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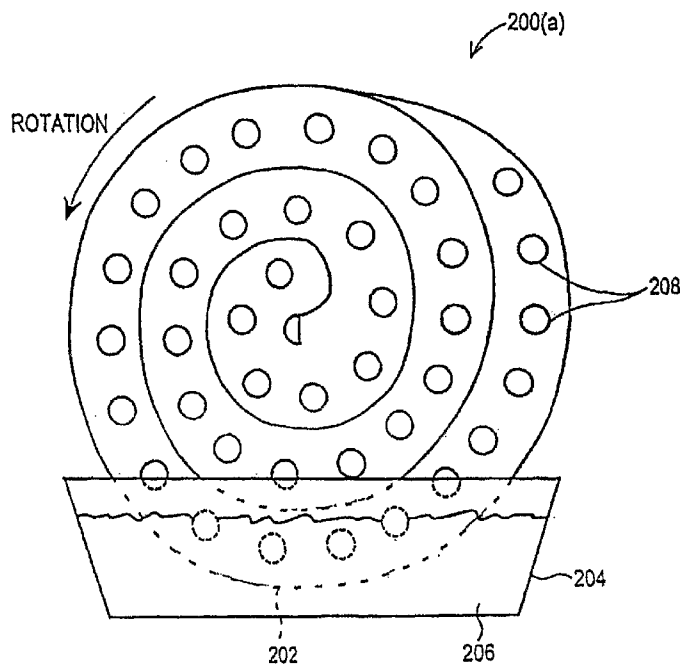
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(54) Title: REMOVAL OF CARBON DIOXIDE FROM AIR



(57) Abstract: The present invention is directed to methods for removing CO<sub>2</sub> from air, which comprises exposing sorbent covered surfaces to the air. The invention also provides for an apparatus for exposing air to a CO<sub>2</sub> sorbent. In another aspect, the invention provides a method and apparatus for separating carbon dioxide (CO<sub>2</sub>) bound in a sorbent.

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**REMOVAL OF CARBON DIOXIDE FROM AIR**

The present invention relates to removal of selected gases from air. The invention has particular utility for the extraction of carbon dioxide (CO<sub>2</sub>) from air and will be described in connection with such utilities, although other utilities are contemplated.

Extracting carbon dioxide (CO<sub>2</sub>) from ambient air would make it possible to use carbon-based fuels and deal with the associated greenhouse gas emissions after the fact. Since CO<sub>2</sub> is neither poisonous nor harmful in parts per million quantities but creates environmental problems simply by accumulating in the atmosphere, it is desirable to remove CO<sub>2</sub> from air in order to compensate for emissions elsewhere and at different times. The overall scheme of air capture is well known.

The production of CO<sub>2</sub> occurs in a variety of industrial applications such as the generation of electricity power plants from coal 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 CO<sub>2</sub> gas, which at present is simply released to the atmosphere. However, as greenhouse gas concerns mount, CO<sub>2</sub> emissions from all sources will have to be curtailed. For mobile sources the best option is likely to be the collection of CO<sub>2</sub> directly from the air rather than from the mobile combustion device in a car or an airplane. The advantage of removing CO<sub>2</sub> from air is that it eliminates the need for storing CO<sub>2</sub> on the mobile device.

Various methods and apparatus have been developed for removing CO<sub>2</sub> from air. In one of these, air is washed with an alkaline solution or sorbent in tanks filled with what are referred to as Raschig rings. For the elimination of small amounts of CO<sub>2</sub>, gel absorbers also have been used. Although these methods are efficient in removing CO<sub>2</sub>, they have a serious disadvantage in that for them to efficiently remove carbon dioxide from the air, the air must be driven by the sorbent at a fairly high pressure, because relatively high pressure losses occur during the washing process. Furthermore, in order to obtain the increased pressure, compressing means of some nature are required and these means use up a certain amount of energy. This additional energy used in compressing the air can have a particularly unfavorable effect with regard to the overall

carbon dioxide balance of the process, as the energy required for increasing the air pressure would produce its own CO<sub>2</sub> that would have to be captured and disposed of.

Thus, since the prior art methods result in the inefficient capture of CO<sub>2</sub> from air because these processes heat or cool the air, or change the pressure of the air by substantial amounts, i.e., the net reduction in CO<sub>2</sub> is negligible as the cleaning process introduces CO<sub>2</sub> into the atmosphere as a byproduct of the generation of electricity used to power the process.

Furthermore, while scrubber designs for separating CO<sub>2</sub> from air already exist, generally they are limited to packed bed type implementations whose goal typically is to remove all traces of an impurity from another gas. One such device, described in U.S. Patent 4,047,894, contains absorption elements comprising porous sintered plates made of polyvinylchloride (PVC) or carbon foam assembled spaced from one another in a housing. Prior to the plates being assembled in the housing, potassium hydroxide is impregnated in the porous plates. Such a device has the disadvantage that the sorbent material used to separate CO<sub>2</sub> from air cannot be replenished without disassembling the device housing.

Processes that collect CO<sub>2</sub> from the air typically rely on solvents that either physically or chemically bind CO<sub>2</sub> from the air. A class of practical CO<sub>2</sub> solvents include strongly alkaline hydroxide solutions such as, for example, sodium and potassium hydroxide. Hydroxide solutions in excess of 0.1 molarity can readily remove CO<sub>2</sub> from air where it becomes bound, e.g., as a carbonate. Higher hydroxide concentrations are desirable and an efficient air contactor will use hydroxide solutions in excess of 1 molar. Sodium hydroxide is a particular convenient choice, but other solvents such as organic amines may be used. Yet another choice of sorbents include weaker alkaline brines such as sodium or potassium carbonate brines.

