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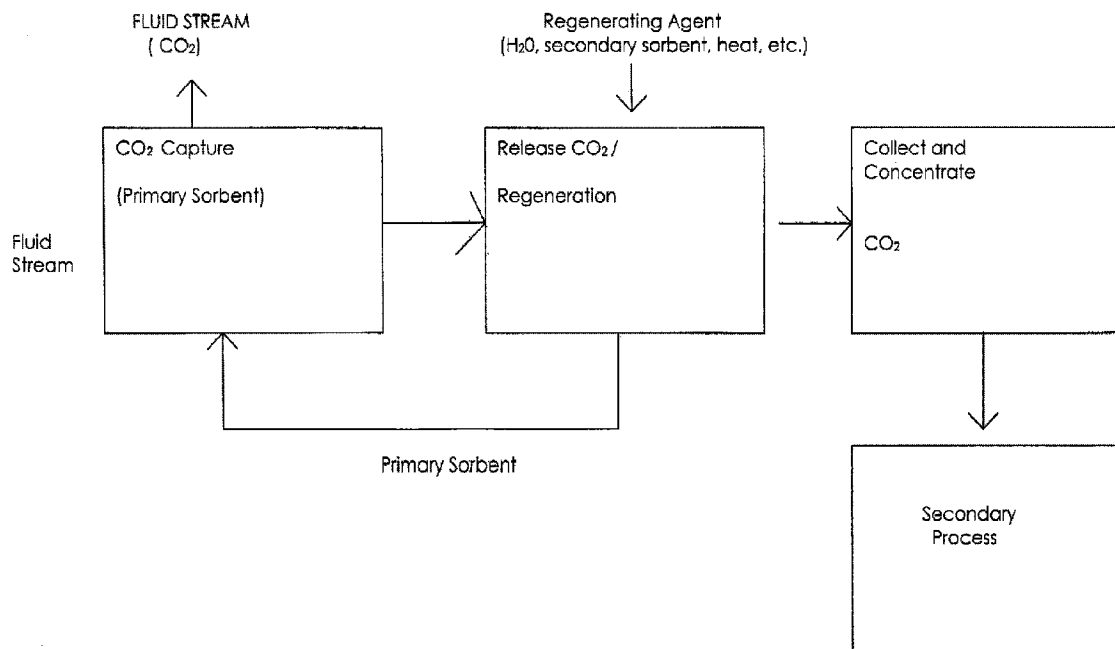
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(54) **Titre : EXTRACTION ET SEQUESTRATION DE DIOXYDE DE CARBONE**

(54) **Title: EXTRACTION AND SEQUESTRATION OF CARBON DIOXIDE**



(57) **Abrégé/Abstract:**

The present disclosure provides a method and apparatus for extracting carbon dioxide (CO2) from a fluid stream and for delivering that extracted CO2 to controlled environments for utilization by a secondary process. Various extraction and delivery methods are disclosed specific to certain secondary uses, included the attraction of CO2-sensitive insects, the ripening and preservation of produce, and the neutralization of brine.

ABSTRACT

The present disclosure provides a method and apparatus for extracting carbon dioxide (CO₂) from a fluid stream and for delivering that extracted CO₂ to controlled environments for utilization by a secondary process. Various extraction and delivery methods are disclosed specific to certain secondary uses, including the attraction of CO₂-sensitive insects, the ripening and preservation of produce, and the neutralization of brine.

EXTRACTION AND SEQUESTRATION OF CARBON DIOXIDE

The present invention relates to a method and apparatus for the removal of selected gases from an environment and the disposal of the selected gases in another environment.

5 The present invention in one aspect relates to removal of selected gases from the atmosphere. The invention has particular utility in connection with the extraction of carbon dioxide (CO₂) from the atmosphere and subsequent sequestration of the extracted CO₂ or conversion of the extracted CO₂ to useful or benign products and will be described in connection with such utilities, although other utilities are contemplated,
10 including the extraction, sequestration or conversion of other gases from the atmosphere including NO_x and SO₂.

 There is compelling evidence of a strong correlation between the sharply increasing levels of atmospheric CO₂ with a commensurate increase in global surface temperatures. This effect is commonly known as Global Warming. Of the various
15 sources of the CO₂ emissions, there are a vast number of small, widely distributed emitters that are impractical to mitigate at the source. Additionally, large-scale emitters such as hydrocarbon-fueled power plants are not fully protected from exhausting CO₂ into the atmosphere. Combined, these major sources, as well as others, have lead to the creation of a sharply increasing rate of atmospheric CO₂ concentration. Until all
20 emitters are corrected at their source, other technologies are required to capture the increasing, albeit relatively low, background levels of atmospheric CO₂. Efforts are underway to augment existing emissions reducing technologies as well as the development of new and novel techniques for the direct capture of ambient CO₂. These efforts require methodologies to manage the resulting concentrated waste streams of
25 CO₂ in such a manner as to prevent its reintroduction to the atmosphere.

 The production of CO₂ occurs in a variety of industrial applications such as the generation of electricity from coal at power plants and in the use of hydrocarbons that are typically the main components of fuels that are combusted in combustion devices, such as engines. Exhaust gas discharged from such combustion devices contains CO₂
30 gas, which at present is simply released to the atmosphere. However, as greenhouse gas concerns mount, CO₂ emissions from all sources will have to be curtailed. For

mobile sources such as motor vehicles and airplanes the best option is likely to be the collection of CO₂ directly from the air rather than from the mobile device in the motor vehicle or airplane. The advantage of removing CO₂ from air is that it eliminates the need for storing CO₂ on the mobile device.

5 Extracting carbon dioxide (CO₂) from ambient air would make it possible to use carbon-based fuels and deal with the associated greenhouse gas emissions after the fact. Since CO₂ is neither poisonous nor harmful in parts per million quantities, but creates environmental problems simply by accumulating in the atmosphere, it is possible to remove CO₂ from air in order to compensate for equally sized emissions elsewhere and
10 at different times.

 The present disclosure provides a system, i.e. a method and apparatus for extracting a contaminant from a flow stream, such as ambient air or an exhaust stack, and for delivering the extracted contaminant for use in a secondary process. The present disclosure is described primarily in regards to the removal and sequestration of
15 CO₂, though the apparatus and method of the present disclosure may be used with various other contaminants.

 In accordance with one aspect of the present disclosure, CO₂ is extracted from air and the extracted CO₂ is delivered to a secondary process where the CO₂ is transformed into an useful or benign product. The CO₂ is delivered in whatever form is
20 required for the secondary process, which may be gaseous, solid, or liquid CO₂. The secondary process may be any manufacturing, food processing, or other industrial process that uses CO₂, such as, machining coolant and lubricant, grit blasting, e.g. for smoothing and paint removal, cryogenic cleaning, quick freeze processes, production and use of R744 refrigerant, CO₂ based dry cleaning solvents, perishable shipping
25 container pre-cooling, perishable shipping inert environment maintenance, beverage carbonation, fire suppression, plant fertilization, horticulture, agriculture, silvaculture, aquatic algae production, enhanced oil recovery, water softening, Solvay process, propellant, pressurizing gas, e.g. for aerosol cans, inflation gas, e.g. for life rafts, supercritical CO₂ extraction, semi conductor manufacturing, organic solvent, perfume
30 aromatics, decaffeinating beverages, e.g. coffee and tea, supramics, pharmaceutical manufacturing, chemical production such as for urea, methanol, inorganic carbonates,

organic carbonates, polyurethanes, paint pigments, foaming agents, carbon based fuels, i.e. synthetic fuels, fumigation, e.g. of grain elevators, neutralization of alkaline water, gas shield, e.g. for welding, which are given as exemplary.

5 A further aspect of the present disclosure provides a method and apparatus for luring CO₂ sensitive insects toward a specific location where a moisture sensitive CO₂ sorbent that is partially or fully loaded with CO₂ is exposed to moisture usually in excess of that present in the ambient air at the location. The sorbent may be held in place by an open basket that is protected with a roof and a floor against accidental wetting by rain.

10 Another aspect of the present disclosure is directed to the control of the concentration of specific gases in a closed environment. While the method and apparatus of this aspect of the present disclosure will be described with specific reference to the control of carbon dioxide in the storage, for example, of bananas, but other fruits and vegetables are also contemplated by this disclosure. The present
15 invention provides a atmosphere-controlled environment for storing produce, wherein other parameters as well as carbon dioxide such as humidity may also be controlled, and a plurality of filters attached to the temperature controlled environment.

Yet another aspect of the present disclosure provides a system, i.e. a method and apparatus for extracting carbon dioxide (CO₂) from ambient air or an exhaust stack and
20 for delivery, sequestration or conversion of the extracted CO₂ into useful or benign products.

