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Plant and method to improve the efficiency of CO.SUB.2 .capture and storage using precipitated calcium carbonate

Abstract

A plant and a method to improve the efficiency of CO.sub.2 capture and storage from the atmospheric air, using precipitated calcium carbonate (PCC) and calcium bicarbonates. The plant includes an electric calciner, a contactor, an apparatus for pH correction, a dosing device for the buffering substance, an absorber/precipitator, a separator, and a PCC dosing device. The system is suitable for receiving at the inlet electric energy, carbonate, water, a flow of atmospheric air and for releasing a flow of CO.sub.2-lean air, a buffered ionic mixture, and a flow of excess PCC. The plant uses the bicarbonates or carbonates as permanent CO.sub.2 storage: this storage allows a cost-effective CO.sub.2 storage in modular plants.

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Background/Summary

FIELD

(1) Object of the present invention is a method and a plant to improve the efficiency of CO.sub.2

capture and storage using precipitated calcium carbonate (PCC).

BACKGROUND

- (2) The effects of the so-called “greenhouse gases” on the climate and especially the correlation between the concentration of CO₂ (carbon dioxide) in the atmosphere and global warming have long been known.
- (3) The efforts of the scientific community and world politics in recent years have been concentrated on trying to counteract the increase in the greenhouse gas emissions into the atmosphere, in order to avoid the phenomenon of global warming, i.e. the rise in the average temperature at a global level.
- (4) In a per se known manner, a number of initiatives have been promoted at international level aimed at limiting the CO₂ emissions into the atmosphere: the Kyoto Protocol in 1997 and the Paris Agreement in 2015, among others, are worth mentioning.
- (5) The forms identified by the scientific community to avoid global warming are many and substantially concern the decrease in the use of fossil fuels such as coal, oil and natural gas favouring the development of renewable energies such as hydraulic, wind, solar energy, from biomass and of zero-emission fuels such as hydrogen or ammonia.
- (6) In addition, many efforts of the international community are focused on improving the efficiency in the use of energy, as in the case of lighting with low-consumption lamps, on the transport with new generations of high-efficiency engines and, in the field of power generation, on replacing old, inefficient coal- or oil-fired power stations with new combined-cycle gas turbine and steam turbine plants with energy efficiencies approaching 60%.
- (7) Despite the on-going technological efforts in the most advanced nations, the forecasts of well-known international institutions on the need for energy globally over the next few years indicate a sharp increase in the demand for electric energy, thermal energy for industry and fuels for transport.
- (8) Consequently, these forecasts indicate a steady increase in the use of fossil sources such as oil, coal and natural gas, especially by emerging, newly industrialized and developing countries. This consumption is in fact favoured by the huge availability of these resources and by the discovery of new deposits and techniques for the extraction thereof, which factors altogether make these energy sources economically advantageous.
- (9) Using the data provided by these authoritative studies, not only a decrease in CO₂ emissions to combat global warming is not expected globally, but a substantial increase in the emissions themselves is instead expected over the next 50 years, mainly due to the increase in world population and to the new industrialization of entire countries.
- (10) The catastrophic effects of such a situation on the climate are easy to understand and difficult to avoid especially because developing nations believe that the renewable energy option is too sophisticated and costly and are more oriented towards short-term economic development programmes than towards CO₂ emission containment and environmental issues.
- (11) The scientific and industrial communities are committed to designing and industrializing processes that allow not only to reduce the CO₂ emissions produced by the process itself but that have as a co-benefit the capture and storage of additional CO₂ through mineralization processes.
- (12) One of the most interesting sectors from this point of view is the one that takes into consideration the calcination of carbonate rocks, the storage of CO₂ and the use of hydroxide for the capture of CO₂ from the air by carbonation.
- (13) In a per se known manner, the main technologies for CO₂ capture and storage by using hydroxides are: the technology proposed by Carbon engineering Ltd. through, but not only, the U.S. Pat. No. 8,728,428B1 the technology proposed by Heirloom through the patent application: PCT/US2020/039265 the technology proposed by Caserini et al. 2019 in the article: “Buffered accelerated weathering of limestone for storing CO₂: Chemical background”
- (14) In a per se known manner the above-mentioned technologies require a permanent storage of

the CO.sub.2 produced by the calcination process that is external to the proposed technology of using the hydroxide as a medium to capture CO.sub.2 by carbonation of hydroxides.

(15) The dependence of said technologies on a permanent storage of CO.sub.2 produced by the process of calcination of the carbonates that severely limits their application and the absence of a commercial use of the carbonate or bicarbonate produced limits their economic viability.

(16) In a per se known manner, the only forms currently available for the permanent storage of CO.sub.2 for the technologies mentioned above are those known as geological CCS (Carbon Capture and Sequestration) which, nonetheless, are encountering considerable difficulties in implementation due to the long timescales for the identification of the geological storage sites, the large size of the projects to obtain economies of scale and the opposition of the population for the CCS made on land.

(17) In a per se known manner, a method for the production of decarbonized hydroxide by storing the CO.sub.2 produced by the calcination process in the form of bicarbonates in seawater has been proposed by means of patent application PCT/IB2021/061832 "Plant and method for the production of decarbonized oxide or hydroxide using carbonate and electric energy".

(18) In a per se known form, one of the most commercially interesting products that can be produced starting from a hydroxide and that represents a permanent mineralization of CO.sub.2 is precipitated calcium carbonate or PCC.

(19) The PCC represents a stable storage of CO.sub.2 that has reacted with the hydroxide and is considered as such also by the European legislation "Commission Implementing Regulation (EU) 2018/2066" of 19 Dec. 2018.

(20) In a per se known form, the PCC is used in various commercial sectors such as, to name the most important, that of paper, plastics, the food sector and the construction one. The PCC market worldwide is greater than 100 million tons/year and represents a product with high added value.

SUMMARY

(21) As can be immediately understood, it is necessary to identify a technology that allows the capture and storage of CO.sub.2 from atmospheric air by carbonation of hydroxides. At the same time, this technology must make it possible to store the CO.sub.2 produced during the calcination process and generate a commercially usable product, possibly with zero impact, "carbon free".

(22) The task of the present invention is to make available a method and a plant that allows the efficient generation of precipitated calcium carbonate (PCC) using the CO.sub.2 present in the air through the electrical calcination of carbonates, the permanent storage of the CO.sub.2 produced in the calcination process in the form of bicarbonates in seawater and the subsequent carbonation of the hydroxide in the form of precipitated calcium carbonate (PCC). The same invention substantially improves the possibilities of industrial application of the carbonation compared to the known technologies.

(23) This object and these tasks are achieved by means of a plant according to claim 1 and by means of a method according to claim 8.

Description

BRIEF DESCRIPTION OF THE DRAWINGS

(1) In order to better understand the invention and appreciate its advantages, some exemplary and non-limiting embodiments thereof are described below, with reference to the attached drawings, in which:

(2) FIG. 1 is a schematic view of a plant to improve the efficiency of CO.sub.2 capture and storage according to the invention;

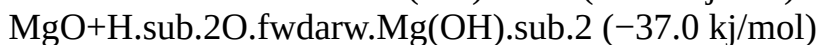
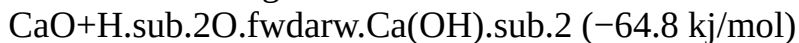
(3) FIG. 2 is a schematic view of another possible embodiment of the plant to improve the efficiency of CO.sub.2 capture and storage according to the invention;

- (4) FIG. 3 is a schematic view of another possible embodiment of the plant to improve the efficiency of CO₂ capture and storage according to the invention;
- (5) FIG. 4 is a schematic view of another possible embodiment of the plant to improve the efficiency of CO₂ capture and storage according to the invention;
- (6) FIG. 5 is a schematic view of another possible embodiment of the plant to improve the efficiency of CO₂ capture and storage according to the invention;
- (7) FIG. 6 is a schematic view of another possible embodiment of the plant to improve the efficiency of CO₂ capture and storage according to the invention;
- (8) FIG. 7 is a graph of the equilibrium of 2270 kg of calcite and 1000 kg of CO₂ in seawater as a function of the pH and of the amount of water;
- (9) FIG. 8 is a mass and energy balance of a possible embodiment of the plant to improve the efficiency of CO₂ capture and storage according to the invention;

