2] and said gaseous stream (14) of chlorine [Cl_2] and thus produce a concentrated acid stream (15) comprising hydrochloric acid [HCl], and electricity and/or heat; and
- a dilution tank (D) arranged to receive a liquid stream (1, 16), preferably a saline stream, and in fluid communication with the H_2/Cl_2 fuel cell (FC) so as to mix said liquid stream (1, 16) with said concentrated acid stream (15) and thus produce the acidic stream (6) comprising hydrochloric acid [HCl].