The extraction of the contaminant from a gas stream in any of the aspects of the present disclosure discussed above may be accomplished by using one of a number of methods such as disclosed in the several patent applications listed in Appendix A,
25 as well as other extraction processes described in the literature and patent art, including processes which capture CO₂ at the stack.

Further features and advantages of the present invention will be seen from the following detailed description, taken in conjunction with the accompanying drawings,
30 wherein

Fig. 1 is a schematic showing a system for capturing CO₂ in accordance with

the present invention wherein CO₂ is delivered to a secondary process;

Fig. 2A is a schematic showing an ion exchange process for capturing CO₂ in accordance with one aspect of the present disclosure wherein multiple chambers are used in succession;

5 Fig. 2B is a schematic showing an ion exchange process for capturing CO₂ where valves are used to control flow between chambers in accordance with the present disclosure;

Fig. 3 is a schematic showing an ion exchange process for capturing CO₂ employing activated carbon in accordance with one aspect of the present disclosure;

10 Fig. 4 is a schematic of an apparatus of the present invention having an electrodialysis cell according to one embodiment of the present disclosure;

Fig. 5 is a schematic showing a system for capturing CO₂ in accordance with the present disclosure wherein the CO₂ capture device works in tandem with an industrial process to create an essentially carbon neutral system;

15 Fig. 6 is a schematic of a method and apparatus for luring CO₂-sensitive insects to a desired location according to one aspect of the present disclosure;

Fig. 7 is a schematic of a method and apparatus for luring CO₂-sensitive insects to a desired location according to one aspect of the present disclosure.

Various methods and apparatus have been developed for removing CO₂ from
20 air. For example, we have recently disclosed methods for efficiently extracting carbon dioxide (CO₂) from ambient air using sorbents that either physically or chemically bind and remove CO₂ from the air. A class of practical CO₂ capture sorbents include strongly alkaline hydroxide solutions such as, for example, sodium or potassium hydroxide, or a carbonate solution such as, for example, sodium or potassium carbonate
25 brine. See for example published PCT Application PCT/US05/29979 and PCT/US06/029238. See also published PCT Application PCT/US07/802229 which describes the use of solid sorbents such as ion exchange resins for removing CO₂ from the air.

In broad concept, the present invention in one aspect extracts carbon dioxide
30 from ambient air using a conventional CO₂ extraction method or one of the improved CO₂ extraction methods disclosed in our aforesaid PCT Applications, or disclosed

herein, and releases at least a portion of the extracted CO₂ to a secondary process employing CO₂. The CO₂ also may be extracted from an exhaust at the exhaust stack.

In our co-pending U.S. Application Publication US 2008-0087165, assigned common assignee there are provided methods and apparatus for extracting carbon dioxide (CO₂) from ambient air and for delivering that extracted CO₂ to controlled environments. Specifically, the aforementioned applications disclose the delivery of CO₂ collected from ambient air or from exhaust gases for use in greenhouses or in algae cultures. The CO₂ is extracted from the gas stream by an ion exchange material that when exposed to dry air absorbs CO₂ that it will release at a higher partial pressure when exposed to moisture. In this process we can achieve concentration enhancements by factors of from 1 to 100.

In a first exemplary embodiment shown in Fig. 1, the present invention provides a system for removing CO₂ from a fluid stream in a capture apparatus, comprising passing the fluid stream in contact with a primary sorbent to absorb CO₂ from the fluid stream. The fluid stream may be ambient air, a flue stream, or any other fluid stream from which the sorbent is capable of withdrawing CO₂. The CO₂ is then released by the primary sorbent and delivered to a secondary process.

The secondary process preferably is connected directly to the CO₂ capture apparatus to minimize transportation costs and potential losses associated therewith. Depending on the intended secondary process, the CO₂ may be transformed into a solid or liquid state. The CO₂ may further be conditioned to a specified pressure and/or temperature.

The secondary process may be any manufacturing, food processing, or other industrial process that uses CO₂, such as for example, machining coolant and lubricant, grit blasting, e.g. for smoothing and paint removal, cryogenic cleaning, quick freeze processes, R744 refrigerant, dry cleaning solvent, perishable shipping container pre-cooling, perishable shipping inert environment maintenance, beverage carbonation, fire suppression, plant fertilization, horticulture, agriculture, silvaculture, aquatic algae production, enhanced oil recovery, water softening, Solvay process, propellant, pressurizing gas, e.g. for aerosol cans, inflation gas, e.g. for life rafts, supercritical CO₂ extraction, semi conductor manufacturing, organic solvent, perfume aromatics,

decaffeinating beverages, e.g. coffee and tea, supramics, pharmaceutical manufacturing, chemical production such as for urea, methanol, inorganic carbonates, organic carbonates, polyurethanes, paint pigments, foaming agents, carbon based fuels, i.e. synthetic fuels, fumigation, e.g. of grain elevators, neutralization of alkaline water, gas shield, e.g. for welding, Many other processes utilizing CO₂ are also possible and are deemed to be within the scope of this disclosure.

Our aforementioned commonly owned applications disclose several potential primary sorbents that may be used to capture and remove CO₂ from the air. In one approach to CO₂ capture, the sorbent is a strong base ion exchange resin that has a strong humidity function, that is to say, an ion exchange resin having the ability to take up CO₂ as humidity is decreased, and give up CO₂ as humidity is increased. Such resins may be regenerated by contact with water, humid air, or pulses of steam. In this approach the CO₂ is returned to a gaseous phase in a more concentrated form, and no liquid media are brought in contact with the collector material.

Other primary sorbents may be regenerated by a secondary sorbent such as weak liquid amine. This amine must be capable of pulling the CO₂ content of gas mixture down so that the CO₂ partial pressure drops to about e.g., 20 to 30 mbar. Thus it can be far weaker sorbent than the primary sorbent and this allows the use of very weak amines.

Still other sorbent materials may be regenerated by the application of heat (utilizing a thermal swing), or vacuum pressure.

In another example, CO₂ is captured and removed from air on a solid phase ion-exchange resin which is placed in a plurality of chambers connected in series. See Fig. 2A. The resins in the different chambers have been exposed for different length of time to the outgassing process. Resins may move from chamber to chamber, or more likely as shown in Fig. 2B, the valving is changed to take a chamber from the purged end of the chain, remove its charge and fill it with a resin which is now put on the unpurged end of the chain. The gas in each chamber is composed of water vapor, CO₂ and possibly an inert sweep gas. The sum of the three partial pressures monotonically declines from the upstream end of the system to the downstream end of the system. The sweep gas pressure can be reduced by increasing the flow speed, but the water

vapor pressure is more or less in equilibrium with the liquid water at this point. The CO₂ pressure should increase in the direction of the sweep. If the water vapor is a large part of the total pressure, the water vapor pressure gradient controls the flow and it would be established by a temperature drop from one chamber to the next, while the

5 CO₂ pressure will rise from one chamber to the next, as each chamber is adding some CO₂ to the flow. The contributions of each chamber will be limited by the rate at which the material can release CO₂ and the equilibrium pressure that particular resin can reach.

The following conceptually describes a CO₂ washing system that is based on

10 immersing the resin into liquid water and moving the water over the resin into a separate chamber where the CO₂ is allowed to be released from the water.

A simple implementation is a set of chamber organized (at least logically into a circle). All but one chamber are filled with water. One chamber (n) is empty and filled with air. Initially chamber n is filled with air, and chamber n+1 is filled with water.

15 Now water is pumped against a minimal pressure drop from chamber k to k+1. This will work for all values of k, except that k=n-1, n, n+1 are special cases which need further consideration. The water in chamber n-1 flows into chamber n, thereby pushing the air inside this chamber out. It is either released to the outside or channeled into chamber n+1 whose water content is moving into chamber n+1. The water pouring into

20 chamber n will inundate the resin that has been replaced into this chamber. The water in chamber n+1 flows into chamber n+2, but rather than obtaining water from chamber n, it pulls in air, which may be the air that resided in chamber n, or fresh air taken from the outside.

At this point we renumber all chambers by replacing n with n-1. Thus it is

25 again chamber n that is filled with air. We now open chamber n, and remove the regenerated resin and replace it with fully loaded resin. Before we load up chamber n, we pump the water from station n-1 to a degassing station and from there to station n+1. This water flow bypasses the currently open chamber n.

This procedure could be used with pure water, in which the process is a simple

30 degassing, but it could also be performed with a carbonate solution which is turned into a bicarbonate and where the CO₂ is removed by other means. CO₂ removal could be

based on an evacuation (which could be achieved by operating an inverted siphon), or based on electrodialysis, or involve a secondary sorbent that is far more compact and thus allows for an easier regeneration option. It also could involve precipitation of bicarbonate from the solution in a thermal swing or a thermal swing for CO₂ release from the mixture. The basic layout is independent of these ideas.