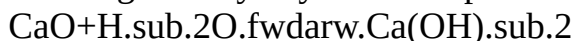
DETAILED DESCRIPTION OF EMBODIMENTS

- (10) In the description, reference will also be made to “carbonic gas” meaning thereby a mixture of gas containing mainly CO₂, and possibly other substances, including N₂, O₂, H₂O, Ar, while when it is intended to refer to the chemical element CO₂ (carbon dioxide) alone in the description, CO₂ will be used.
- (11) In the description, reference will also be made to “non-soluble” gases, meaning thereby the set of gases that are poorly soluble in water, including N₂ and Ar.
- (12) In the description reference will also be made to “atmospheric air” meaning thereby the atmospheric air having a CO₂ content of about 420 ppm at the time of writing the present document.
- (13) In the description, reference will also be made to “lean air”, meaning thereby air with a lower amount of CO₂ than the “atmospheric air”: this “lean air” is obtained by passing the “atmospheric air” through an “absorber/precipitator” where at least CO₂ is removed in whole or in part.
- (14) In the description, reference will also be made to “water”, meaning thereby seawater in the liquid phase with the chemical and physical characteristics necessary for use in the process according to the invention, while when it is intended to refer to the chemical element H₂O alone in the description, H₂O will be used.
- (15) In the description, reference will also be made to the “sea”, meaning thereby the sea as such but also the ocean, or any body of salt water.
- (16) In the description, reference will also be made to “carbonate”, meaning thereby any calcareous or dolomitic sedimentary rock such as calcite, aragonite, dolomite, siderite, magnesite, marble, but also any other carbonate material such as shells or corals.
- (17) In the description, reference will also be made to “water vapour”, meaning thereby water in the gaseous phase with the chemical and temperature characteristics necessary for use in the process according to the invention.
- (18) In the description reference will also be made to the “electric calciner” (or electric kiln), meaning thereby any controlled-atmosphere electric apparatus, known per se, capable of calcining the carbonate according to the reactions $\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$ (+183 kJ/mol) or $\text{MgCO}_3 \rightarrow \text{MgO} + \text{CO}_2$ (+118 kJ/mol). The calcination process, per se known, takes place at temperatures preferably comprised between 600° C. and 1200° C. and is an endothermic process. The controlled-atmosphere electric calciner does not allow direct contact of the calcination zone with the ambient air whilst it allows flushing the calcination zone possibly with water vapour.
- (19) In the description, reference will also be made to the “oxide”, meaning thereby the product of the calcination formed mainly by calcium oxide CaO or magnesium oxide MgO and to a lesser extent by other materials present in the carbonate rock with which the calciner is fed.
- (20) In the description, reference will also be made to the “hydroxide”, meaning thereby the product of the hydration of calcium oxide Ca(OH)₂ or of magnesium oxide Mg(OH)₂.

with the following chemical reactions:

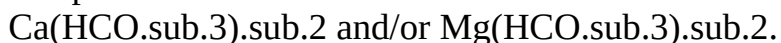


(21) In the description, reference will also be made to the “hydroxide production unit” (slaker), meaning thereby any device capable of reacting calcium oxide with water according to the reaction:



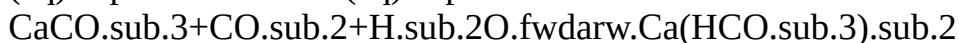
where Ca can be replaced with Mg in case it was present in the carbonate rock.

(22) In the description, reference will be made to “bicarbonates”, meaning thereby the chemical compounds:



(23) In the description, reference will be made to “impurities”, meaning thereby the foreign substances present in the carbonate that do not take part in the chemical reactions in the reactor according to the invention.

(24) In the description, reference will be made to the “contactor”, meaning thereby a reactor in which CO_2 , water and possibly carbonate are reacted according to the reactions:



where Ca can be replaced with Mg in case it was present in the carbonate rock. This reactor is known as “limestone contactor” or “calcite contactor” and is normally used for remineralizing drinking water from reverse osmosis plants and can be with fixed bed (updraft or downdraft), fluidized bed, either pressurised or atmospheric.

(25) In the description, reference will be made to the “ionic mixture”, meaning thereby a mixture where the carbonate, if present, has dissolved and Ca^{2+} or Mg^{2+} are in ionic form. By “ionic mixture” is meant also the mixture of water and CO_2 alone.

(26) In the description, reference will be made to the “buffered ionic mixture”, meaning thereby an ionic mixture in which the pH has been corrected to the desired value by addition of an oxide or a hydroxide.

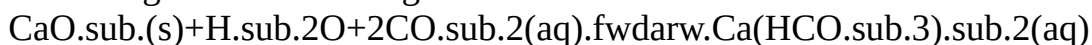
(27) In the description, reference will be made to the “aqueous solution” meaning thereby any aqueous solution as such but also an ionic mixture, buffered ionic mixture or water coming from the sea.

(28) In the description, reference will be made to the “process parameters meter” meaning thereby any device suitable for measuring the chemical parameters such as pH and/or the alkalinity and/or the hardness and/or DIC (dissolved inorganic carbon) and/or TOC (total organic carbon) and/or the conductivity of an aqueous solution but also physical parameters such as temperature and/or flow rate of the fluid and/or pressure and/or turbidity.

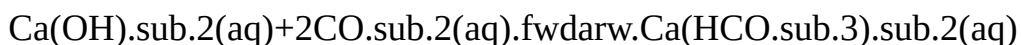
(29) In the description, reference will be made to the “control unit”, meaning thereby any device, preferably electronic, capable of controlling, processing, storing and interpreting information coming from one or more process parameters meters.

(30) In the description, reference will be made to the “dosing device”, meaning thereby any device capable of dosing and introducing a specific amount of material or substance into a system or circuit, such as peristaltic pumps, eccentric screw pumps, augers and extruders. The “dosing device” can be controlled by specific control units thanks to the information coming from process parameters meters.

(31) In the description, reference will also be made to the “apparatus for pH correction”, meaning thereby a reactor in which the ionic mixture is reacted with the oxides or hydroxides coming from the dosing device according to the reactions:

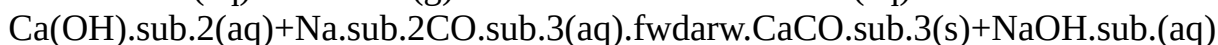


or

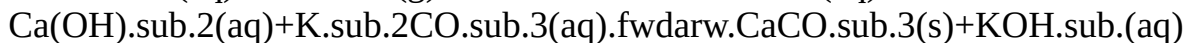


in order to obtain a buffered ionic mixture, where Ca can be replaced by Mg in case it was present in the carbonate rock.

(32) In the description, reference will be made to the “absorber/precipitator”, meaning thereby any device or plant capable of causing, simultaneously or in successive steps, the absorption CO.sub.2-liquid and the precipitation of PCC following one of the following chemical reactions:



or



(where Ca can be replaced with Mg if present in the carbonate)

The absorber/precipitator can be, in a per se known form, a plant formed by washing towers, Venturi scrubbers, filling columns, horizontal scrubbers, the bubble columns integrated with a mixing zone with the buffering substance.

(33) In the description, reference will also be made to the “separator”, meaning thereby any apparatus capable of separating a solid from a liquid such as filters, centrifuges, hydrocyclones or decanters.

(34) In the description, reference will also be made to the “basic solution”, meaning thereby the aqueous solution deriving from the separation of the PCC from the PCC suspension (described below) and with a pH higher than 8: this basic solution can be an aqueous solution of NaOH and Na.sub.2CO.sub.3 or an aqueous solution of KOH and K.sub.2CO.sub.3.

(35) In the description, reference will be made to “Ω.sub.cal”, meaning thereby the calcite saturation state in seawater.

(36) In the description, reference will be made to the “pH”, meaning thereby the measurement scale that indicates the acidity or the basicity of a liquid which is defined by the following formula:

$$\text{pH} = -\log.\text{sub}.\text{10} [\text{H}.\text{sub}.\text{3O}.\text{sup}.\text{+}]$$

(37) In the description, reference will be made to the “alkalinity”, meaning thereby the amount of hydroxides OH.sup.-, carbonates CO.sub.3.sup.2- and bicarbonates HCO.sub.3.sup.2- present in seawater.

(38) In the description, reference will be made to the “hardness”, meaning thereby a value that expresses the total content of Ca.sup.2+ and Mg.sub.2.sup.+ ions present in seawater.

(39) In the description, reference will be made to “bara”, meaning thereby the measurement of the absolute pressure measured in bar, where 1 bar=100000 Pa.

(40) In the description, the comma “,” will be used as a thousands separator and point “.” as a decimal separator.

(41) In the description, reference will also be made to the “buffering substance”, meaning thereby both the oxide and the hydroxide.

(42) In the description, reference will also be made to the “alkaline substance”, meaning thereby both the oxide and the hydroxide.

(43) In the description, reference will also be made to the “atmosphere”, meaning thereby any place in contact with the atmospheric air.

(44) In the description, reference will also be made to the concept of “decarbonized”, meaning thereby a product or a service that does not entail CO.sub.2 emissions into the atmosphere, i.e. where the CO.sub.2 produced by the production process has been sequestered and then stored permanently.

(45) In the description, reference will also be made to the concept of “PCC” (precipitated calcium carbonate) meaning thereby not only the precipitated calcium carbonate formed by calcite, aragonite, vaterite crystals but also the “PMC” (precipitated magnesium carbonate), i.e. the precipitated magnesium carbonate formed by magnesite, barringtonite, nesquehonite and lansfordite crystals ranging in size from 0.01 micron to 50 microns.

(46) In the description, reference will be made to the concept of “PCC suspension”, meaning thereby an aqueous suspension of PCC. The aqueous suspension can be formed by PCC in an aqueous solution of NaOH and Na.sub.2CO.sub.3 or by PCC in an aqueous solution of KOH and K.sub.2CO.sub.3.