See also, PCT Published Applications PCT/US2005/015453 and PCT/US2005/015454.

The foregoing discussion of the prior art derives primarily from our earlier Published PCT Application PCT/US05/29979 in which there is proposed a system for removing carbon dioxide from air, which comprises exposing solvent covered surfaces to airstreams where the airflow is kept laminar, or close to the laminar region. The carbon dioxide gas is absorbed by the solvent and removed from the air. In a preferred embodiment, the solvent comprises an alkaline sorbent solution such as a strong hydroxide solution. See also, our earlier published PCT Application Serial No.

PCT/US06/03646 in which we describe an air/liquid exchanger comprising an open-cell foam for supporting a liquid sorbent.

5 The present invention provides improvements over the prior art as described above. More particularly, the present invention provides several processes and systems for removing carbon dioxide or other gases of interest from air.

10 In accordance with one embodiment of the invention, there is provided an ion exchange material to capture or absorb CO<sub>2</sub>. In one aspect, the invention employs a solid anionic exchange membrane as the primary CO<sub>2</sub> capture matrix. The ion exchange material may comprise a solid matrix formed of or coated with an ion exchange material. Alternatively, the material may comprise a cellulose based matrix coated with an ion exchange material.

15 Yet another embodiment of the invention employs a wetted foam air exchanger that uses a sodium or potassium carbonate solution, or other weak carbon dioxide sorbent, to absorb carbon dioxide from the air to form a sodium or potassium bicarbonate. The resulting sodium or potassium bicarbonate is then treated to refresh the carbonate sorbent which may be recovered and disposed of while the sorbent is recycled.

20 In yet another embodiment of the invention, carbon dioxide is removed from the air using an ion exchange material which is regenerated using a liquid amine solution which is then recovered by passing the amine solution into an electrodialysis cell.

In still yet another aspect of the invention, carbon dioxide is removed from the air by modifying the alkalinity of seawater which in turn increases the flux of carbon dioxide from the atmosphere into the water.

25 Further features and advantages of the present invention will be seen from the following detailed description, taken in conjunction with the accompanying drawings, wherein like numerals depict like parts, and wherein

30 FIG. 1(a) is a side elevational view, in partial cross-section and FIG. 1(b) is a perspective view of yet alternative forms of air scrubbers made in accordance with another embodiment of the present invention;

FIGs. 2(a)-2(c), 3(a)-3(b) and 4(a)-4(c) are perspective or side elevational views, as the case may be, of air scrubbing units made in accordance with yet other embodiments of the present invention;

FIG. 5 is a block flow diagram illustrating a process for removing CO<sub>2</sub> from air in accordance with one embodiment of the invention;

FIGs. 6-8 graphically illustrate the CO<sub>2</sub> capture over time;

FIG. 9 is a process flow diagram in accordance with an embodiment of the invention;

FIG. 10 is a schematic flow diagram showing an integrated system for CO<sub>2</sub> removal from air in accordance with another aspect of the invention; and

FIGs. 11-14 are schematic diagrams of cells for treating seawater in accordance with alternative aspects of the invention.

The present invention generally relates to carbon dioxide (CO<sub>2</sub>) extraction, reduction, capture, disposal, sequestration or storage, particularly from air, and involves new processes and apparatuses to reduce or eliminate CO<sub>2</sub> from the environment. Both extraction and sequestration of CO<sub>2</sub> are encompassed by the invention.

In our earlier U.S. Patent Application Serial No. 60/603,811, we outlined a strategy for contacting air with sorbent coated surfaces. We showed, that with the slow reaction kinetics typical of hydroxide or carbonate solutions absorbing CO<sub>2</sub>, one should provide straight channels for laminar flow to maximize the uptake of CO<sub>2</sub> for a given energy investment in pressure drop across the collecting structure. If the liquid side reaction kinetics could be improved, more complex channels would reduce the air side limitation, but for low reaction kinetics straight channels with smooth surfaces appear most effective.

This invention in one aspect provides an approach for absorbing carbon dioxide from an air stream that can proceed efficiently even with weak sorbents and at low uptake rates. By wetting a foam, which has straight channels cut through it, in a manner that internal foam surfaces are fully or partially covered with a weak sorbent, it is possible to create a large area of sorbent surface that is exposed to a slow gas flow. The gas flow through the channels and through the bulk foam can be adjusted so as to optimize the uptake of dilute carbon dioxide for a given pressure drop across multiple layers of foam. For the extraction of low concentration gas admixtures to a gas stream this technique obviates the need for strong sorbents with a fast rate of absorption. As a consequence one can take advantage of weak sorbents like sodium carbonate for capturing CO<sub>2</sub> from air, rather than having to rely on strong sorbents like sodium

hydroxide. The lower binding energy of carbon dioxide to the weak sorbent greatly simplifies subsequent sorbent recovery steps. This disclosure describes the principles involved and outlines a method and apparatus to create moist foam surfaces and to extract the CO<sub>2</sub> laden sorbent from the foam. These methods can be used with any applicable sorbent recovery method. They are not limited to the capture of carbon dioxide from the air, but could be extended easily to the capture of trace gas admixtures from any gas stream. As outlined below, the details of the implementation will depend on the concentration of the trace gas, the rate of the adsorption or absorption reaction and the flow speeds involved. It also matters whether the goal of the process is to capture all of the trace gas out of the mixture in order to clean up the gas, or whether the goal is to collect a valuable stream of trace gas from the mixture without attempting to eliminate nearly all traces from the carrier gas.