A variation of this idea has all chambers evacuated with the exception of chamber n-1 which is filled with water, n which is open to the air, and n+1 which is again filled with water. The nominally evacuated chambers are filled with a mixture of water vapor and CO₂. In this case, we pump water from chamber n-1 into n, displacing the air to the outside and immersing the resin in water. The pump does not need to do much work, because at the same time the water in chamber n+1 is sucked into chamber n+2, while chamber n+1 fills itself with air. At the end of this process chamber n+1 is filled with air and open to the outside. Chamber n is filled with water and at vacuum pressure. Chamber n+2 is filled with water and at vacuum pressure, and all other chambers are still under vacuum conditions. No net work was done, but all chambers moved by one. We can now renumber all chambers, and repeat the cycle.

In this case we use the water to stimulate the gas release and the freshly wetted resin in the last chamber is now topping off the CO₂ which is pumped out of this chamber, letting gas flow from all other chambers into this one. The CO₂ content of the water is likely to be high, however, it remains more or less constant over time as we do not extract this CO₂, so after some initial transients, this CO₂ reservoir will remain constant and not remove CO₂ from the resin (we ignore here some small losses to the outside air which are not completely avoidable) check valves can be installed to prevent backward flow. As a result we have a water driven implementation of the CO₂ release which is significantly simpler than a water vapor driven system.

Optionally, some of the water vapor may be recovered from the system during the compression stage. This will provide sufficient heat that the system can operate at slightly elevated temperatures. Indeed it is possible to use the last step of pumping out of the gas to severely cool the resin and remove all excess water.

Yet other possibilities exist. For example, it is possible to create a buffer storage for the water which makes it possible to slowly withdraw water from chamber

n-1 and in a second step fill chamber n very rapidly so as to minimize the amount of time the water is in contact with air and thus can exchange gas with the outside air. The buffer itself must be able to change volume. It takes on an additional volume as it takes on the fluid from chamber n-1. It then contracts again as it pushes the same
5 volume into chamber n. Again mechanical work is related to friction losses, inertial losses, and losses to slight pressure mismatches between the various chambers. This can be adjusted for with careful thermal management.

In yet another example CO₂ is captured and removed from air by employing hydrophobic activated carbon materials with strong base ion exchange resins. See Fig.
10 3. This latter process is based on observation that activated carbon has been observed to absorb CO₂ when wet, and release the absorbed CO₂ as it dries. This is the opposite behavior from ion exchange resins. Accordingly, this makes it possible to couple solid phase ion exchange resin extractors and activated carbon extractors in sequence. Starting with dry activated carbon and moistened resin materials air is passed through
15 the system. As the air dries the resin, it transports the water vapor to the carbon. The resin picks up CO₂ as it dries, and the activated carbon picks up CO₂ as it accepts moisture. Once the resin is dry, the system is reversed, and fresh air is flowed through the activated carbon, and releases moisture back to the ion exchange resins. As the carbon dries it gives off CO₂, raising the CO₂ partial pressure where it can be
20 concentrated and removed. A feature and advantage of coupling ion exchange material and activated carbon in this manner is that water is preserved, and is a simple matter of valving to reverse air flow. Alternatively, zeolite materials may be used in place of activated carbon. By stringing several air capture devices together, the ambient CO₂ removed may be concentrated before passing to a secondary process.

25 The same ion exchange resins may be used to remove excess CO₂ build-up from closed containers such as storage containers for fresh fruit or vegetables, e.g., bananas, in order to maintain a maximum level of CO₂ in the container and avoid excessive ripening or spoilage, as will be described in greater detail below.

In another aspect of the present invention shown in Fig. 4, CO₂ is captured
30 using ion exchange materials and concentrated using an electrodialysis (ED) cell. The overall process is as follows: The ion exchange resin is washed using a basic solution,

such as sodium carbonate (Na_2CO_3), preferably having a pH of 11-12. The resulting effluent, which in the example of a sodium carbonate wash will be primarily sodium bicarbonate (NaHCO_3), will preferably have a pH of 9-10. The effluent is then supplied to the acid side of an ED cell, where the reaction is controlled through bipolar and cationic membranes. After an initial run, the acidic side of the cell stabilizes at a near neutral pH, at which point CO_2 evolves and is captured. Osmotic pressure drives water towards the base side of the cell. The basic solution is maintained near a pH of 12 and may also be used to replenish the wash fluid.

In another exemplary embodiment shown in Fig. 5, the present invention provides a system that is substantially carbon neutral, wherein an air capture device, such as those described herein, collects CO_2 that is released by an industrial process employing CO_2 as described above. For example, such processes include the use of CO_2 as a refrigerant, as a dry cleaning agent or other solvent, as a fire suppression material, as an oxidation preventing shield-gas in welding or electronics manufacture, as an alternative to sand-blasting, e.g., for smoothing, or paint or rust removal, as a freezing agent in food processing, or any other process where CO_2 is utilized and is later released to the atmosphere. The system effectively creates a loop that is substantially carbon neutral. The air capture device may, for example, be connected the HVAC system of a building where CO_2 is released by processes therein. With the present invention, CO_2 is captured, concentrated and recycled for reuse on site.

The invention also may be used to generate carbon credits. Thus, a manufacturer may extract CO_2 , and obtain a carbon credit which may be traded or sold, and then use the extracted CO_2 in a secondary process, eliminating the cost of purchasing or generating CO_2 for the secondary process.

Another aspect of the present disclosure provides an apparatus and method for using captured CO_2 to attract CO_2 sensitive insects, such as mosquitoes. It is known that certain insect pests like mosquitoes are attracted to sources of CO_2 , which for them is a way to find a potential victim. In recent years lures have been developed for mosquitoes that release CO_2 in the environment in order to attract mosquitoes and potentially other insects. A drawback of most of these devices is that they require gas cartridges of CO_2 or natural gas, propane or butane to produce CO_2 . In related

applications it has been shown how certain ion exchange materials can be used to absorb CO₂ when they are in a dry state and release it again when they get wet. Here an application of such a material is described wherein the controlled CO₂ release is used to attract mosquitoes to a device at certain times while at other times the device
5 recharges its CO₂ stores.

Referring to FIG. 6, this aspect of the present disclosure describes a method of luring CO₂ attracted insects by using a CO₂ capture resin that when dry will collect CO₂ from the air and release it again when exposed to moisture. A number of such materials have been described in previous disclosures. This disclosure describes how
10 these resin materials can be used to lure mosquitoes to the device at certain times.

It is possible to expose an amount of resin to air so as to load it with CO₂. When the device is activated, e.g. in the evening the resin is exposed to humid air, or is directly wetted for example by a small water spray. As a result the resin will begin releasing CO₂ therefore creating an environment that will attract mosquitoes. One
15 implementation, for example, would be a small container filled with polymer strands of the ion exchange resins and similar materials that can be used to absorb CO₂. The purpose of the CO₂ release is to attract certain insects, like mosquitoes that are attracted by CO₂.

The device exposes resin to the air, and containing the resin in a way that is protected from water and rain. During times the device is inactive, it is dry and the
20 resin will collect CO₂. The device includes a means of applying moisture to the resin material. Moisture application could be achieved by spraying water onto the resin surface, by wicking water into a woven wick that contains the resin material, or by any other means known in the art.

The device acts as a lure to attract mosquitoes away from people. In this case the device can be completely open, because no part needs to be kept away from people. In another implementation the device includes means of killing the pest once it enters the device. This includes but is not limited to electric discharges, or by contact
25 insecticides embedded into the resin matrix.

It is possible to combine the CO₂ lure with other means of attracting insects, including insects that do not respond to the presence of CO₂. These means include, but
30

are not limited to light and heat sources, sounds, odors or pheromones. Devices of this nature can be designed for indoor and outdoor use. Indoor use in malaria regions may help suppress the incidence of mosquitoes and hence malaria.

Another aspect of the present disclosure relates to the capture and release of
5 gases generated by the ripening and preservation of fruits and vegetables. Many produce items, i.e., fruits and vegetables, are often stored in a temperature-controlled environment in order to control the ripening process. Methods for the packaging and shipping of such fruits and vegetables have been developed to maximize the amount of time that the produce may be stored. Many methods for storing and ventilating produce
10 are known that provide various types of bags and containers, including gas permeable membranes, that allow some control of the exposure of the produce to gases such as oxygen, ethylene, and carbon dioxide. However, these methods do not provide optimal storage conditions and long-term storage options are still desired.