(47) In the attached figures, the plant according to the invention is indicated as a whole with reference number **100**.

(48) A first aspect of the invention concerns a plant **100** to improve the efficiency of CO.sub.2 capture and storage using precipitated calcium carbonate PCC. With reference to FIGS. **1** to **6**, the plant **100** comprises an electric calciner **10**, a contactor **20**, an apparatus for pH correction **30**, a dosing device for the buffering substance **40**, an absorber/precipitator **50**, a separator **70** and a PCC dosing device **90** wherein: the electric calciner **10** is suitable for receiving at the inlet a flow of carbonate **110**, a flow of electric energy **120** and for releasing at the outlet at least a flow of carbonic gas **140** and at least a flow of oxide **130**; the flow of oxide **130** is suitable for providing a flow of buffering substance **440**, **460** and a flow of alkaline substance **450**, **470**; the contactor **20** is suitable for receiving at the inlet the flow of carbonic gas **140** released by the electric calciner **10**, a flow of dosed PCC **920** and a flow of water **210**; the contactor **20** is suitable for reacting the CO.sub.2 present in the flow of carbonic gas **140** with the flow of water **210** and the flow of dosed PCC **920** coming from the PCC dosing device **90** according to the reactions:

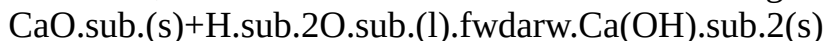
$$\text{CO.sub.2(aq)} + \text{H.sub.2O.sub.(l)} \rightleftharpoons \text{H.sub.2CO.sub.3(aq)} \rightleftharpoons \text{H.sub.(aq).sup.++} + \text{HCO.sub.3(aq).sup.-}$$
 and

$$\text{CaCO.sub.3(s)} + \text{CO.sub.2(aq)} + \text{H.sub.2O.sub.(l)} \rightleftharpoons \text{Ca(HCO.sub.3).sub.2(aq)}$$
 (where Ca can be replaced with Mg if present in the carbonate) and for releasing at the outlet at least a flow of ionic mixture **230** and a flow of non-soluble gases **221**; the apparatus for pH correction **30** is suitable for receiving at the inlet at least a flow of buffering substance **440**, **460** and the flow of ionic mixture **230**; the apparatus for pH correction **30** is suitable for reacting the flow of ionic mixture **230** with the flow of buffering substance **440**, **460** and for releasing at the outlet a flow of buffered ionic mixture **340**; the dosing device for the buffering substance **40** is suitable for receiving at the inlet a flow of buffering substance **130** or a flow of hydroxide **630** and for releasing at the outlet the predetermined flow of buffering substance **440**, **460** to feed the apparatus for pH correction **30** and the flow of alkaline substance **450**, **470** to feed the absorber/precipitator **50**; the absorber/precipitator **50** is suitable for receiving at the inlet the flow of alkaline substance **450**, **470** released by the dosing device for the buffering substance **40**, a flow of atmospheric air **510**, a flow of basic solution **710** and for releasing a flow of lean air **520** and a flow of PCC suspension **550** to feed the separator **70**; the separator **70** is suitable for receiving at the inlet the flow of PCC suspension **550** and for releasing at the outlet at least a flow of PCC **750** available to the PCC dosing device **90** and the flow of basic solution **710**; the PCC dosing device **90** is suitable for receiving at the inlet the flow of PCC **750** and for releasing: a flow of dosed PCC **920** available to feed the contactor **20**; a flow of excess PCC **950** available for any use; and wherein the basic solution **710** is an aqueous solution comprising one or more of: NaOH, Na.sub.2CO.sub.3, KOH, and K.sub.2CO.sub.3.

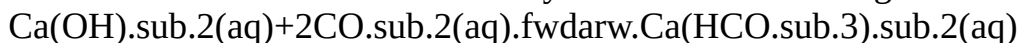
(49) In some embodiments of the plant **100** according to the invention (see for example FIGS. **1**, **2** and **3**), the flow of buffering substance and the flow of alkaline substance are flows of oxide **440**, **450** originating from the electric calciner **10** and the apparatus for pH correction **30** is suitable for reacting the flow of ionic mixture **230** with the flow of oxide **440** according to the reaction:
$$\text{CaO.sub.(s)} + \text{H.sub.2O.sub.(l)} + 2\text{CO.sub.2(aq)} \rightleftharpoons \text{Ca(HCO.sub.3).sub.2(aq)}$$
 and the absorber/precipitator **50** is suitable for reacting the flow of basic solution **710** with the flow of oxide **450**.

(50) In some embodiments of the invention (see for example FIGS. **4**, **5**), the plant **100** further comprises a hydroxide production unit **60** installed between the electric calciner **10** and the apparatus for pH correction **30**, wherein: the hydroxide production unit **60** is suitable for receiving

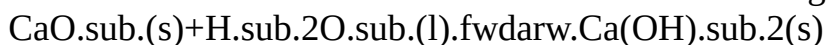
at the inlet at least the flow of oxide **130; 440** originating from the electric calciner **10** and a predetermined flow of water **610**; the hydroxide production unit **60** is suitable for reacting a flow of oxide **130; 440** with the flow of water **610** according to the reaction:



(where Ca can be replaced with Mg if present in the carbonate) and for releasing at the outlet a flow of hydroxide **630; 460**; the apparatus for pH correction **30** is suitable for reacting the flow of ionic mixture **230** with the flow of hydroxide **460** according to the reaction:



(51) In some embodiments of the invention (see for example FIG. 6), the plant **100** further comprises a hydroxide production unit **60** installed between the dosing device for the buffering substance **40** and the absorber/precipitator **50**, wherein: the hydroxide production unit **60** is suitable for receiving at the inlet at least a flow of oxide **450** originating from the electric calciner **10** and the predetermined flow of water **610**; the hydroxide production unit **60** is suitable for reacting the flow of oxide **450** with the flow of water **610** according to the reaction:

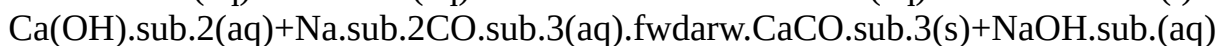


(where Ca can be replaced with Mg if present in the carbonate) and for releasing at the outlet a flow of hydroxide **470**.

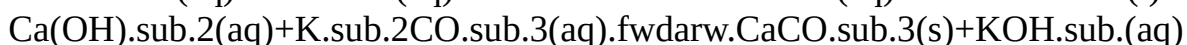
(52) In accordance with an embodiment of the plant **100** according to the invention and with reference to FIG. 2 the plant **100** further comprises a control unit **80** and a process parameters meter **81** for the flow of ionic mixture **230** or for the buffered ionic mixture **340**. The process parameters meter **81** is also suitable for providing the measurement to the control unit **80** and the control unit **80** is suitable for controlling the dosing device for the buffering substance **40** so that it feeds to the apparatus for pH correction **30** the exact amount of flow of buffering substance **440; 460** that is adequate to obtain the buffered ionic mixture **340** with the desired pH.

(53) In accordance with an embodiment of the plant **100** according to the invention and with reference to FIGS. 2 and 3 the plant **100** further comprises a control unit **85**, one or more process parameters meters **86** for the flow of water **210** entering the contactor **20**, one or more process parameters meters **87** for the flow of ionic mixture **230** leaving the contactor **20**. The process parameters meters **86, 87** are further suitable for providing the measurements to the control unit **85** and the control unit **85** is suitable for controlling the PCC dosing device **90** so that it feeds to the contactor **20** the amount of flow of dosed PCC **920** that is adequate to obtain the flow of ionic mixture **230** with the desired pH.

(54) In accordance with an embodiment of the plant **100** according to the invention and with reference to FIG. 4 the plant **100** further comprises a control unit **82** and one or more process parameters meters **83; 84** for the physical/chemical parameters of the flow of atmospheric air **510** and/or for the flow of lean air **520** suitable for measuring CO.sub.2 flow rate and/or concentration. The meters of the physical/chemical parameters of the flow of atmospheric air **510** and/or of the flow of lean air **520** are also suitable for providing the measurement to the control unit **82** which is suitable for controlling the dosing device for the buffering substance **40** so that it feeds to the absorber/precipitator **50** the exact amount of flow of alkaline substance **450; 470** that is adequate to optimize the production of a flow of PCC suspension **550** respectively according to the reactions:



or the reactions:



(where Ca can be replaced with Mg if present in the carbonate)

or is suitable for controlling the flow of atmospheric air **510** so that the absorber/precipitator **50** has the adequate amount of CO.sub.2 to react the amount of flow of alkaline substance **450; 470** fed to the absorber/precipitator **50** according to the reactions described above to optimize the production

of a flow of PCC suspension **550**.