In collecting carbon dioxide from the air, two distinct transfer steps could potentially set the rate limit. The first is the uptake of carbon dioxide into the sorbent, the second is the transport of carbon dioxide through an airside boundary layer to the surface of the sorbent. In the first case the capture system is sorbent-side limited in the second it is air-side limited. In an earlier published PCT Application Serial No. PCT/US06/03646, we outlined one approach to optimizing a CO<sub>2</sub> capture device from a dilute stream. Here we outline another approach that takes advantage of a very different principle. Both approaches aim to minimize the pressure drop required across a scrubbing device for removing a certain fraction of the CO<sub>2</sub> from the air flow. Since CO<sub>2</sub> in the air is very dilute, it is important to minimize the energy penalty for pushing air through the air scrubbing system. Ideally, the pressure drop is so small, that the partial stagnation of natural wind flows is sufficient to provide the energy for making contact between the air and the sorbent material.

The aforesaid previous invention provides a method of minimizing the pressure drop for a fixed flow velocity, by assuring that the CO<sub>2</sub> transport is at least partially airside limited. For weak sorbents like alkaline solutions this suggests a laminar flow which generates boundary layers thick enough to roughly equalize the air-side mass transport coefficient and the sorbent side transfer coefficient. This invention by contrast is concerned with partitioning the air flow into fast moving and slowly moving streams and inserting the scrubber into the stream where it flows slowly.

As a particular design we consider a filter device in which the distances between

nearest neighbor absorbing surfaces are small compared to the allowable boundary layer thickness. In that case the CO<sub>2</sub> concentration on the surface is not much reduced and consequently the system can be considered sorbent side limited. In such a system the fractional loss of momentum is large compared to the fractional loss of carbon dioxide.

5 As one lowers the speed of the airflow, the system remains sorbent-side limited and the fractional loss of momentum still remains high, but the available momentum drops rapidly. Hence the total loss in momentum is reduced for a given thickness of the filter system. The pressure drop can be even further reduced, as the longer residence time of the air in the filter will lead to a higher reduction in CO<sub>2</sub> content of the air. If one holds  
10 the fractional CO<sub>2</sub> extraction constant the filter can be made thinner and thus the required pressure drop is even further reduced.

However, if the total flow through the collector is to remain constant the slowdown of the flow in the filter must be accompanied by a speed-up of another stream. This can be accomplished by partitioning an air stream into two streams. Both streams  
15 simultaneously are run through a filter. The system experiences a pressure drop which is governed by the thickness of the filter, and the flow speed of the air. In panel B) the flow pattern has been reorganized so that one stream is first expanded out, while the other part is made to converge. As a result the air in the widening section slows down, while the air in the narrowing section speeds up. At the point of maximum cross section  
20 a filter is installed into the slow flow. Downstream from this point, the expanded air flow is made to converge again and the other air stream fans out to the same extended cross section the first flow had higher upstream. At this point the air in the second stream is scrubbed of all or part of its CO<sub>2</sub>. A final section follows where both streams are readjusted to their initial cross-section. In order to achieve the same filter affiance,  
25 the filters in this new design can be substantially thinner. If the system is sorbent side limited, then the volume of the filter does not need to change, but since the cross section increased the thickness of the filter can be reduced accordingly. The pressure drop is reduced because the flow speed is lower and the resistance of the filter is reduced.

The above example serves to explain a basic physical principle. In the following  
30 we outline a specific method of approximating such a behavior with simple blocks of foam like filter material. Foam blocks have many advantages: They can be shaped into arbitrary forms, they can hold some liquid and they are easily wetted; and open cell foams present a large internal surface area that can be used to absorb CO<sub>2</sub> from air flowing through the foam.



A large foam block wetted with a liquid sorbent like NaOH or Na<sub>2</sub>CO<sub>3</sub> will absorb CO<sub>2</sub> from the air. If we assume a typical pore size of about 1 mm and a specific area of about 4000m<sup>-1</sup>, then a typical uptake rate for a sorbent surface of about 2 μmol m<sup>-2</sup>s<sup>-1</sup> would provide an uptake capacity of 8 mmol s<sup>-1</sup> for a foam block of one cubic meter. If we intend to extract 5 mmol/m<sup>3</sup> from the air stream, the thickness of the apparatus at flow speeds of 3m/sec would be about 2m. However, the pressure drop of solid block of foam would be far too large to maintain such a high flow speed. If, however, one opens up channels through the foam that let 90% of the air bypass a foam layer, and then mix the air again and go through another layer with 90% bypass, then the effective flow speed in the foam is ten times smaller, the pressure drop is reduced by a factor of ten, and the uptake rate is virtually unchanged as it is not limited by the rate at which air flows through the thin slices, but by the rate at which the surfaces inside these foam slices can absorb CO<sub>2</sub>.

By forming small straight channels through a layer of foam, one opens a pathway through the foam that will allow the bulk of the air a path that avoids going through the foam. By adjusting the total cross section of the holes, and the diameter of the holes it is possible to control the relationship between pressure drop and flow speed, and the fraction of the flow that actually goes through the holes.

Small diameter holes at a fixed flow rate will lead to a higher pressure drop, or alternatively at a fixed pressure drop they will lead to a higher flow rate. A practical system operates between the two limits where adjustment of the hole diameter and the number of holes will change the overall resistance to flow and thus change pressure drop and flow speed.

Increasing the number of holes will increase the flow rate, and hence reduce the pressure drop across the foam block. The pressure drop across the foam block in turn controls the flow speed through the bulk of the foam. It is therefore possible to adjust the parameters of this system in a way that optimizes a specific apparatus in that one controls its pressure drop, across the foam block, and independently the size of the bypass flow.