U.S. Patent Publication No. 2008/0008793,
15 discloses a method for storing bananas in a controlled environment where oxygen and carbon dioxide levels are optimized in addition to the temperature. Longer periods of storage may be achieved in this environment and improved flavor characteristics may be achieved. The reference fails, however, to discuss how such levels would be reached and maintained.

20 This aspect of the present disclosure provides a method for stabilizing the CO₂ in a room at any level between 5 ppm and 100,000 ppm. The invention also serves to achieve a low absolute humidity (usually below 25 ppt of water vapor, preferably below 15 ppt, with improved performance as the absolute humidity drops even lower).

Referring to FIG. 7, the method comprises circulating air through a filter box
25 that follows one of the methods for CO₂ absorption describes in one of our aforesaid previous applications. For example, the filter may employ an ion exchange resin that is subject to a humidity swing to absorb CO₂ at the partial pressure representing the desired CO₂ level. The apparatus may include a plurality of such filters operating, wherein each filter will run until the CO₂ uptake rate has slowed down to a
30 predetermined level at which we consider the resin to be essentially fully loaded. This will probably be less than the maximum loading for the resin that can be physically be

achieved, but the predetermined level may be optimized for performance at some lower level to improve the collective uptake rate. The uptake rate of the resin will depend primarily on absolute humidity and to some extent on temperature, and can approach one CO₂ per positive elementary fixed charge in the resin.

5 Once the resin is loaded the air intake is closed or the resin filter may be moved into a separate chamber. A humidity swing regeneration step follows. Regeneration is accomplished by a change in temperature and absolute humidity, or by wetting the resin, e.g., as described, for example, in U.S. Pat. No. 4,711,645; U.S. Pat. No. 5,318,758; U.S. Pat. No. 5,914,455; U.S. Pat. No. 5,980,611; U.S. Pat. No. 6,117,404;
10 and U.S. Patent Publication No. 2007-0217982 and WO 2009/061836.

 Wetting can be accomplished by either dipping the resin into DI or condensation water; by spraying or flowing such water over the resin, (such condensation water may be available from the refrigeration unit operating the storage facility, and may be augmented by condensation water recovered from our unit); by
15 generating steam in a blast of warm air that results in water condensation on the resin material; or by exposing the resin to warm moist air (such warm air may be available from the hot side of the refrigeration unit, it may already be moist or need additional moisture.) If the moisture is added as humidity or by generating steam, it is not necessary to use DI or condensation water.

20 The moist air loaded with CO₂ is then purged from the unit. Heat and water may be recovered in a heat exchange unit that reduces heating demand and water consumption.

 The present disclosure as discussed above may be used to cover a range of applications from extremely low levels of CO₂ to extremely high levels of CO₂. It is in
25 principle possible to remove CO₂ from a gas stream that contains CO₂ far in excess of the levels discussed above. Levels around 1 to 10 volume percent could easily be accommodated, and operating above about 10 volume percent CO₂ is also possible. It is advantageous for this design to operate at temperatures below about 15°C, because the loading and unloading characteristics of the resin improve under these conditions.

Alternative options at elevated levels of CO₂ include the use of activated carbon, the use of zeolites, the use of weak based amine, or other physical sorbents such as actuated alumina for CO₂ capture instead of ion exchange resin.

5 In broad aspect the present invention provides a method and apparatus for the extraction of a contaminant from a gas stream. The present invention will be described in reference to a method and apparatus for capturing CO₂ from ambient air; however, the invention is also applicable to handling exhaust air or other gas streams and may be used to capture hydrogen sulfide, ammonia, or other common contaminants from such gas streams.

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In PCT International Patent Publication WO 2008/061210

we discuss a CO₂ capture process that utilizes a humidity swing to regenerate a sorbent, releasing a mixture of CO₂ and water vapor. The water vapor may be removed from the mixture by compression or cooling, either
15 of which will cause the water vapor to condense and precipitate out of the mixture.

To perform the humidity swing, it often is useful to expose the sorbent to low pressure water vapor. In order to achieve the required minimum water vapor pressure, it is may be necessary to operate above ambient temperatures as the maximum water vapor pressure is significantly dependent on temperature. To that end, the
20 aforementioned co-pending applications discuss how to transfer heat to loaded sorbents that need to be inserted into an environment that is at a higher temperature.

In regenerating the sorbent it is necessary to dry the resin material. This opens an opportunity to combine such system with a vacuum distillation system, and use the heat of evaporation that is released when the material is drying to remove heat from the condenser inside the vacuum distillation system. Whereas the recovery of the CO₂ in
25 most applications requires entering the resin material into a vacuum chamber, the present invention also may be used to drive a complimentary distillation process.

As explained in the aforementioned co-pending applications, the CO₂ sorbent is often an anionic exchange resin, but here we intend to consider all humidity-sensitive
30 CO₂ sorbents that can absorb carbon dioxide from the air when they are dry and release carbon dioxide when they have been exposed to humidity in the form of liquid water

and/or partial pressures of water vapor which exceed those at ambient conditions. We will generally refer to such materials as water-sensitive CO₂ sorbents.

Vacuum distillation is a standard method of creating fresh water from a brine, such as seawater, brackish water or other salt rich brines pumped from underground.

5 For purposes of this disclosure, brine is also used to refer to contaminated water that is otherwise unsuitable as fresh water, such as for example, waters contaminated with biological waste materials. Thus, the term "brine" encompasses all waters contaminated with materials from which water can be separated by vacuum distillation.

Vacuum distillation begins with a chamber that has been at least partially
10 evacuated. Brine is introduced into the chamber and is separated into two components: concentrated brine and fresh water product. There are many ways to supply a fluid into a vacuum chamber that are known to practitioners of the state of the art. By adding and subtracting from the vacuum chamber equal volumes of incompressible fluid it is possible to design a continuous flow system that requires only minimum amount of
15 mechanical work.

The apparatus comprises a vacuum chamber that is divided into at least two parts; an evaporator unit and a condenser unit. As brine is introduced into the evaporator unit, it is allowed to evaporate. In this manner the water vapor becomes separated from the contaminants in the brine. The water vapor is then passed to a
20 condenser unit, where it is allowed to condense. It is necessary to remove heat of condensation to keep from impeding further condensation in the condenser unit. This heat may be passed to the evaporator unit, enabling the evaporation to occur, by counterflow or some other method.

The evaporator unit, which is initially evacuated, fills with water vapor. The
25 equilibrium partial pressure over the brine in the evaporator unit is a function of the temperature and of the salt content of the brine. The equilibrium partial pressure over the condensate in the condenser unit is a function of the temperature. At equal temperature, the equilibrium partial pressure over the condensate is slightly higher than over the brine. Thus, in a system with constant temperature the brine would gradually
30 dilute itself with water extracted from the condensate. The system left to itself would

operate in reverse, just as saltwater will become more dilute when it is separated from fresh water with a semi-permeable osmotic membrane.

One way to condense the water vapor in the condenser unit is to raise the pressure, wherein the water vapor will condense at ambient temperatures. This may be accomplished using a compressor to drive up the pressure. The heat of condensation will cause the temperature to rise in the condenser unit, wherein the heat deposited by the condensation can then be transferred to the evaporator unit. The compression acts in effect as a heat pump which transfers heat from the brine to the condensate, and a return heat flow balances out the total heat fluxes inside the system.

Where compression is used to condense the water out of the resulting gas mixture, the heat produced by that process can be transferred to the sorbent to raise its temperature as required. Alternatively, the heat required to drive the sorbent to the requisite temperature can also be derived from the condensation of water that has been allowed to evaporate at ambient conditions.

Another approach is to maintain by some other system a temperature gradient between the evaporator unit and the condenser unit, which is enough to cause a gradient in the equilibrium partial pressure that causes vapor to flow from the evaporator unit to the condenser unit. In order to maintain such a temperature differential, it is necessary to provide the heat of evaporation on the evaporator unit, and remove the heat of condensation on the condenser unit of the chamber. The required temperature differences are small; a few degrees between the evaporator and the condensate are sufficient. Operational temperatures can be low and could be well within the range of ambient temperatures, particularly in warmer climates.

One way of establishing the temperature gradient is to generate heat and transfer it to the evaporator. Another way of establishing the temperature gradient is to actively remove heat on the condenser unit. This requires a heat exchange system that removes heat from the condensate. In such an operation of the device, the temperature of the brine is higher than that of the condenser unit the heat is passed through and cannot be recovered within the system. In principle it is possible to couple one or more additional heat pumps to the system, which pumps the heat removed at the condenser unit and returns it to the evaporation side.