(55) A skilled person will certainly be able to understand that the size of the contactor **20** depends on the flow rates of the flow of carbonic gas **140**, of the flow of water **210**, of the flow of dosed PCC **920** and on the kinetics of the chemical reactions that take place. The ratios between the flow rates of the flow of carbonic gas **140**, the flow of water **210** and the flow of dosed PCC **920** are established with physical-chemical criteria that allow the completion of the reactions:

$\text{CO.sub.2(aq)} + \text{H.sub.2O.sub.(l)} \rightleftharpoons \text{H.sub.2CO.sub.3(aq)} \rightleftharpoons \text{H.sub.(aq)} + \text{HCO.sub.3(aq).sup.-}$

and

$\text{CaCO.sub.3(s)} + \text{CO.sub.2(aq)} + \text{H.sub.2O.sub.(l)} \rightleftharpoons \text{Ca(HCO.sub.3).sub.2(aq)}$

(where Ca can be replaced with Mg if present in the carbonate) avoiding the precipitation of carbonates in the apparatus for pH correction **30** during the insertion of the flow of buffering substance **440**; **460** due to too high Ω .sub.cal.

(56) A skilled person will therefore be able to agree that the necessary contact time between the flow of water **210**, the flow of carbonic gas **140** and possibly the flow of dosed PCC **920** is the main parameter that allows sizing the contactor **20**. If for a contact time of 10 s, at a flow rate of the flow of carbonic gas **140** of 1 kg/s, it was needed 1 m.sup.3/s of flow of water **210**, it means that the contactor **20** must have a size of about 10 m.sup.3; whereas if a flow rate of the flow of carbonic gas **140** was 10 kg/s, 10 m.sup.3/s of water would be needed and the size of the contactor would be about 100 m.sup.3.

(57) In accordance with an embodiment of the plant **100**, the amount of the flow of dosed PCC **920** introduced into the contactor **20** is null and the contactor **20** has a volume that allows a minimum contact time of the water with the flow of carbonic gas **140** of 10 s, preferably comprised between 60 s and 180 s and that allows to have a partial pressure of CO.sub.2 greater than 0.1 bara, preferably comprised between 0.2 bara and 2 bara.

(58) In a per se known form and in accordance with experimental results and with the scientific literature, the time for CO.sub.2 to fully hydrate in water to form carbonic acid H.sub.2CO.sub.3 according to the reaction:

$\text{CO.sub.2(aq)} + \text{H.sub.2O.sub.(l)} \rightleftharpoons \text{H.sub.2CO.sub.3(aq)} \rightleftharpoons \text{H.sub.(aq).sup.++} + \text{HCO.sub.3(aq).sup.-}$

has a characteristic time ranging from a few seconds to a few minutes.

(59) It should be noted here that the buffering substance fed to the apparatus for pH correction **30**, can be a flow of oxide (indicated with **440**; FIGS. **1**, **2**, **3** and **6**) or can be a flow of hydroxide (indicated with **460**; FIGS. **4** and **5**).

(60) It should be noted here that the buffering substance fed to the dosing device for the buffering substance **40** can be both a flow of oxide (indicated with **130**; FIGS. **1**, **2**, **3**, **5** and **6**) released by the electric calciner **10** and a flow of hydroxide (indicated with **630**; FIG. **4**) released by the hydroxide production unit **60**, and that the buffering substance released by the dosing device for the buffering substance **40** can be both a flow of oxide (indicated with **440** and **450**) and a flow of hydroxide (indicated with **460** and **470**).

(61) It should be noted here that the buffering substance fed to the absorber/precipitator **50**, can be a flow of oxide (indicated with **450**; FIGS. **1**, **2**, **3** and **5**) or can be a flow of hydroxide (indicated with **470**; FIGS. **4** and **6**).

(62) A second aspect of the invention concerns a method to improve the efficiency of CO.sub.2 capture and storage using precipitated calcium carbonate. The method according to the invention comprises the steps of: providing an electric calciner **10**; feeding to the electric calciner **10** a flow of electric energy (**120**) and a flow of carbonate **110** to obtain the calcination of the flow of carbonate **110** according to the reaction:

$\text{CaCO.sub.3(s)} \rightleftharpoons \text{CaO.sub.(s)} + \text{CO.sub.2(g)}$

(where Ca can be replaced with Mg if present in the carbonate); releasing at the outlet from the

electric calciner **10** a flow of carbonic gas **140** and a flow of oxide **130**; providing the contactor **20**; conveying the flow of carbonic gas **140** to the contactor **20**; providing a dosing device for the buffering substance **40**; conveying the flow of oxide **130** or a flow of hydroxide **630** to the dosing device for the buffering substance **40**; from the dosing device for the buffering substance **40** obtaining a flow of buffering substance **440**; **460** and a flow of alkaline substance **450**; **470**; feeding to the contactor **20** the flow of carbonic gas **140** produced by the electric calciner **10**, a predetermined flow of water **210** and a flow of dosed PCC **920** to obtain a flow of ionic mixture **230** via reactions:

$\text{CO.sub.2(aq)} + \text{H.sub.2O.sub.(l)} \rightleftharpoons \text{H.sub.2CO.sub.3(aq)} \rightleftharpoons \text{H.sub.(aq)} + \text{HCO.sub.3(aq).sup.-}$

e

$\text{CaCO.sub.3(s)} + \text{CO.sub.2(aq)} + \text{H.sub.2O.sub.(l)} \rightleftharpoons \text{Ca(HCO.sub.3).sub.2(aq)}$ (where Ca can be replaced with Mg if present in the carbonate) releasing at the outlet from the contactor **20** the flow of ionic mixture **230**; conveying the flow of ionic mixture **230**; conveying the flow of buffering substance **440**; **460**; providing an apparatus for pH correction **30**; feeding the apparatus for pH correction **30** with the flow of ionic mixture **230** and with the predetermined flow of buffering substance **440**; **460**; releasing at the outlet of the apparatus for pH correction **30** a flow of buffered ionic mixture **340**; providing an absorber/precipitator **50**; feeding the flow of alkaline substance **450**; **470** to the absorber/precipitator **50**; feeding a flow of atmospheric air **510** to the absorber/precipitator **50** so that the reaction of the CO.sub.2 present in it can take place with the flow of alkaline substance **450**; **470** following the reactions:

$2\text{NaOH.sub.(aq)} + \text{CO.sub.2(aq)} \rightleftharpoons \text{Na.sub.2CO.sub.3(aq)} + \text{H.sub.2O.sub.(l)}$
 $\text{Ca(OH).sub.2(aq)} + \text{Na.sub.2CO.sub.3(aq)} \rightleftharpoons \text{CaCO.sub.3(s)} + \text{NaOH.sub.(aq)}$

or the reactions:

$2\text{KOH.sub.(aq)} + \text{CO.sub.2(aq)} \rightleftharpoons \text{K.sub.2CO.sub.3(aq)} + \text{H.sub.2O.sub.(l)}$
 $\text{Ca(OH).sub.2(aq)} + \text{K.sub.2CO.sub.3(aq)} \rightleftharpoons \text{CaCO.sub.3(s)} + \text{KOH.sub.(aq)}$

(where Ca can be replaced with Mg if present in the carbonate); releasing at the outlet from the absorber/precipitator **50** a flow of PCC suspension **550** and a flow of lean air **520**; providing a separator **70**; feeding the flow of PCC suspension **550** to the separator **70** so that a flow of PCC **750** can be separated from a flow of basic solution **710**; providing a PCC dosing device **90**; feeding the flow of PCC **750** to the PCC dosing device **90**; releasing at the outlet from the PCC dosing device **90** the predetermined flow of dosed PCC **920** and a predetermined flow of excess PCC **950**; feeding the predetermined flow of dosed PCC **920** to the contactor **20** so that the reaction can take place:

$\text{CaCO.sub.3} + \text{CO.sub.2} + \text{H.sub.2O} \rightleftharpoons \text{Ca(HCO.sub.3).sub.2}$

(where Ca can be replaced with Mg if present in the carbonate); making available the predetermined flow of excess PCC **950**.

(63) In accordance with some embodiments of the invention, the flow of buffering substance fed to the apparatus for pH correction **30** is a flow of oxide **440**.

(64) In accordance with some embodiments of the invention, the flow of buffering substance fed to the absorber/precipitator **50** is a flow of oxide **450**.

(65) In accordance with some embodiments of the invention, the method further comprises the steps of: providing a hydroxide production unit **60**; feeding the flow of oxide **130**; **440** and a predetermined flow of water **610** to the hydroxide production unit **60** so that the reaction can take place:

$\text{CaO.sub.(s)} + \text{H.sub.2O.sub.(l)} \rightleftharpoons \text{Ca(OH).sub.2(s)}$ (where Ca can be replaced with Mg if present in the carbonate); releasing at the outlet from the hydroxide production unit **60** at least a flow of hydroxide **630**; **470**.

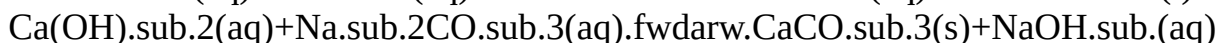
(66) In accordance with such embodiments of the method, the flow of buffering substance fed to the apparatus for pH correction **30** can be a flow of hydroxide **460**.