Finally, one generalization of these concepts: The concepts are not limited to extracting CO<sub>2</sub> from air, but they can be easily generalized to the extraction of any trace gas from any gas stream. Finally, while in most of the above discussion we assumed that the absorber is a liquid that is absorbed by the foam, it is of course also possible to

consider foam like solid materials, including mats of fibers or other structures, that can absorb CO<sub>2</sub> as it passes through the system.

In contrast to experiments performed with AQUAFOAM<sup>®</sup>, which is a very hydrophilic phenolic foam that easily retains liquid and thus has pores completely filled with liquid, the polyurethane foams were essentially stripped of 80 to 90% of the volume of liquid it contained at the point of immersion. In contrast to the experiments on phenolic foams (AQUAFOAM<sup>®</sup>), in experiments with polyurethane foam the duration of uptake was greatly reduced from days or weeks to tens of minutes. In return the rate of uptake was greatly enhanced for a weak sorbent like a half molar sodium carbonate solution. The critical difference between the two experiments is that in the former experiments the foam is filled with fluid, whereas in the latter the foam volume is in its majority filled with gas. Intermittent soaking of the polyurethane foam block during the experiment, which would fill the pore space with liquid, lead to an immediate reduction in CO<sub>2</sub> uptake which only recovered after the liquid level contained in the foam had been appropriately reduced.

While the CO<sub>2</sub> uptake of a carbonate solution is greatly enhanced, the rate of water evaporation is essentially unchanged. Water evaporation is not sorbent side limited and hence the gas stream moving through the foam block is immediately water saturated and thus stops soaking up additional water. However, in most designs it will not be possible to take advantage of this effect, as a system that maximizes CO<sub>2</sub> uptake will contact all of the air and thus saturate all of the air with water vapor.

The role of hydrophilic vs. hydrophobic vs. mixed surfaces is at this point not fully understood. Each have advantages and disadvantages. Hydrophobicity controls the amount of liquid retained in the foam and the ease with which this liquid can be applied evenly. Thus, it is believed that a hydrophilic phenolic foam with slightly larger than usual pore sizes could combine excellent wetting properties with an appropriate low water retention level. Most commercially available phenolic foams are designed to retain water, and thus are not well suited to this application.

Various foams are commercially available and can be used. These include hard foams that would crush and be mechanically destroyed if subjected to significant compression, soft elastic foams that can be "squeezed." Hard foams can only be flushed with fluid. In order to maintain an appropriate level of saturation, it is necessary to let such foams drain. On the other hand, it is possible to push liquid out of the foam by driving a gas like air under pressure into the foam matrix.

Unevenness in flow patterns, draining and drying rates can render the use of these foams very challenging. In the case of soft, elastic foams it is possible to move liquid into and out of the foam by compressing the foam matrix. In the case of hard foams turning the foams will help in evenly distributing fluid throughout the volume of the foam.

A second aspect of this first embodiment thus is concerned with the application and extraction of liquid from soft and elastic foam structures as well as from foams that cannot be compressed without damaging the foam structure.

The simplest approach to wetting the foam would be the application of liquid on the top and letting it drain by gravity. Particularly large celled foams, or reticulated foams which drain easily are suitable for this approach. If wetting a foam is accomplished through flowing fluids and gravity based drainage, then slowly rotating the foam aids in obtaining even fluid coverage inside the foam. The direction of the axis of rotation must have a component in the horizontal direction, so that rotation does change the flow direction inside the foam as it changes the alignment of the foam with the direction of gravity. Rotation speeds are matched to the foam and fluid flow properties such that the bulk of the fluid but not all in the time of a rotation can flow to the bottom of the foam volume. By shaping the foam appropriately it is even possible to transfer fluid in the process of rotating the foam piece. As an example, the foam may be formed into a closed spiral shape 200 as depicted in FIG. 1(a), and slowly rotated about its axis with its rim or periphery 202 dipping into a pan or sump 204 containing liquid sorbent fluid 206. Channels 208 may be formed through the foam to allow passage of air. Alternatively, the foam may be formed into an open spiral shape 210 as depicted in FIG. 1(b) and slowly rotated with its periphery into a pan or sump 214 containing liquid sorbent fluid. Also, if desired, the central axis end of the foam spiral may be mounted in a sorbent collection tray 216 which rotates with the foam spiral. The rotation in this case will gradually move the fluid from the rim of the shape to its center where it may be extracted from the foam.

In foams that can be elastically compressed, it is possible to assure fluid mixing by moving the fluid by compressing and relaxing the foam. Referring to FIGs. 2(a)-2(c), in order to move liquid through the foam structure external pressure may be applied by moving rollers 42 over the surface of the foam 44 or by compressing foam blocks between flat plates. Rollers 42 may be smooth cylindrical surfaces that roll on both sides of the foam. The rollers push the external foam surfaces toward each other and thus

force fluid to flow and mix throughout the volume. Alternatively, one can use a single roller on one side, and a rigid surface on the back of the foam holding the foam in place. This arrangement would be particularly useful for relatively thin foams, where the additional cost of a second roller and the concomitant structural complications would not be justified.

Instead of having smooth surfaces the surfaces of the rollers can be structured and shaped so as to increase the fluid movement in the foam by varying the degree of compression locally. Options include, simple fluting with ridges that follow the roller axis. Alternatively one can consider ridges that run circumferential around the rollers, or surfaces with dimples and protrusions. With any of these structured surfaces, it would be useful to match the surfaces on the opposing rollers (or shapes in the structured walls) so as to optimize fluid flow patterns. Attention must be paid to maximizing volume change in the foam while minimizing shear strain in the foam.