In combination with the CO₂ capture system described above, the water vapor is evaporated from the brine and is partly absorbed onto the resin. This will release a substantial portion of the CO₂ or other targeted contaminant from the sorbent. When this step is performed in a vacuum chamber, the atmosphere of the chamber will be
5 filled primarily with water vapor and CO₂. The vacuum chamber will also aid in the evaporation of the water vapor in the brine. The concentrated brine is then removed and the water is then condensed out of the CO₂. Thus, the present invention produces a distilled water stream as well as concentrated CO₂.

Providing heat to the drying resin is advantageous and one can therefore
10 integrate a heat exchange system operating between the drying resin collector and the condenser inside the vacuum system. In a typical implementation the evaporation of the water from the resin would not produce quite enough water to make up the water losses from the system; therefore it would have to be augmented by additional brine evaporation.

15 Another aspect of the present disclosure provides a different process whereby ambient environmental temperatures are used to maintain a constant temperature at the condenser unit, i.e. by flowing ambient air, or ambient water through the heat exchanger on the brine evaporation side, and we use additional brine, e.g. seawater, to operate an evaporative cooler that creates the temperature drop necessary to force the
20 condensation of clean water inside the vacuum chamber. The amount of seawater that needs to be evaporated on the outside of the chamber to maintain a low temperature is approximately equal to the amount of brine that is converted in the vacuum stiller.

The system disclosed herein comprises a vacuum chamber with means of introducing and removing a brine, with means for removal of clean water condensate,
25 with internal surfaces on which the brine is allowed to evaporate, and surfaces of a lower temperature where the water vapor is allowed to condense. The surfaces on which the brine is evaporating are in close contact with a heat exchanger that provides the necessary heat to maintain evaporation. It is advantageous to use free heat, i.e., heat from the ambient environment, which may have been augmented by heat, e.g.
30 from sunshine, or, e.g. waste heat. The surfaces on which water vapor is allowed to

condense are in close contact with a heat exchanger that uses additional brine to provide evaporative cooling required to force the condensation.

In the above embodiment, brine is consumed both inside and outside the chamber. The maximum acceptable concentration of the discharge brine will limit the amount of evaporation that is acceptable. The rate of consumption in both cases is similar. The two waste streams can be combined and mixed for return to the ocean or brine reservoir. The returned concentrated brine is slightly cooler than ambient temperatures.

Where ocean water or any water from a large body of water is used, it is not unusual for the input water is already cooler than ambient temperatures. In this case, it is possible to take advantage of the additional cooling power derived from the cool water that is in the system.

In addition, one might use a CO₂ membrane that separates CO₂ from nitrogen and oxygen. One option would be to use a carbonic anhydrase based membrane separation technology. Of particular utility are membranes with similar properties to the ion exchange resin discussed more fully in our other applications, (see Appendix A). The thin resin membrane would transfer CO₂ according to a pressure gradient in CO₂ and against a pressure gradient in water vapor. The two combined create a net flow of CO₂ across the membrane and thus by keeping the outside of the membrane wet or in high humidity one would create two chemical potentials that will drive CO₂ across the membrane.

Finally, there is a great synergy with the climate control of the current chamber. The CO₂ management is preferably integrated with de-humidification, or humidification of the air as the case may be, and it may also be integrated with the temperature control and AC handling of the air. The CO₂ stabilization unit, shares the air handling and blowing equipment with the other tasks, and it may be built into the same set of ducts. It can take advantage of heat and condensation water produced in the refrigeration unit.

The present disclosure in another aspect provides an additional use for extracted CO₂. According to the present invention, the extracted CO₂ is employed to neutralize carbonic acid. The present invention takes advantage of the fact that in sequestration, if

one can drive the partial pressure of CO₂ up by about a factor of about 100, the concentrated CO₂ may then be injected into alkaline brines, to neutralize the brine.

The resins disclosed in our previous US Patent Publication No. 2009-0120288 and PCT International Patent Publication WO 2008131132, assigned to a
5 common assignee, make it possible to capture CO₂ from the air and drive it off the sorbent with no more than excess water vapor. It also is possible to wet the resin directly with liquid water and form a carbonate, and transfer the carbonate in a second step through a membrane between the two fluids. However, in most cases, it is preferable to create a concentrated CO₂ gas that then can be transferred directly into a
10 more alkaline brine. Here again we can make direct contact between the gas and the brine, or keep them separated by a hydrophobic, porous membrane.

There are many applications where one has access to alkaline underground brines that can be used to drive a humidity swing with ionic exchange sorbents, even if their ion content make them unsuitable for direct contact with the resin. The present
15 invention takes advantage of the humidity swing and transfers the CO₂ through the gas phase. Alternatively, hydrophobic membranes may be used to create a gas phase interface between two liquids, or between a liquid and a gas. If the brine covers one side of the membrane it is possible to pull CO₂ gas through the membrane without bringing contaminant ions in contact with the sorbent resin.

20 A particular application of this technology can be realized where some other industrial process has created a highly alkaline waste stream that needs to be neutralized before disposal. In that case, we can introduce carbonic acid, which will either cause the precipitation of insoluble carbonates, or produce soluble but neutral carbonate salts. Similar processes are disclosed in (PCT) Publication Number
25 WO/2005/047183. As an example, consider waste streams from bauxite processing, e.g. in the Bayer process, which produces "red mud" at pH 13. According to the PCT Application cited above, between 1990 and 2003 six to seven million tons of red mud have been produced. Another example mentioned in the reference is the reprocessing or disposal of potassium hydroxide solutions from alkaline batteries. The process of
30 the present invention would create potassium carbonate or bicarbonate producing materials that are indeed quite harmless.

In one aspect of the neutralization process according to the present disclosure, we propose to use an alkaline brine which is preferably in a temperature range between 40 and 60°C, and use the water vapor to recover CO₂ from our resins. We then wash the CO₂ out of the gas mixture with the help of the alkaline brine. The heated alkaline
5 brine will provide a high level of moisture which induces the resin to give off CO₂ while it at the same time prevents the CO₂ level from rising substantially. If operated in a vacuum the process should not be transport limited. In the presence of atmospheric pressures, however, the process could be transport limited.

One possible approach is to have the liquor be soaked up in open cell foams
10 such as AQUAFOAM® floral retention foam as described in our PCT Published Application No. WO2006/084008. Another is to have it trickle through a packed bed that is installed parallel to the resin recovery unit and cycles gas from the recovery unit through it. Another option is to contain the resins in a tube whose outside is covered with a material that soaks up the brine. In such a design heat transfer between inside
15 and outside the tube is optimized.

The resin, which has been saturated with CO₂ in ambient air, is brought into a chamber connected to a second chamber containing wetted surfaces over which the brine flows. The brine will establish a high level of humidity and the resulting high humidity air is blown over the sorbent material. In one aspect of this invention this
20 exchange will occur with humid air entering the chamber. In another aspect, residual air in the chamber is at least partially removed by evacuation prior to running water vapor through the chamber. As the water vapor is circulated between the wetted surfaces and the sorbent material, it carries CO₂ that is released to the alkaline brine where it is absorbed into the brine. In this implementation the resin functions to speed
25 up the transfer of CO₂ from ambient air into the alkaline brine. Further acceleration of the transfer of CO₂ may be achieved with other materials, such as, for example, with carbonic anhydrase that thereby would open the use of brines with relatively low levels of alkalinity e.g with a pH of 8-11. In this range one could even use seawater, even though the accelerated acidification of seawater would in many cases be counter-
30 productive. However, this would not be the case, for example, where the source of an alkaline brine is an underground aquifer, from which brine is removed and to which it

is returned once the CO₂ is absorbed. The brine could also be water that has been exposed to alkaline mineral rocks such as basalt or peridotite or serpentinite rock. For example, one could percolate the water through a pile of serpentine tailings or other tailings that can release alkalinity.

5 The use of serpentine tailings to increase alkalinity is known in the art. Alternatively, the serpentine could be mined for this purposes. It also is possible in some formations to inject water into alkaline underground systems for the purpose of enriching it with base cations. The presence of CO₂ in the water may speed up this process.

10 In the case of serpentine and olivine as well as basalt, this particular use of mineral sequestration would likely result in the precipitation of magnesium and/or calcium carbonate. The advantage of this method over previous attempts to directly sequester CO₂ from the atmosphere is that the CO₂ concentrations can be enriched by about a factor of 100, which will greatly help with the reaction kinetics.