(67) In accordance with such embodiments of the method, the flow of alkaline substance feeding the absorber/precipitator **50** can be a flow of hydroxide **470**.

(68) In accordance with some embodiments of the invention, the method further comprises the step of: recirculating the flow of basic solution **710** released by the separator **70** to the absorber/precipitator **50**.

(69) In accordance with some embodiments of the invention, the method further comprises the steps of: providing a control unit **80** and a process parameters meter **81** for the flow of ionic mixture **230** or for the buffered ionic mixture **340**; providing the measurement of the process parameters meter **81** to the control unit **80**; controlling the dosing device for the buffering substance **40** by means of the control unit **80** so that it feeds to the apparatus for pH correction **30** the exact amount of flow of buffering substance **440**; **460** to obtain a buffered ionic mixture **340** with a desired pH.

(70) In accordance with some embodiments of the invention, the method further comprises the steps of: providing a control unit **82** and one or more process parameters meters **83**; **84** for the flow of atmospheric air **510** and/or for the flow of lean air **520**; providing the measurement of the process parameters meters **83**; **84** to the control unit **82**; controlling the dosing device for the buffering substance **40** by means of the control unit **82** so that it feeds to the absorber/precipitator **50** the amount of the flow of alkaline substance **450**; **470** that is adequate to optimize the production of a flow of PCC suspension **550** respectively according to the reactions:



or the reactions:



$\text{Ca(OH).sub.2(aq)} + \text{K.sub.2CO.sub.3(aq).fwdarw.CaCO.sub.3(s)} + \text{KOH.sub.(aq)}$ (where Ca can be replaced with Mg if present in the carbonate) controlling the flow of atmospheric air **510** so that the absorber/precipitator **50** has the adequate amount of CO.sub.2 to react the amount of flow of alkaline substance **450**; **470** fed to the absorber/precipitator **50** according to the reactions described above to optimize the production of a flow of PCC suspension **550**.

(71) In accordance with some embodiments of the invention, the method further comprises the steps of: providing a control unit **85** and one or more process parameters meters **86**; **87** a flow of water **210** entering the contactor **20** and/or for the flow of ionic mixture **230** and of the buffered ionic mixture **340**; providing the measurement of the process parameters meters **86**; **87** to the control unit **85**; controlling the PCC dosing device **90** and the dosing device for the buffering substance **40** by means of the control unit **85** so that it feeds the contactor **20** respectively with the correct amount of the flow of dosed PCC **920**.

(72) With reference to FIGS. **1**, **2**, **3**, **4**, **5**, **6** a skilled person will be able to see that the electric calciner **10** is fed with the flow of carbonate **110** and a flow of electric energy **120** and releases a flow of oxide **130** and the flow of carbonic gas **140**. The electric calciner **10** is fed by electric energy to generate the heat necessary for calcination. The electric energy can be used in electrical resistors, microwave generators, plasma torches or induction systems.

(73) In a per se known form, the calcination of the flow of carbonate **110** takes place according to the reaction:



(where Ca can be replaced with Mg if present in the carbonate), at temperatures comprised between about 600° C. (MgCO.sub.3) and 1200° C. (CaCO.sub.3) and at intermediate values as a function of the chemical composition of the carbonate which can also be a $\text{CaMg(CO.sub.3).sub.2}$ dolomite and of the chemical composition of the atmosphere in the calciner.

(74) In a per se known form, the calcination reaction is an endothermic reaction requiring 118 KJ/mol of heat in the case of calcination of MgCO.sub.3 and 183 KJ/mol in the case of CaCO.sub.3 .

(75) A skilled person can understand that the CO.sub.2 produced by a controlled-atmosphere electric calcination generates a flow of carbonic gas **140** formed by CO.sub.2 and traces of non-soluble gases **221** possibly entered with the flow of carbonate **110** inside the electric calciner **10** or gases intentionally fed to the electric calciner **10** to improve the process conditions.

(76) With reference to the embodiment of FIGS. **1, 2, 3, 4, 5, 6**, the plant **100** according to the invention comprises the contactor **20**.

(77) In a per se known form, the contactor **20** uses a flow of water **210** and a flow of dosed PCC **920** as a medium to absorb CO.sub.2 from the flow of carbonic gas **140** and to form the flow of ionic mixture **230** according to the reaction:

$$\text{CO.sub.2(g)} + \text{CaCO.sub.3(s)} + \text{H.sub.2O} \Rightarrow \text{Ca.sup.2+.sub.(aq)} + 2\text{HCO.sub.3.sub.-.sub.(aq)}$$
where the Ca can be replaced by Mg if present in the flow of dosed PCC **920**.

(78) In a per se known form, there are different types of contactors (limestone contactors or calcite contactors), generally used for the re-mineralization of drinking water downstream of desalination treatments.

(79) In a per se known form, the permanent storage of CO.sub.2 in the form of bicarbonates in the sea using contactors has been proposed in several scientific articles and patents, among which it is worth mentioning the U.S. Pat. No. 6,890,497 B2 entitled "Method for extracting and sequestering carbon dioxide" and the Italian patent application 10202000000037 entitled "Impianto e metodo per il sequestro di CO.sub.2 con un condotto reattore a pressione crescente" ("Plant and method for sequestering CO.sub.2 with a growing pressure reactor conduit").

(80) In a per se known form, the contactors used for the re-mineralization of water or whose use has been proposed for the permanent storage of CO.sub.2 in the form of bicarbonates must keep the water that is in contact with the carbonate sufficiently under-saturated, with an Ω_{cal} preferably comprised between 0.01 and 0.6, to allow a dissolution kinetics of the carbonate that is sufficiently rapid and acceptable for an industrial plant. For this reason, the commercial contactors use an excess of CO.sub.2 in the water, a pH generally comprised between 5 and 6, and a final degassing of the CO.sub.2 to bring the pH of the water back to values above 7.

(81) In a per se known form, the technologies for CO.sub.2 storage by means of bicarbonates in the sea have, as mentioned above, the discharge of an acid effluent (pH comprised between 6 and 7), with still a significant amount of CO.sub.2 not reacted with the carbonate. This fact turns out to be environmentally harmful if the discharge of the effluent takes place in the depths of the sea where there is no possibility of degassing the CO.sub.2 or it is very inefficient (CO.sub.2 storage efficiencies of about 50%) where the discharge takes place on the surface with degassing of the residual CO.sub.2.

(82) A skilled person will understand that by neutralizing such acidity present in the flow of ionic mixture **230** with a flow of buffering substance **440** or **460**, one could discharge into the sea an effluent with the same natural pH as the seawater and store all the residual CO.sub.2 in the form of bicarbonates according to the reaction:

$$550.\text{sub.2(aq)} + 2\text{CO.sub.2(aq)} \xrightarrow{\text{Ca}} \text{Ca(HCO.sub.3).sub.2(aq)}$$

(where Ca can be replaced with Mg if present in the carbonate). The neutralization of this acidity eliminates the environmental issues and achieves a CO.sub.2 storage efficiency of about 100%.

(83) In a per se known form, the reaction of Ca(OH).sub.2 (where Ca can be replaced by Mg if present in the carbonate) with seawater is a complex reaction because of the presence of other chemical elements and therefore it turns out that for each mole of Ca(OH).sub.2 one can neutralize about 1.50-1.79 moles of CO.sub.2 instead of the 2 moles provided for by the equation:

$$\text{Ca(OH).sub.2(aq)} + 2\text{CO.sub.2(aq)} \xrightarrow{\text{Ca}} \text{Ca(HCO.sub.3).sub.2}$$

(84) (where Ca can be replaced with Mg if present in the carbonate)

(85) With reference to the embodiment of FIGS. **1, 2, 3, 4, 5** and **6**, the plant **100** according to the invention comprises the apparatus for pH correction **30** wherein the flow of ionic mixture **230** is mixed with a predetermined amount of flow of buffering substance **440** or **460** sufficient to obtain

the desired pH of the buffered ionic mixture **340**.

(86) A skilled person can easily understand that the composition of the flow of ionic mixture **230** released by the contactor **20** may contain impurities that are convenient to be filtered from the flow of ionic mixture **230** by means of appropriate filters (not shown in the figure) placed between the mixer **20** and the apparatus for pH correction **30** or downstream of the apparatus for pH correction **30**.

(87) With reference to the embodiment of FIG. 2, the plant **100** according to the invention is provided with a process parameters meter **81** and with a control unit **80** for the management of the dosing device for the buffering substance **40** that allows to feed to the apparatus for the correction of the pH **30** the correct amount of flow of oxide **440** or hydroxide **460**. In the case of the flow of hydroxide **460**, the dosing device for the buffering substance **40** may be a dosing pump as the flow of hydroxide **460** may be fed to the apparatus for pH correction **30** in the form of a slurry or of ionic solution.

(88) A skilled person will certainly be able to agree that the maximum amount of CO.sub.2 captured and stored from a flow of atmospheric air **510** in the absorber/precipitator **50** is the greater, the greater the amount of carbonate of the flow of dosed PCC **920** dissolved in the contactor **20** is as the amount of the flow of buffering substance **440**; **460** necessary to feed the apparatus for pH correction **30** is smaller. Consequently, the amount of the flow of alkaline substance **450**; **470** available to the absorber/precipitator **50** will be greater.