Referring to FIGs. 2(a)-2(c) particular implementation which we discuss here for illustrative purposes would be a foam matrix 44 rectangular in shape, with large width and height and a relatively small thickness, as an example consider a foam block collector pad, 2 meters high, 1 meter wide, and 0.3m in thickness. Narrow tubular channels cross through the block in the 0.3m thickness of the block. Air would flow through the foam in the direction of the channels, traversing the foam in the direction of its smallest dimension. Liquid could be applied to its two sides or to the top, and rollers 112, 114 would span the rectangular faces 2 m tall and 1 meter wide. The rolling action would squeeze liquid in place, a downward stroke with a high degree of compression could be used to squeeze liquid downward and let it drain from the bottom of the block.

Rollers 112, 114 would move up and down the sides of the foam, and they might move in or out to modify the compression on the foam collector pad. An upward stroke with less compression could be used to establish a uniform fluid filling throughout the brick.

Liquid 116 could be applied on the top of the brick and pushed down by the rollers. Some fluid will be pushed downward, and depending on the gap between the rollers a certain amount of fluid is left behind in the foam matrix. If the height of the foam is not too large all fluid could be applied on the top and pushed down to the bottom. Alternatively, we can spray the fluid onto the sides of the foam in advance of the rollers. If the compression is set high the rollers can be used to squeeze out liquid that is either captured directly in front of the rollers as it pushes out of the sides of the

rollers or if the speed of the rollers is sufficiently slow, the fluid will be pushed to the bottom of the foam pad, where it will be extruded and collected. It is thus possible to remove liquid from the pad by either injection additional carrier fluid, or just squeezing out liquid from the foam. In a second application fresh fluid is applied to the foam,  
5 which with a lower level of compression is evenly applied over the volume of the foam pad.

It also is possible to move the pads through the rollers and install the rollers in a fixed position.

Referring to FIGs. 3(a)-3(b), an alternative to rollers would be flat plates 118-120  
10 squeezing the entire area of the foam collector pads 110. This would work particularly well for arrangements in which the airflow is aligned in the vertical direction and the compression of the foam is used to squeeze fluid in and out of the foam parallel to the air flow direction, which usually represents the smallest dimension of the foam pad. It is also possible to turn the foam pad prior to squeezing and move it from an upright  
15 position into a horizontal position.

A particular implementation where the foam is moving rather than the rollers would be design where the foam moves as a continuous loop, like a belt over rollers that saturate and squeeze the foam, while the foam moves in an endless loop. These loops could be arranged in various ways, in particular it is possible to run the loop vertically up  
20 and down, or run it horizontally.

In yet another aspect of the invention, illustrated in FIGs. 4(a)-4(c), the collector may comprises a plurality of foam collector pad 50, each rotatably suspended from a support post 132 which support posts 132 are in turn horizontally movable between an operating and open position as shown in FIGs. 4(a)-4(b), respectively, and a closed  
25 position showed in FIG. 4(c) in which a liquid sorbent may be applied from a spray and excess sorbent squeezed via end plates 48. The amount of liquid present is chosen such that gas flow through the foam sees little impediment, the bulk of the pore volume is filled with gas, and gas filled pore spaces are interconnected so as to make it possible to transfer CO<sub>2</sub> by diffusion or other means from one pore to the next, until it gets  
30 absorbed.

For air side limited flows, channels are ideally straight, but the effective rate of migration of sorbate gas into the foam structure may be enhanced by creating pressure fluctuations in the flow field.

While sodium hydroxide solution may be employed as the sorbent in the above described apparatus, i.e. in accordance with the teachings of our aforesaid published PCT Application Serial No. PCT/US06/03646, in accordance with one embodiment of our invention we may employ a wetted foam air extractor system that uses a sodium or potassium carbonate solution – or any other weak CO<sub>2</sub> sorbent, to absorb carbon dioxide from the air and in the process forms sodium or potassium bicarbonate; a sorbent recovery step that refreshes the carbonate sorbent by percolating the bicarbonate brine over a solid sorbent, which in a preferred implementation is an ion exchange resin; a resin recovery step using a liquid sorbent, which in a preferred implementation is a liquid amine solution, and a CO<sub>2</sub> release which is accomplished either by thermal swing, pressure swing or electrodialysis.

Following CO<sub>2</sub> from the air through the apparatus, can thus be described as follows: the air comes in contact with a weak sorbent, like sodium carbonate, that by virtue of its distribution over a foam surface can achieve uptake rates that are so high that air side transport starts limiting the CO<sub>2</sub> uptake. Once the solution has taken up sufficient amounts of CO<sub>2</sub>, it percolates over a solid sorbent, for example an amine based ion exchange resin that removes bicarbonate from the solution and thus restores its alkalinity. The CO<sub>2</sub> is now attached to the resin and is removed from the resin in a subsequent step, by washing the resin with a another liquid sorbent, preferably an amine solution from which one can then in a final step recover the CO<sub>2</sub>. Here the options are a thermal swing, a pressure swing, or an electrodialysis process.

Referring to FIG. 5, the steps of the process are as follows: capture of carbon dioxide from air on a carbonate wetted foam at step 250. In this process, a wetted foam structure is exposed to ambient air which flows through the system at speeds ranging from 0.1m/sec to 100m/sec, the preferable range being from 0.5m/sec to 10m/sec and an optimal range of from 0.5 to 4m/sec. These foam structures are shaped or arranged such as described above so that they have passageways through which air flows and comes in contact with the wetted foam surfaces. The wetted foam surfaces absorb carbon dioxide. In such case the CO<sub>2</sub> laden sorbent contains bicarbonate ions. The following steps of the process will have to recover the carbonate from a very dilute bicarbonate stream that is mixed in with a possibly much larger concentration of CO<sub>3</sub><sup>=</sup>.