15 Another source of alkalinity could be Mg(OH)₂ that has resulted from the processing of serpentine and olivine.

It is also possible to use the CO₂ to dissolve calcium carbonate rock that then can be put into the ocean as calcium bicarbonate. In this example it is possible to directly use seawater to drive the dissolution, and the presence of carbonic anhydrase may speed up this process dramatically. See, e.g. PCT International Patent Appln. Serial No. PCY/US08/60672, assigned to a common assignee, for a discussion of the use of carbonic anhydrase to accelerate the CO₂ capture process.

20 The dissolution of limestone with air captured CO₂ is analogous to a process in which the CO₂ comes from a power plant. The present invention provides a substantial advantage over a power plant in that we do not have to bring enormous amounts of lime stone to a power plant, or distribute the CO₂ from a power plant to many different processing sites, but that we can instead develop a facility where seawater, lime and CO₂ from the air come together more easily. One specific implementation would be to create a small basin that is periodically flushed with seawater. The CO₂ is provided by
25 air capture devices located adjacent to or even above the water surface. Of particular
30 interest are sites where limestone or other forms of calcium carbonate (such as empty

mussel shells) are readily available as well. If we have calcium carbonate, seawater and air capture devices in one place, we can provide a way of disposing of CO₂ in ocean water without raising the pH of the water.

5 Indeed, it is possible to install such units adjacent a coral reef area by bringing additional limestone to the site or by extracting limestone debris near the reef. If the units operate in a slight ocean current upstream of the reef, they can generate conditions that are more suitable to the growth of the coral reef. Growth conditions can be improved by raising the ion concentration product of Ca⁺⁺ and CO₃⁻. This product governs the rate of coral reef growth.

10 It should be emphasized that the above-described embodiments of the present device and process, particularly, and “preferred” embodiments, are merely possible examples of implementations and merely set forth for a clear understanding of the principles of the invention. Many different embodiments of the invention described herein may be designed and/or fabricated.

15

APPENDIX A

WRIGHT 04.01 PCT	PCT/US05/29979
GLOBAL 05.01	11/346,522
GLOBAL 05.01 PCT	PCT/US06/03646
GLOBAL 05.01-P	60/649,341
GLOBAL 05.02 PCT	PCT/US06/29238
GLOBAL 05.02-P	60/703,098
GLOBAL 05.03-P	60/703,099
GLOBAL 05.04-P	60/703,100
GLOBAL 05.05-P	60/703,097
GLOBAL 05.06-P	60/704,791
GLOBAL 05.07-P	60/728,120
GLOBAL 06.01-P	60/780,466
GLOBAL 06.01/06.03	11/683,824
GLOBAL 06.01/06.03	PCT/US07/63607
GLOBAL 06.03-P	60/780,467
GLOBAL 06.04-P	60/827,849
GLOBAL 06.04/06.05	11/866,326
GLOBAL 06.04/06.05	PCT/US07/80229
GLOBAL 06.05-P	60/829,376
GLOBAL 06.06 PCT	PCT/US07/084880
GLOBAL 06.06-P	60/866,020
GLOBAL 07.01 PCT	PCT/US08/60672
GLOBAL 07.01-P	60/912,649
GLOBAL 07.02-P	60/912,379
GLOBAL 07.03-P	60/946,954
GLOBAL 07.04 CIP-P	60/985,596
GLOBAL 07.04-P	60/980,412
GLOBAL 07.05-P	60/985,586
GLOBAL 07.06-P	60/989,405
GLOBAL 08.01-P	61/058,876

GLOBAL 08.02-P	61/058,881
GLOBAL 08.03-P	61/058,879

What is claimed is:

1. A method for removing carbon dioxide from a gas, comprising:
bringing said gas in contact with a resin contained in a plurality of chambers,
wherein the plurality of chambers are connected in series;
wetting said resin with water, wherein the water enters a first chamber and exits
through a last chamber;
collecting water vapor and carbon dioxide from said resin;
separating said carbon dioxide from said water vapor; and
delivering said separated carbon dioxide for use in a secondary process.
2. The method of claim 1, wherein the secondary process is selected from a group
consisting of machining coolant and lubricant, grit blasting for smoothing and rust
removal, grit blasting for smoothing and paint removal cryogenic cleaning, quick freeze
processes, R744 refrigerant, dry cleaning solvent, perishable shipping container pre-
cooling, perishable shipping inert environment maintenance, beverage carbonation, fire
suppression, plant fertilization, horticulture, agriculture, silvaculture, aquatic algae
production, enhanced oil recovery, water softening, Solvay process, propellant,
pressurizing gas, pressurizing gas for aerosol cans, inflation gas, inflation gas for life
rafts, supercritical CO2 extraction, semiconductor manufacturing, organic solvent,
perfume aromatics, decaffeinating coffee, decaffeinating tea, supramics, pharmaceutical
manufacturing, chemical production of urea, methanol, inorganic carbonates, organic
carbonates, polyurethanes, paint pigments, foaming agents, carbon based fuels, synthetic
fuels, fumigation of farm products, neutralization of alkaline waters, neutralization of
slurries, neutralization of solid materials, gas shield for welding, and electronics
manufacturing.

3. The method of claim 1, wherein said plurality of chambers are connected via a plurality of valves that allow any of said plurality of chambers to serve as said first chamber or said last chamber.

4. The method as of claim 1, wherein said first chamber contains resin that was most recently saturated or partially saturated with carbon dioxide from said gas, and each successive chamber contains resin which has been wetted and carbon dioxide collected from for a greater period of time than the previous chamber, and so on, to said last chamber.