(89) A skilled person will certainly be able to understand that in order to maximize the amount of CO.sub.2 captured from a flow of atmospheric air **510** it is necessary to maximize the amount of the flow of dosed PCC **920** dissolved in the contactor **20**.

(90) In a per se known form, the dissolution of the flow of dosed PCC **920** in the contactor **20** depends on the amount of water and on the pH according to the equilibrium curve presented in FIG. 7 which refers to the complete dissolution of 2270 kg of CaCO.sub.3 in seawater in the presence of 1000 kg of CO.sub.2.

(91) A skilled person will certainly be able to calculate, with the information available in the literature, the dissolution rate of the carbonate as a function of the amount of water and of the pH, the sizes of the contactor **20** and the sizes and specific surface of the carbonate crystals that make up the flow of dosed PCC **920**.

(92) A skilled person will certainly be able to agree that the dissolution rate of the carbonate increases proportionally to the increase in the surface of the carbonate particles and that therefore the use, with the same mass, of small-sized carbonate particles with a high area/volume ratio increases the surface where the dissolution reactions take place and hence the dissolution rate compared to the use of large-sized particles.

(93) A skilled person will certainly be able to verify that the contact times between the flow of water **210** and the carbonate inside the contactor **20** necessary for a complete dissolution of the carbonate depend on the sizes of the carbonate itself and on the ratio between the amounts of CO.sub.2 present in the flow of carbonic gas **140** and the amount of the flow of water **210**.

(94) A skilled person will certainly be able to verify that by using a ratio between the mass flow of the flow of water **210** and CO.sub.2 present in the flow of carbonic gas **140** of less than 2000:1, and a carbonate particle of less than 1 micron, the minimum contact time between the flow of water **210** and the carbonate inside the contactor **20** that are necessary to have a residual amount of CO.sub.2 in the flow of ionic mixture **230** of about 50% are less than 1,000 s while for a particle greater than 10 microns, the minimum contact time between the flow of water **210** and the carbonate inside the contactor **20** necessary to have a residual amount of CO.sub.2 in the flow of ionic mixture **230** of about 50% are higher than 50,000 s.

(95) A skilled person will therefore certainly understand that, in order to contain the sizes and the costs of the contactor **20**, it is convenient to use small-sized carbonate particles, smaller than 5 microns and preferably comprised between 0.1 and 1 micron and to leave a residual amount of

CO.sub.2 in the flow of ionic mixture **230** higher than 50%.

(96) A skilled person will therefore certainly understand that, with the same size of the contactor **20**, it is possible to dissolve more carbonate if the particle is smaller than 1 micron compared to the case in which it is greater than 10 microns.

(97) A skilled person will certainly understand the advantage of using in the contactor **20** the micron or submicron-sized carbonate crystals obtained from a PCC precipitation process in the absorber/precipitator **50** instead of particles of carbonate ground by mechanical processes.

(98) A skilled person will certainly be able to agree that the micron-sized carbonate grinding process involves considerable investments in machinery which, in addition to considerable energy consumptions, entails high maintenance costs.

(99) In a per se known form and with reference to the scientific article by Rinder et al (2021) —“The influence of particle size on the potential of enhanced basalt weathering for carbon dioxide removal-Insights from a regional assessment. Journal of Cleaner Production”, the energy consumption for the grinding of carbonate up to the size of 1 micron is about 560 Kwh/ton while, as will be explained later, the energy consumption for the production of 1 ton of PCC produced using an industrial flow of atmospheric air **510** with 14 molar % of CO.sub.2 is about 100 Kwh/ton.

(100) A skilled person will certainly be able to agree that, having available a flow of alkaline substance **450**; **470**, an absorber/precipitator **50**, a separator **70** and a flow of atmospheric air **510** according to the invention, the production of precipitated carbonate crystals such as the flow of dosed PCC **920** with micron or submicron sizes is more energetically convenient and from a plant point of view easier than installing a mechanical grinding plant.

(101) In a per se known form and as already anticipated above, the dissolution rate of the carbonate decreases asymptotically to zero as equilibrium conditions are approached and therefore, in order to maintain the sizes of the contactor **20** within commercially acceptable limits, it is necessary to maintain process conditions away from the equilibrium. Consequently, it is reasonable to use in the contactor **20** a pH of the water preferably comprised between 5 and 6.5, which corresponds to a residual CO.sub.2 higher than 50% of the CO.sub.2 initially present in the carbonic gas **140** in the ionic mixture **230** with amount of water **210** from 500 m.sup.3/ton.sub.CO2 to 4000 m.sup.3/ton.sub.CO2.

(102) A skilled person can certainly understand that the flow of ionic mixture **230** released by the contactor **20**, if not subjected to a CO.sub.2 degassing with loss of storage efficiency, generally has a pH comprised between 5 and 6.5, lower than the pH of the sea which is about pH 8.

(103) A skilled person will certainly understand that, in order to avoid acidifying the sea by releasing a flow of acidic ionic mixture **230**, it is necessary to buffer the pH with a basic substance such as a flow of oxide **440** or of hydroxide **460**.

(104) A skilled person will then understand that the chemical reactions that take place in the apparatus for pH correction **30** are fundamental for the storage in the form of calcium bicarbonates of the residual CO.sub.2 in the ionic mixture **230** and are not a trivial addition of alkaline substance for a small pH correction.

(105) A skilled person will easily be able to verify that with the same mass ratio between the flow of water **210** and the CO.sub.2 present in the flow of carbonic gas **140** and by decreasing the quantities of the flow of dosed PCC **920** used in the contactor **20** according to the invention, the necessary contact time between the flow of water **210**, the CO.sub.2 and the flow of dosed PCC **920**, progressively decreases up to reaching a few seconds necessary only for the hydration of the CO.sub.2 in the particular case in which the flow of dosed PCC **920** used is null. A skilled person will certainly understand that the choice of the contact time between the flow of water **210**, the CO.sub.2 present in the flow of carbonic gas **140** and the flow of dosed PCC **920** or the choice of not using the flow of dosed PCC **920** to buffer the CO.sub.2 present in the carbonic gas **140** but only the flow of buffering substance **440** or **460** are choices of economical type. In fact, by

decreasing the amount of the flow of dosed PCC **920** used with the same CO.sub.2 present in the flow of carbonic gas **140** and the flow of water **210**, the sizes and the plant cost of the contactor **20** are decreased to the detriment of a greater consumption of electric energy necessary to produce greater amounts of flow of oxide **440** or hydroxide **460** that are necessary to buffer the CO.sub.2 present in the flow of ionic mixture **230** but with greater amounts of flow of excess PCC **950** available for sale and smaller amounts of CO.sub.2, present in the flow of lean air **520**, captured and stored.

(106) With reference to FIG. **8**, a skilled person can certainly understand the simplified mass and energy balance of a particular plant **100** for CO.sub.2 capture and storage by PCC production according to the invention wherein: the electric calciner **10** is fed by 2,270 kg of flow of carbonate **110** (CaCO.sub.3) and 2,000 kw.sub.e of a flow of electric energy **120** and releases at the outlet 1,000 kg of flow of carbonic gas **140** (CO.sub.2) and 1,271 kg of flow of oxide **130** (CaO); the contactor **20** is fed by 1,000 m.sup.3 of flow of water **210** (considered with a density of 1 kg/dm.sup.3), by 1,135 kg of flow of dosed PCC **920** and 1,000 kg of flow of carbonic gas **140** (CO.sub.2) and releases, at the outlet, after a residence time of 600 s at an average pressure of 2 bara, 1,002,135 kg of flow of ionic mixture **230** in which there are still present 500 kg of CO.sub.2 and a pH of about 6.2; the hydroxide production unit **60** is fed by 1,271 kg of flow of oxide **130** released by the electric calciner **10** and by a predetermined flow of water (not shown) and releases at the outlet 1,680 kg of flow of hydroxide **630** Ca(OH).sub.2; the dosing device for the buffering substance **40** receives at the inlet 1,680 kg of flow of hydroxide **630** released by the hydroxide production unit **60** and releases at the outlet 560 kg of flow of hydroxide **460** to the apparatus for pH correction **30** and 1,100 kg of flow of hydroxide **470** available for feeding the absorber/precipitator **50**; the apparatus for pH correction **30** receives at the inlet 1,002,130 kg of flow of ionic mixture **230** released by the contactor **20** and 560 kg of flow of hydroxide **460** released by the dosing device for the buffering substance **40** and releases 1,002,690 kg of buffered ionic mixture **340** with pH of 8 exploiting the reaction:

$$\text{Ca(OH).sub.2(aq)} + 2\text{CO.sub.2(aq)} \rightarrow \text{Ca(HCO.sub.3).sub.2(aq)}$$

(where Ca can be replaced with Mg if present in the carbonate). In the case of seawater, as a function of its chemical composition, 1 mole of Ca(OH).sub.2 neutralizes 1.50-1.79 moles of CO.sub.2. In the case under examination, a ratio of 1.5 moles of CO.sub.2 per mole of Ca(OH).sub.2 is considered; the absorber/precipitator **50** receives at the inlet 1,100 kg of flow of hydroxide **470** and 1,059,680 kg of a flow of atmospheric air **510** containing 0.0412 mol % of CO.sub.2, 146,523 kg of basic solution **710** and releases at the outlet 1,059,003 kg of flow of lean air **520** and 148,000 kg of a flow of PCC suspension **550**; the separator **70** receives at the inlet 148,000 kg of flow of PCC suspension **550** and releases at the outlet 1,477 kg of flow of PCC **750**; and the PCC doser **90** receives at the inlet 1,477 kg of flow of PCC **750** and releases at the outlet 1,100 kg of flow of dosed PCC **920** to feed the contactor **20** and 377 kg of commercially available flow of excess PCC **950**.