The ratio of carbonate to bicarbonate depends on the total carbon concentration. In order to have sorbent liquid move into and out of the foam, liquid is flushed out of the foam by one of several methods described elsewhere. The preferred method would be a

design where gravity drainage of the liquid by itself will remove the spent sorbent, or a water flush will mobilize the spent sorbent and collect it at the bottom of the device. For implementations in which the optimal capture design does not lend itself to gravity drainage, other methods that utilize motion or compression of the foam are possible such as described above.

In any case, the resulting solution contains a dilute stream of sodium bicarbonate. Given the low concentration, direct sorbent and CO<sub>2</sub> recovery from this brine is usually not the most advantageous approach. As an alternative we provide a three stage approach where the low concentration bicarbonate is first concentrated by bringing the solution in contact with an amine based ion exchange resin.

In the next step 252, ion exchange resins in contact with bicarbonate solutions will absorb bicarbonate ions from the brine, and replace them with hydroxide ions, which in turn are neutralized by reacting with a second bicarbonate ion resulting in the formation of carbonate ions and water. Resins could be of various types, but several suitable resins are available commercially. Preferred are resins functionalized with amine groups. The important consideration is the binding energy of the bicarbonate (or carbonate) to the resin. It must be large enough to transfer CO<sub>2</sub> from the liquid to the resin, but weak enough to relinquish the carbon dioxide in the subsequent processing step. Typical binding energy would range from 20 to 60 kJ/mole but wider ranges are possible. While for practicality, organic resins are preferred, other solid sorbents equally could be utilized to perform this transition. One particularly preferred material is magnesium hydroxide, although other solid materials that can be carbonated may be used, such as lithium silicates and lithium zirconates which are given as examples. Such materials are capable of absorbing CO<sub>2</sub> and may be used as solid sorbents in accordance with the present invention. Similarly, various commercially available ion exchange resins are capable of recovering the carbonate brine, by raising the alkalinity back to that of the starting material may be used in the practice of the present invention.

A particular implementation is a resin bed through which CO<sub>2</sub> laden sorbent is cycled. As the sorbent flows through the bed the resin is gradually saturated with carbon dioxide. If flows are kept relatively slow, the absorption front will move gradually through the resin until it breaks out at the far end of the bed, at which stage one would observe a sudden increase in the concentration of bicarbonate in the effluent and thus know when the resin has been spent. Once this point has been reached, the resin is due to be refreshed.

The partial pressure of carbon dioxide in the air is very low, around 380 micro bar. As a result for most resins, this front will be rather wide and ill defined, in that case it would be advantageous to break the resin bed into multiple beds, and use a nearly spent bed, to begin the removal of carbon dioxide and thereby maximize saturation of the bed, use a one or more cascading beds to remove the bulk of the CO<sub>2</sub> from the sorbent and percolate the sorbent fluid finally through a last fresh bed, to maximize extraction. By plumbing and valving stationary beds together, it is possible to cycle their logical position in the chain of sorbent refreshing or in the resin recovery step. As a result, the steps of the operation move gradually through a ring of tanks. For some resins, the binding energy of different sites varies, and in that case it would be disadvantageous to push the resin to its limits. Instead in such a case the resin would swing back and forth within a range of binding energies that are easily accessible.

The resin is recovered in a step 254 by washing it with a different CO<sub>2</sub> sorbent, for example, an amine solution that binds carbon dioxide strongly enough to recover it from the resin. This will lead to a transfer of the bicarbonate, carbamate or carbonate ion from the resin to the amine solution. The advantage of this last step is that the amine solution can achieve far higher load factors, i.e., ratio of amine solution-to-CO<sub>2</sub> weight than the resin itself. The improvement is even larger, when compared to the initial carbonate brine. Thus less energy is wasted in heating and cooling the sorbent, than if the heat recovery step would be performed on the resin itself or if recovery were attempted from the original weak sorbent.

The amine solution loaded with CO<sub>2</sub> is transformed in a thermal swing to release carbon dioxide from the amine in a step 256. There are several options available for this step, since amine solutions are used in other carbon dioxide absorption systems. In one option, steam is used in transferring heat to the process. Preferably, heat for forming the steam will be from carbon neutral energy sources such as solar energy, or absent these sources, from the combustion of carbon based fuels with pure oxygen, thereby creating an additional stream of concentrated CO<sub>2</sub> that reflects the energy demand of the CO<sub>2</sub> recycling process. Of course, other heat sources including geothermal heat sources, solar energy heat sources, as well as waste heat energy sources may be used.

The invention is susceptible to modification. For example, instead of using inactive foam with a liquid sorbent percolating through it, it is possible to use a functionalized foam or resin without the use of a carbonate sorbent. In such case, the wetted foam would be used to directly collect carbon dioxide from the air. In such case,



the foam should not be allowed to dry completely, but for some foams it may not be necessary to inject liquid water, since a minimum amount of moisture in the air may be sufficient to have the amine react with carbon dioxide from the air. Once the foam is saturated with CO<sub>2</sub>, a flush with a secondary CO<sub>2</sub> sorbent may be used to regenerate the resin. This could be a carbonate solution, but with a higher concentration of sodium carbonate than in the system discussed above. The resin wash could also be an amine wash, in which case the process becomes a streamlined version of the main process discussed above.

Alternatively, instead of using carbonate sorbents in the foam one could use amine solutions directly in the foam. That would eliminate the second and third step of the process. The result is a process that is streamlined down to a single process step for capture followed by a single process step for sorbent recovery and CO<sub>2</sub> release.