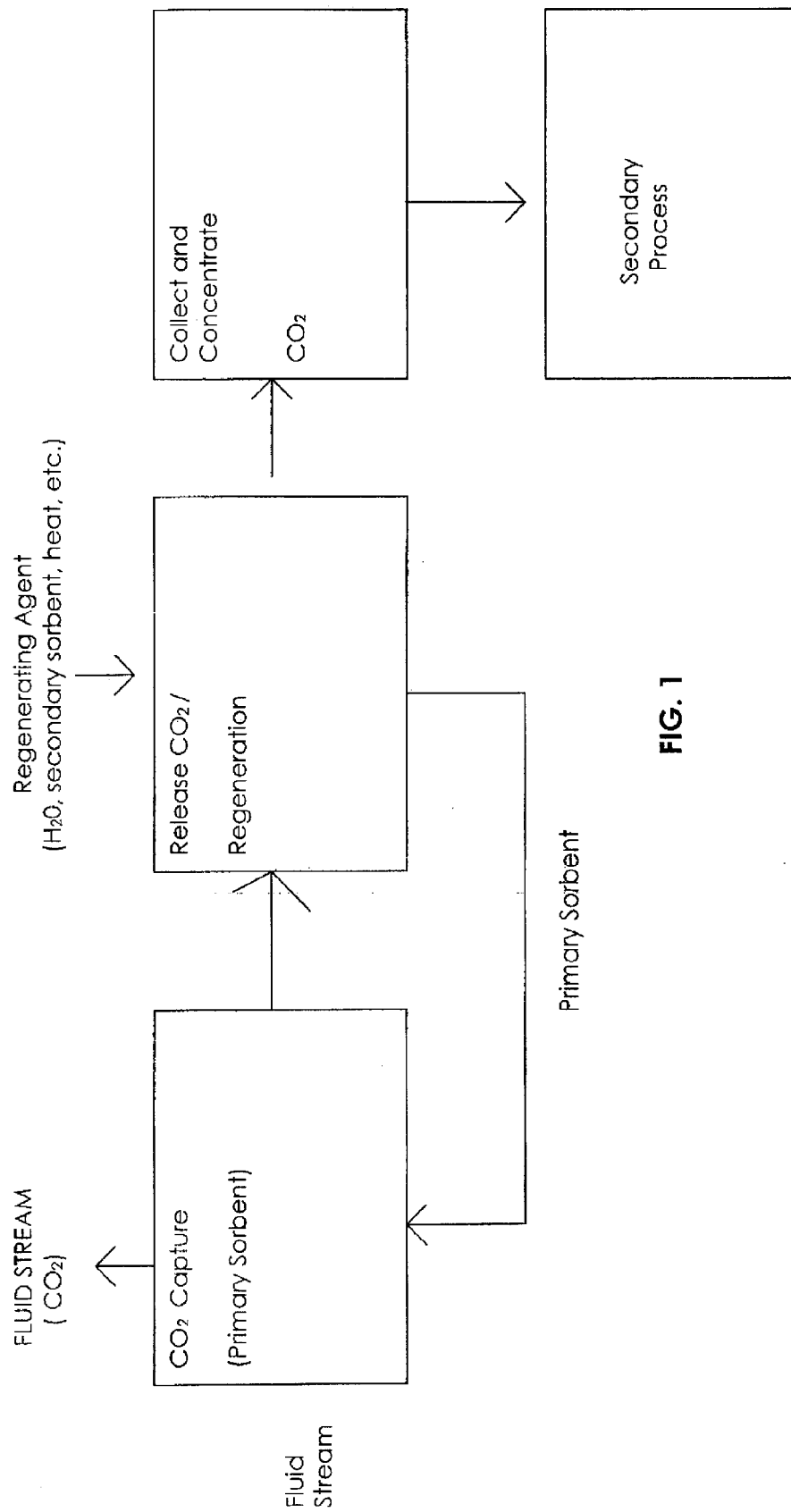


FIG. 1

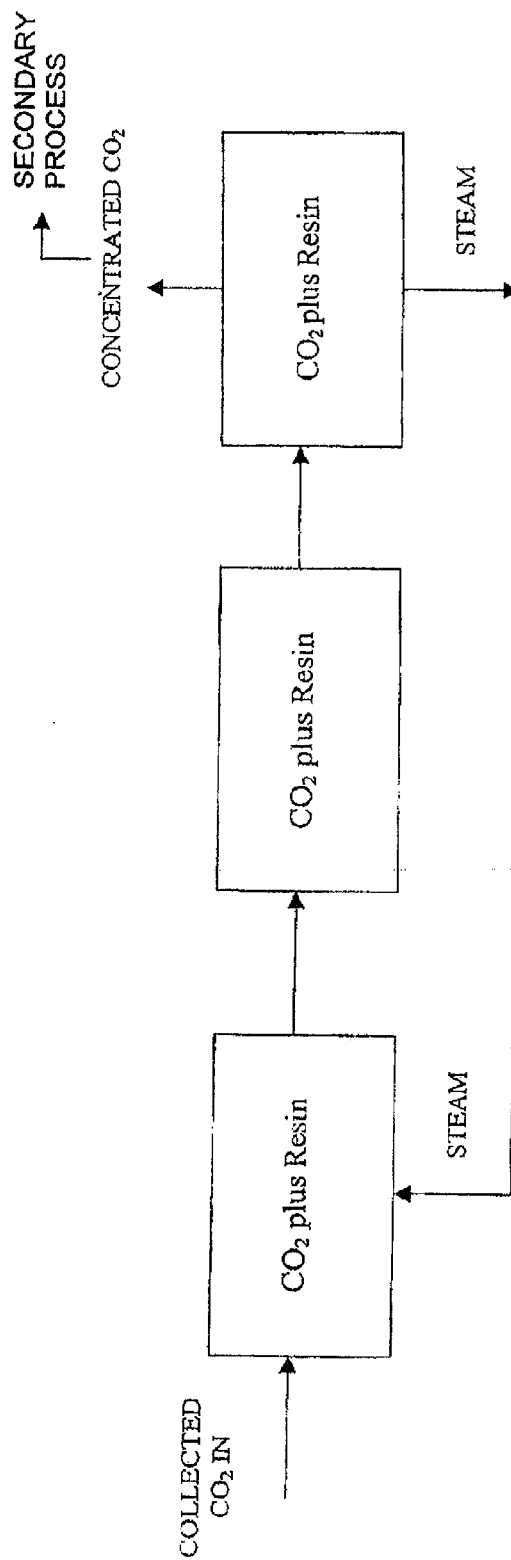


FIG. 2A

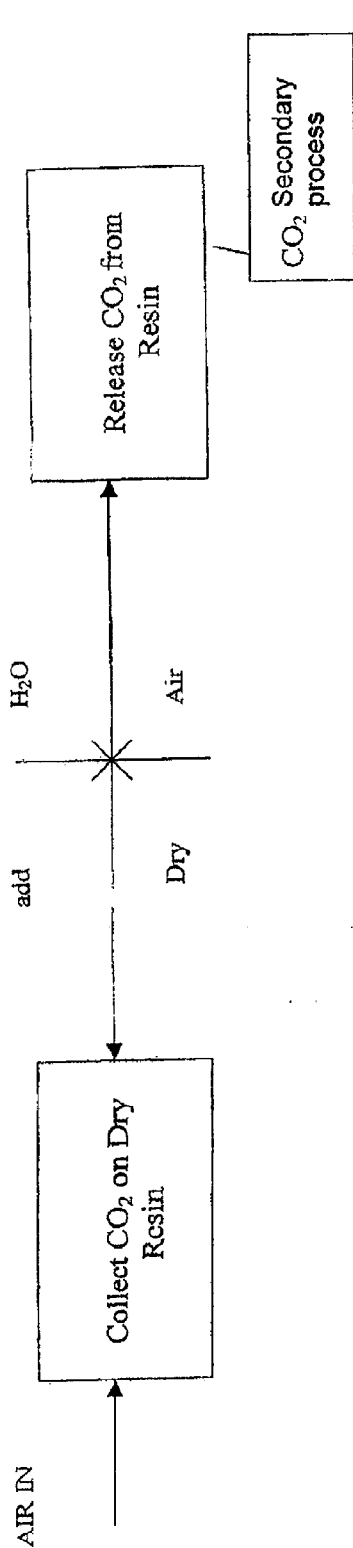


FIG. 2B

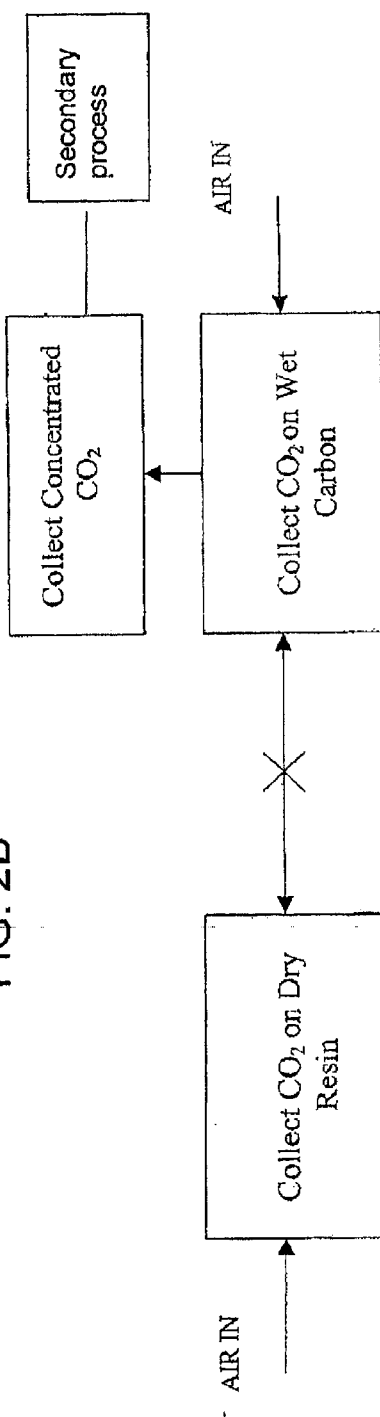


FIG. 3