(107) Still with reference to FIG. **8**, a skilled person can certainly calculate the energy necessary for the ventilation of the flow of atmospheric air **510** from 1 bara to 2 bara (pressure necessary to generate bubbles in a 10-meter-high bubble absorber/precipitator) which, for the case in question is 55 kWh.sub.e.

(108) Still with reference to FIG. **8**, a skilled person will be able to calculate the energy necessary for the recirculation of the flow of basic solution **710** between the absorber/precipitator **50** and the separator **70** which, in the particular case, turns out to be 35 kWh.sub.e.

(109) Still with reference to FIG. **8**, a skilled person will be able to calculate the energy necessary for pumping the flow of water **210** which, in the particular case, turns out to be 60 kWh.sub.e.

(110) Still with reference to FIG. **8**, a skilled person will be able to notice that the total electrical consumption (compression of the flow of atmospheric air **510**, water pumping between the separator **70** and the absorber/precipitator **50** and possibly other minor consumptions not shown in

the drawing) to produce 1,135 kg of flow of dosed PCC **920** and 350 kg of excess PCC flow **950** with a size of 1 micron amount to about 100 kWh.sub.e whilst, as written above, if one had to grind the carbonate to the size of 1 micron, one would have an electrical consumption of 635 kWh.sub.e.

(111) As a skilled person can understand, using the flow of dosed PCC **920** instead of mechanically micronized carbonate for capturing and storing CO.sub.2 present in the flow of atmospheric air **510** entails a considerable increase in energy efficiency of the plant according to the invention.

(112) Still with reference to FIG. **8**, a skilled person can well understand that there may also be the production of a certain amount of flow of excess PCC **950** usable for other uses as a function of the process parameters used in the contactor **20** and hence of the amount of the flow of dosed PCC **920** used.

(113) A skilled person may understand that in the plant according to the invention it is possible to maximise the capture and storage of the CO.sub.2 present in the flow of atmospheric air **510** in the absorber/precipitator **50** by sending all the flow of PCC suspension **550** produced in the absorber/precipitator **50** to the contactor **20** as a flow of dosed PCC **920**. Conversely, it is possible to maximize the production of a flow of excess PCC **950** by bringing to zero the amount of the flow of dosed PCC **920** sent to the contactor **20**.

(114) As a skilled person can well understand from the above reported example, the flow of excess PCC **950** available for other uses is a completely decarbonized PCC in case the flow of electric energy **120** feeding the calciner and the electric energy (not shown in the example) feeding the extraction, the transport and the crushing of the carbonate and the pumping of the water were completely renewable; conversely, the flow of excess PCC **950** would be decarbonized except for the share that is part of the emissions due to the energy contribution mentioned above.

(115) As a skilled person can understand, the flow of excess PCC **950**, can be conveniently used in various industrial sectors such as those of paper, plastics, rubber and food for both human and animal consumption.

(116) A skilled person can certainly understand that the plant according to the invention allows to directly capture the atmospheric CO.sub.2 by storing it in calcium carbonate and generating negative emissions.

(117) As the skilled person can well calculate using market values, the cost per ton of decarbonized PCC depends mainly on the cost of the carbonate and of the electric energy while the plant and labour costs have a marginal impact on the final result. In particular, about 2100 kWh.sub.e of electric energy and 2270 kg of carbonate are needed to produce 1 ton of decarbonized PCC. If the cost of carbonate were 7.5 €/ton and the cost of renewable electric energy were 30 €/MWh (it is the LCOE—Levelized Cost Of Energy of wind energy), the variable cost of the flow of PCC **750**, in the case analysed in FIG. **8**, would be 225 €/ton.sub.PCC from which one should subtract the benefit obtained from the capture and storage of quantifiable 1.95 tons of CO.sub.2 present in the flow of atmospheric air **510**, at 80 €/ton.sub.CO2, in 156 €/ton, resulting in a final variable cost of about 69 €/ton.sub.PCC.

(118) A skilled person, again for the case analysed in FIG. **8**, could therefore calculate that the installation costs of the electric calciner, the contactor, the dosing device, the carbonate mill, the civil works and the services have an impact of about €15/ton on the flow of excess PCC **950**, while personnel costs turn out to be negligible.

(119) Still with reference to FIG. **8**, a skilled person will then be able to calculate that the final cost of a ton of flow of excess PCC **950** is €84/ton.sub.CO2. Considering that a ton of flow of excess PCC **950** can be sold on the market at values higher than 300 €/ton.sub.PCC, the plant according to the invention allows to have an economic margin equal to or greater than about 200 €/ton.sub.PCC which corresponds to a margin of about 100 €/ton.sub.CO2 captured and sequestered in the flow of atmospheric air **510**.

(120) As a skilled person can understand, the plant according to the invention allows to generate revenues from the capture and permanent storage of CO.sub.2 present in a flow of atmospheric air

510, being much more competitive than the plants of CO.sub.2 capture and storage present on the market that consider CO.sub.2 capture and storage as a cost.

(121) As a skilled person can certainly understand, the process for capturing and storing the CO.sub.2 present in a flow of atmospheric air **510** according to the invention allows to permanently store CO.sub.2 both in the sea in the form of bicarbonates and in the form of carbonates at a cost that is competitive with the cost of geological CCS.

(122) As a person will certainly be able to understand, the availability of carbonate, water and renewable electric energy are not limitations to produce enough decarbonized PCC according to the invention to permanently store all the anthropogenic CO.sub.2 and to generate the negative CO.sub.2 emissions necessary to comply with the 2015 Paris agreements.

(123) As the skilled person can well conclude, the method and the plant according to the invention allow to produce decarbonized PCC using exhaust gases of industrial plants or atmospheric air contributing to the decarbonization of industrial sectors where it is difficult to reduce CO.sub.2 and to generate negative emissions.

(124) It is clear that the specific characteristics are described in relation to different embodiments of the plant and of the method by way of non-limiting example. Obviously, in order to satisfy contingent and specific needs, a person skilled in the art may make numerous modifications and variants to the plant and method according to the present invention, all nevertheless contained within the scope of protection, as defined by the following claims.

Claims

1. A plant to improve the efficiency of CO.sub.2 capture and storage using precipitated calcium carbonate PCC, the plant comprising: an electric calciner, a contactor, an apparatus for pH correction, a dosing device for the buffering substance, an absorber/precipitator, a separator, and a PCC dosing device, wherein: the electric calciner is configured for receiving at the inlet a flow of carbonate, a flow of electric energy and for releasing at the outlet at least a flow of carbonic gas and at least a flow of oxide; the flow of oxide is configured for providing a flow of buffering substance, and a flow of alkaline substance; the contactor is configured for receiving at the inlet the flow of carbonic gas released by the electric calciner, a flow of dosed PCC and a flow of water; the contactor is further configured for reacting the CO.sub.2 present in the flow of carbonic gas with the flow of water and the flow of dosed PCC coming from the PCC dosing device according to the reactions:

$$\text{CO.sub.2(aq)} + \text{H.sub.2O.sub.(l)} \rightleftharpoons \text{H.sub.2CO.sub.3(aq)} \rightleftharpoons \text{H.sub.(aq).sup.++} + \text{HCO.sub.3(aq).sup.-}$$
 and

$$\text{CaCO.sub.3(s)} + \text{CO.sub.2(aq)} + \text{H.sub.2O} \rightarrow \text{Ca(HCO.sub.3).sub.2(aq)}$$
 and for releasing at the outlet at least a flow of ionic mixture and a flow of non-soluble gases; the apparatus for pH correction is configured for receiving at the inlet at least a flow of buffering substance and the flow of ionic mixture; the apparatus for pH correction is configured for reacting the flow of ionic mixture with the flow of buffering substance and for releasing at the outlet a flow of buffered ionic mixture; the dosing device for the buffering substance is configured for receiving at the inlet a flow of buffering substance or a flow of hydroxide and for releasing at the outlet the predetermined flow of buffering substance to feed the apparatus for pH correction and the flow of alkaline substance to feed the absorber/precipitator; the absorber/precipitator is configured for receiving at the inlet the flow of alkaline substance released by the dosing device for the buffering substance, a flow of atmospheric air, a flow of basic solution and for releasing a flow of lean atmospheric air and a flow of PCC suspension to feed the separator; the separator is configured for receiving at the inlet the flow of PCC suspension and for releasing at the outlet at least a flow of PCC available to the PCC dosing device and the flow of basic solution; the PCC dosing device is configured for receiving at the inlet the flow of PCC and for releasing: a flow of dosed PCC available to feed the contactor; the

flow of excess PCC available for any use; and wherein the basic solution is an aqueous solution comprising one or more of: NaOH, Na_2CO_3 , KOH, and K_2CO_3 .