It also is possible to replace the thermal swing for CO<sub>2</sub> recovery with an electro dialysis process. Electro dialysis could follow several distinct approaches, as disclosed, for example in our published PCT Application PCT/US06/03646. Electro dialysis could be applied to the bicarbonate solution generated in the first step, or alternatively, it could be applied to the amine solution that is generated in the final step.

In yet another aspect of the invention, we utilize solid phase anion exchange materials (AEM) for the direct capture of CO<sub>2</sub> and other acid gases from air. The application of AEMs as discussed herein with regards to its utility for low (ppm) absorption of CO<sub>2</sub> from air, but readily is usable for capturing other low concentration gases such as NO<sub>x</sub> absorption, and SO<sub>4</sub>, as well as concentrated CO<sub>2</sub> or other gas removal.

Two alternatives are possible.

One alternative is to use an intermediate solid substrate that is able to be exposed to large volumes of air and collect CO<sub>2</sub> at low concentrations while acting as a solid with little or no vapor pressure. The solid substrate can be envisioned to act as a sort of net, storing the CO<sub>2</sub> chemically until it is released into solution at a later time. Further the solid substrate is able to release the newly collected CO<sub>2</sub> back into a solution that also regenerates the solid surface. The solution containing the captured CO<sub>2</sub> is regenerated in an energetically feasible way. A volatile or high vapor pressure solution can be utilized to collect the CO<sub>2</sub> from the substrate and can be regenerated at low energy penalty. This intermediate step allows us to cleave CO<sub>2</sub> attached to a substrate without exposing the substrate to the open environment, preventing atmospheric contamination and loss.

The above process exchanges anions to and from a solid substrate. Here we are utilizing the anion exchange partner fastened to a solid substrate participating in ion transfer. An example of this is the reaction of methylamine onto a styrene backbone via chloro-methylation (a common ion exchange resin used in deionized water systems). In this type of systems a nitrogen group such as an amine is attached to a polymer backbone via a covalent bond. This covalent bond pins the ammonia type molecule to the substrate while allowing it to dissociate (to form a cation and anion). If all four of the possible covalent bonds that can be attached to the nitrogen are filled with carbon groups, the nitrogen is forced into an electron deficient state and acquires a permanent positive charge. The permanent charge on the ammonium ion turns it into a cation which must then be satisfied by the ionic attachment of a neighboring anion. This is a salt that is covalently attached to a solid polymer substrate.

The ability to create a solid surface that acts like a strong base solution provides several features and advantages not limited to the following:

1. The CO<sub>2</sub> net utilizes the anion exchange properties of the amine salt while capitalizing on the zero vapor pressure of the solid polymer backbone. Essentially the amine salt can be forced into a hydroxide form (OH<sup>-</sup>) by replacing all of its anions via concentration gradient leaving a surface of OH<sup>-</sup> attached to the solid. The attached OH<sup>-</sup>s are now readily available for reacting with incoming CO<sub>2</sub>. Since most of the techniques to capture CO<sub>2</sub> exploit the reaction of the acid gas with a liquid base, or OH<sup>-</sup> surface, this method shares in the fast acid/base reaction kinetics.
2. The elimination of a liquid film intermediate allows for large increases in surface area as compared to current methods. In gas liquid contactors the challenge is to spread the liquid in such a way as to contact as much air as possible. This normally involves spreading the liquid over a solid surface to increase its surface while not inducing such a large pressure drop that the gas is not able to properly flow. The solid OH<sup>-</sup> surface allows for maximum surface area with minimal pressure drop.
3. Minimal water is required for the reaction to occur and overall, essentially no water is consumed. The membrane is able to cleave water from the air in order to facilitate the capture. When large volumes of air are concerned this is a major benefit.
4. Because the OH<sup>-</sup> is attached to the polymer substrate, it is no longer able to react with the environment unless there is an anion available to replace it or an acid is available to react with it. This is a benign surface that is highly reactive with acid gases

only. This allows the complete removal of a strong oxidizer from direct contact with the environment while still facilitating capture.

5. Another problem with contacting large volumes of open air is airborne contamination of the collector itself. The buildup of dirt and bacteria within the system is inevitable. As long as there is no anion transfer to the solid itself from the contaminants, the surface can be washed with water before being treated or regenerated, eliminating contaminants from entering the rest of the separation process.

6. Little or no liquid pumping is required between surface renewals. This significantly reduces pumping costs from distributing the fluid over a surface to create contact area.

7. Since the process for attaching anion exchange groups to polymers is relatively well understood, there is no limit to the types or shapes of materials to which the anion exchange material could be applied.

In one aspect our invention employs solid anionic exchange membranes as the primary capture matrix for the capture and subsequent delivery of atmospheric CO<sub>2</sub>. The membranes are spaced closely together with spacings from 1-25 mm. This spacing allows for the passage of ambient air with a pressure drop sufficiently low to preclude the use of machines to move the air. This is in accordance with the matrix construction discussed our aforesaid PCT Application Serial No. PCT/US05/29979.

The advantages of using ion exchange membranes as the material for the matrix are several. One advantage lies in the fact that the membranes can be operated in such a way as to be nearly dry, thus removing the risk of spreading caustic materials through the environment in the form of aerosols. Another advantage in operating in an essentially dry mode is the absence of water loss due to evaporation. This water loss is significant not only in the amounts of water lost to evaporation, but also in all the attendant costs of pumping, purchasing and plumbing of the water delivery systems. Another advantage is the membrane's ability to store the captured CO<sub>2</sub> at a concentration greater than that possible with an aqueous surface of the same area. The increased apparent active area exceeds the equivalent aqueous area. This allows capture at rates that exceed those possible by using aqueous solutions. Additionally, the total capture capacity is in excess of that possible with aqueous solutions.