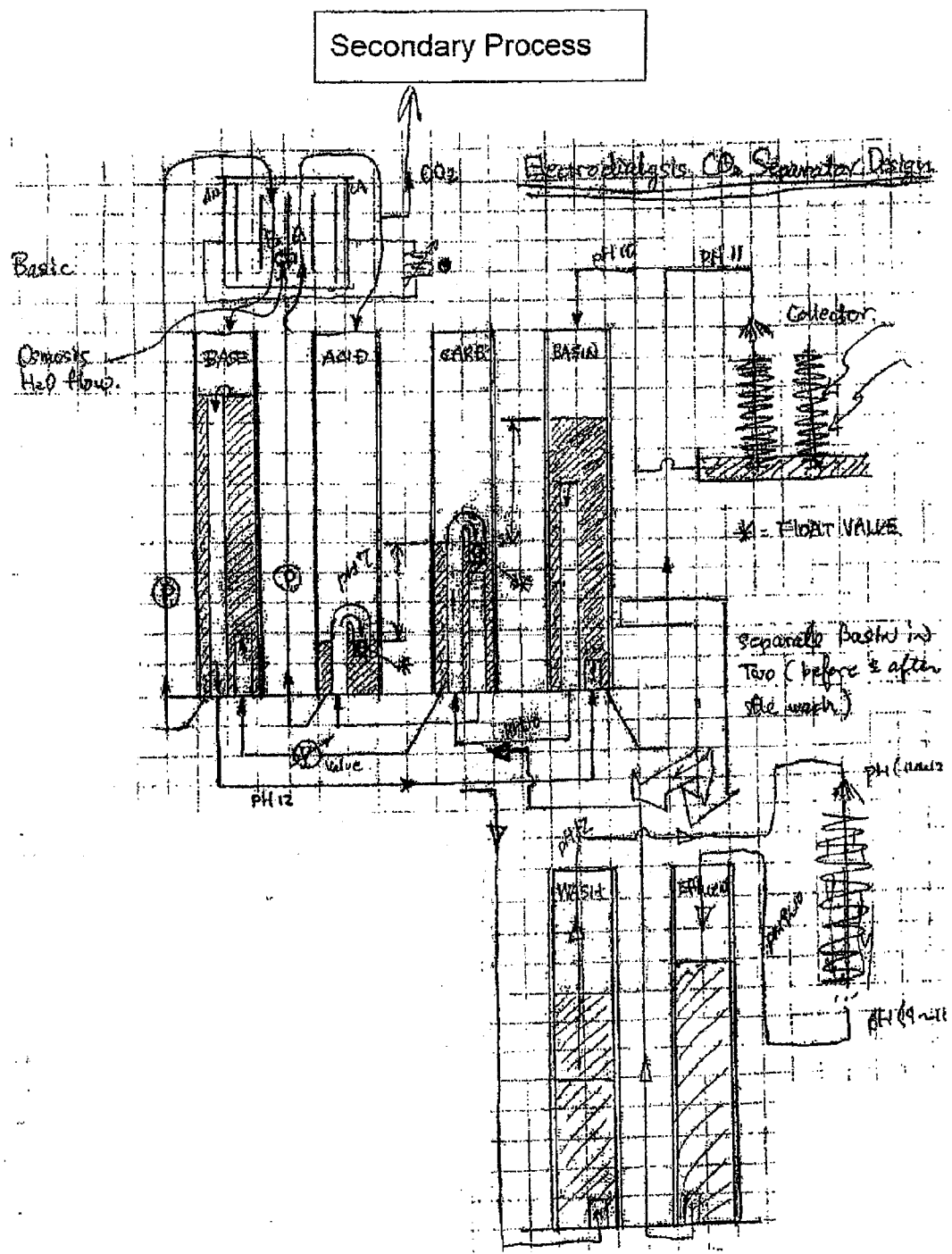


FIG. 4

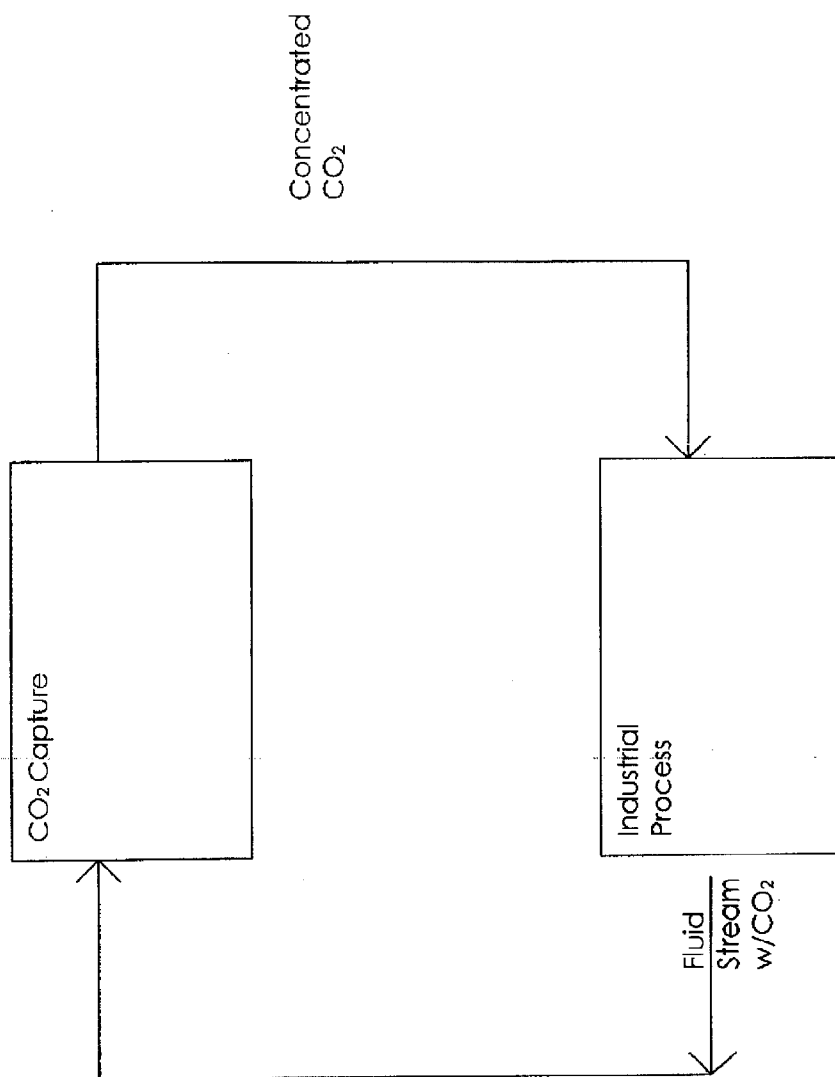


FIG. 5

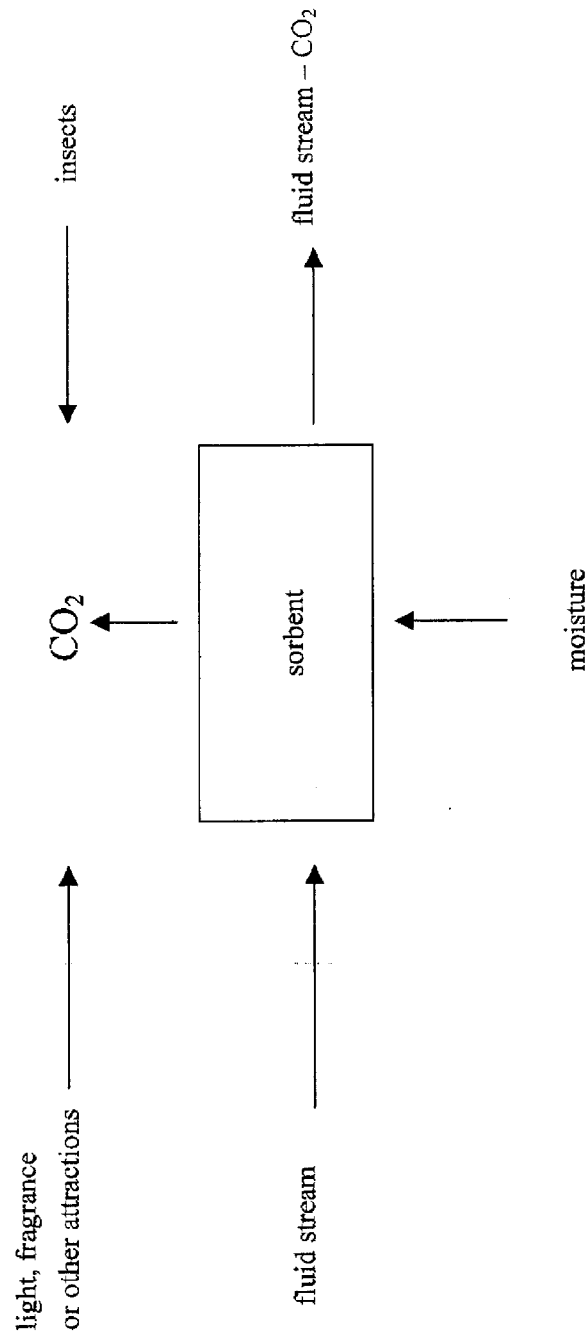


FIG. 6

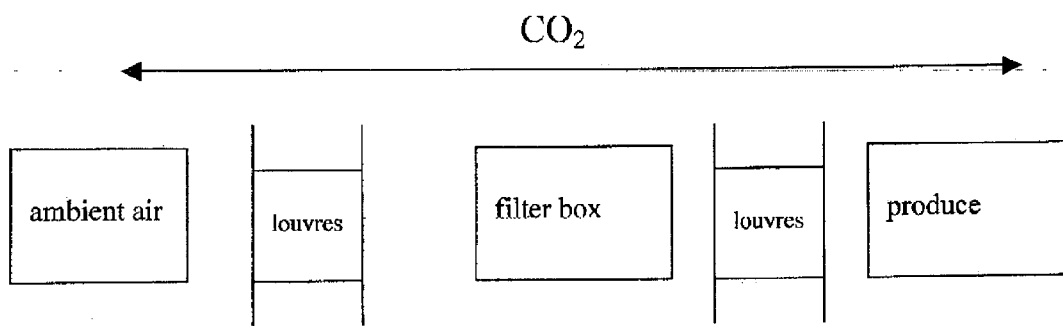


FIG. 7