2. The plant according to claim 1, wherein the flow of buffering substance and the flow of alkaline substance are flows of oxide originating from the electric calciner and the apparatus for pH correction is suitable for reacting the flow of ionic mixture with the flow of oxide according to the reaction:

$\text{CaO}(\text{s}) + \text{H}_2\text{O}(\text{l}) + 2\text{CO}_2(\text{aq}) \rightarrow \text{Ca}(\text{HCO}_3)_2(\text{aq})$ and the absorber/precipitator is suitable for reacting the flow of atmospheric air with the flow of oxide.

3. The plant according to claim 1, further comprising a hydroxide production unit installed between the electric calciner and the apparatus for pH correction, wherein: the hydroxide production unit is configured for receiving at the inlet at least the flow of oxide originating from the electric calciner and a predetermined flow of water; and the hydroxide production unit is configured for reacting the flow of oxide with the flow of water according to the reaction:

$\text{CaO}(\text{s}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{Ca}(\text{OH})_2(\text{s})$ and for releasing at the outlet the flow of hydroxide; the apparatus for pH correction is configured for reacting the flow of ionic mixture with the flow of hydroxide according to the reaction:

$\text{Ca}(\text{OH})_2(\text{aq}) + 2\text{CO}_2(\text{aq}) \rightarrow \text{Ca}(\text{HCO}_3)_2(\text{aq})$.

4. The plant according to claim 1, further comprising a hydroxide production unit installed between the dosing device for the buffering substance and the absorber/precipitator, wherein: the hydroxide production unit is configured for receiving at the inlet at least a flow of oxide originating from the electric calciner and the predetermined flow of water; and the hydroxide production unit is configured for reacting the flow of oxide with the flow of water according to the reaction:

$\text{CaO}(\text{s}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{Ca}(\text{OH})_2(\text{s})$ and for releasing at the outlet a flow of hydroxide.

5. The plant according to claim 1, further comprising a control unit and a process parameters meter for the flow of ionic mixture or for the buffered ionic mixture; the process parameters meter is also configured for providing the measurement to the control unit, and the control unit is configured for controlling the dosing device for the buffering substance so that it feeds to the apparatus for pH correction the exact amount of flow of buffering substance that is adequate to obtain the buffered ionic mixture with the desired pH.

6. The plant according to claim 1, further comprising a control unit, one or more process parameters meters for the flow of water entering the contactor, one or more process parameters meters for the flow of ionic mixture leaving the contactor; the process parameters meters are further configured for providing the measurements to the control unit and the control unit is configured for controlling the PCC dosing device so that it feeds to the contactor the amount of flow of dosed PCC that is adequate to obtain the flow of ionic mixture with the desired pH.

7. The plant according to claim 1, further comprising a control unit and one or more process parameters meters for the physical/chemical parameters of the flow of atmospheric air and/or for the flow of lean atmospheric air suitable for measuring the CO_2 flow rate and/or concentration, and meters of the physical/chemical parameters of the flow of atmospheric air and/or of the flow of lean atmospheric air are also configured for providing the measurement to the control unit which is configured for controlling the dosing device for the buffering substance so that it feeds to the absorber/precipitator the exact amount of flow of alkaline substance that is adequate to optimize the production of a flow of PCC suspension respectively according to the reactions:

$2\text{NaOH}(\text{aq}) + \text{CO}_2(\text{aq}) \rightarrow \text{Na}_2\text{CO}_3(\text{aq}) + \text{H}_2\text{O}(\text{l})$

$\text{Ca}(\text{OH})_2(\text{aq}) + \text{Na}_2\text{CO}_3(\text{aq}) \rightarrow \text{CaCO}_3(\text{s}) + \text{NaOH}(\text{aq})$

or the reactions:

$2\text{KOH}(\text{aq}) + \text{CO}_2(\text{aq}) \rightarrow \text{K}_2\text{CO}_3(\text{aq}) + \text{H}_2\text{O}(\text{l})$

$\text{Ca}(\text{OH})_2(\text{aq}) + \text{K}_2\text{CO}_3(\text{aq}) \rightarrow \text{CaCO}_3(\text{s}) + \text{KOH}(\text{aq})$; or is suitable for controlling the flow of atmospheric air so that the absorber/precipitator has the adequate amount of

CO.sub.2 to react the amount of flow of alkaline substance fed to the absorber/precipitator according to the reactions described above to optimize the production of a flow of PCC suspension.

8. A method to improve the efficiency of CO.sub.2 capture and storage using precipitated calcium carbonate, the method comprising steps of: providing an electric calciner; feeding to the electric calciner a flow of electric energy and a flow of carbonate to obtain the calcination of the flow of carbonate according to the reaction:

$\text{CaCO}_3(\text{s}) \rightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$; releasing at the outlet from the electric calciner a flow of carbonic gas and a flow of oxide; providing a contactor; conveying the flow of carbonic gas to the contactor; providing a dosing device for the buffering substance; conveying the flow of oxide or a flow of hydroxide to the dosing device for the buffering substance; from the dosing device for the buffering substance obtaining a flow of buffering substance and a flow of alkaline substance; feeding to the contactor the flow of carbonic gas produced by the electric calciner, a predetermined flow of water and a flow of dosed PCC to obtain a flow of ionic mixture via reactions:

$\text{CO}_2(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_2\text{CO}_3(\text{aq})$
 $\text{H}_2\text{CO}_3(\text{aq}) + \text{HCO}_3^-(\text{aq}) \rightleftharpoons \text{HCO}_3^-(\text{aq}) + \text{H}^+(\text{aq})$

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$\text{CaCO}_3(\text{s}) + \text{CO}_2(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{Ca}(\text{HCO}_3)_2(\text{aq})$ releasing at the outlet from the contactor the flow of ionic mixture; conveying the flow of ionic mixture; conveying the flow of buffering substance; providing an apparatus for pH correction; feeding the apparatus for pH correction with the flow of ionic mixture and with the predetermined flow of buffering substance; releasing at the outlet of the apparatus for pH correction a flow of buffered ionic mixture; providing an absorber/precipitator; feeding the flow of alkaline substance to the absorber/precipitator; feeding a flow of atmospheric air to the absorber/precipitator so that the reaction of the CO.sub.2 present in it takes place with the flow of alkaline substance) following the reactions:

$2\text{NaOH}(\text{aq}) + \text{CO}_2(\text{aq}) \rightleftharpoons \text{Na}_2\text{CO}_3(\text{aq}) + \text{H}_2\text{O}(\text{l})$

$\text{Ca}(\text{OH})_2(\text{aq}) + \text{Na}_2\text{CO}_3(\text{aq}) \rightleftharpoons \text{CaCO}_3(\text{s}) + 2\text{NaOH}(\text{aq})$;

or the reactions:

$2\text{KOH}(\text{aq}) + \text{CO}_2(\text{aq}) \rightleftharpoons \text{K}_2\text{CO}_3(\text{aq}) + \text{H}_2\text{O}(\text{l})$

$\text{Ca}(\text{OH})_2(\text{aq}) + \text{K}_2\text{CO}_3(\text{aq}) \rightleftharpoons \text{CaCO}_3(\text{s}) + 2\text{KOH}(\text{aq})$; releasing at the outlet from the absorber/precipitator a flow of PCC suspension and a flow of lean atmospheric air; providing a separator; feeding the flow of PCC suspension to the separator so that a flow of PCC is separated from a flow of basic solution; recirculating the flow of basic solution released by the separator to the absorber/precipitator; providing a PCC dosing device; feeding the flow of PCC to the PCC dosing device; releasing at the outlet from the PCC dosing device the predetermined flow of dosed PCC and a predetermined flow of excess PCC; feeding the predetermined flow of dosed PCC to the contactor so that the reaction takes place:

$\text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{Ca}(\text{HCO}_3)_2$; and making available the predetermined flow of excess PCC.

9. The method in accordance with claim 8, to improve the efficiency of CO.sub.2 capture and storage using precipitated calcium carbonate comprising the steps of: providing a hydroxide production unit; feeding the flow of oxide and a predetermined flow of water to the hydroxide production unit so that the reaction takes place:

$\text{CaO}(\text{s}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{Ca}(\text{OH})_2(\text{s})$; and releasing at the outlet from the hydroxide production unit at least a flow of hydroxide.

10. The method in accordance with claim 8, wherein the flow of alkaline substance that feeds the absorber/precipitator is a flow of hydroxide.