The attached FIGs. 6-8 which illustrate the CO<sub>2</sub> capture performance of an anionic membrane exposed to both a continuous ambient air flow and also a closed

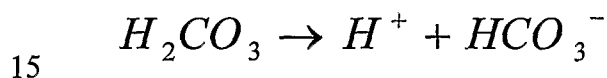
container (18.9L) within which a small piece (2x2cm) of active membrane is suspended and the drawdown of the CO<sub>2</sub> in the enclosed bottle is measured and logged.

Another data set shows a small piece of active membrane suspended within a larger (128L) closed container with same data measured and logged.

5 In yet another aspect, the present invention employs cellulose based pads as substrates for ion exchange media (IEM). As noted *supra*, IEM works by allowing ions to exchange from a solution with like charged ion within the IEM. This exchange can be accomplished via several routes.

10 In one process a high concentration fluid induces like charged ions on the IEM to migrate away from the resins' ion receptive sites into the solution and allow the higher concentration ions in the solution to occupy the sites. This can be envisioned as overpowering the resin via a concentration gradient.

The absorption of CO<sub>2</sub> on an IEM takes place via the following mechanism:



Cellulose based IEM's have become very efficient. Using the EDM method of animolysis to functionalize cellulose into an IEM has shown almost equivalent storage attributes as the commercially available IEM that are based on styrene divinylbenzene. This provides the pathway for cellulose utilization.

20 We have found that IEM's have the ability to capture CO<sub>2</sub> directly from the air and release it via concentration gradient into an amine wash solution. This has many implications

25 Due to the large regeneration energy requirements of carbonated earth alkaline solutions, the use of amine based alkaline solutions has shown a significant energy advantage. The problem, however, is that most amine solutions that exhibit the desirable qualities required, such as high kinetic rate and absorption capacity, also exhibit a high partial pressure. Due to the large amounts of air that must be contacted to facilitate the absorption, (around 2 million cubic meters per ton of CO<sub>2</sub> assuming 200ppm uptake), even low vapor pressure solutions have a very high loss rate. Without an intermediate

between the liquid amine and the air most amine solutions would not be applicable to the direct capture of CO<sub>2</sub> from the air.

The IEM is just that intermediate, which allows us to minimize the contact time of the absorbent solution with large volumes of air but still take advantage of the low regeneration costs of the liquid amine solution.

Since the surface of the contactor is produced from the sorbent itself, there is no need to constantly wet a surface with sorbent liquid to facilitate absorption. This is possible because the IEM's retain significant amounts of water (some as high as 50% by mass). This coupled with an internal concentration gradient allows the IEM to act as a solution. As CO<sub>2</sub> is absorbed onto the IEM a concentration gradient is induced that causes the migration of HCO<sub>3</sub><sup>-</sup> away from the surface to a lower concentration and the counter migration of OH<sup>-</sup> to replace it. This effectively allows the IEM to store HCO<sub>3</sub><sup>-</sup> deep within its structure while not losing effective surface area. Of course, once the IEM becomes saturated after a set amount of time, the amine wash solution could be used to regenerate the media to its OH<sup>-</sup> state and lose very little amine in the process. Our experiments have shown absorption periods of greater than 8 hours.

By eliminating the use of a continuous free passing ionic liquid solvent we also eliminate the formation of crystals on the collector surface which ultimately will lead not only to decreases in the collector performance but also in the lifetime of the substrate.

The IEM will circumvent this issue molecularly by storing the ionic products within the substrate itself. Instead of the salt residing on the surface of the substrate where it can form scale and cause fouling, the anions that are produced in the CO<sub>2</sub> absorption process have no counter ions which will enable them to sit independently on the surface of the media. When the CO<sub>2</sub> is absorbed to the surface of the media, it effectively neutralizes the OH<sup>-</sup> anion portion of the resin replacing it with an HCO<sub>3</sub><sup>-</sup> effectively storing it in the substrate.

Yet another embodiment of the invention is a process for regenerating an ion exchange resin used in capturing CO<sub>2</sub>. FIG. 9 exhibits the general process flow diagram.

To achieve separation and recovery of Na<sub>2</sub>CO<sub>3</sub>, CO<sub>2</sub> is removed from the NaHCO<sub>3</sub> in passing the liquid through an ion exchange media, in which CO<sub>2</sub> is released, which undergoes an acid/base reaction with the NaHCO<sub>3</sub> remaining in the liquid, thus regenerating Na<sub>2</sub>CO<sub>3</sub>. The Na<sub>2</sub>CO<sub>3</sub> solution then exits the ion exchange column and is returned to the upstream process.

The ion exchange media will over time become saturated with CO<sub>2</sub> and must be regenerated. This is achieved by passing a liquid amine solution through the bed after the Na<sub>2</sub>CO<sub>3</sub> + NaHCO<sub>3</sub> stream has been removed. The liquid amine solution will release an OH<sup>-</sup> to the ion exchange resin, which in turn releases the CO<sub>2</sub>, effectively

5 regenerating the ion exchange media. The amine-CO<sub>2</sub> solution is then removed and the process is repeated as a cyclic system.

The amine-CO<sub>2</sub> solution must also go through a recovery step in order to complete the cycle. The amine-CO<sub>2</sub> recovery is accomplished in a distillation in which the CO<sub>2</sub> is separated and captured in the gas phase and the amine-OH solution is returned  
10 to the bed.

The following non-limiting example further illustrates this aspect of the invention. A strong base macro-reticulated ion exchange resin was used to cleave HCO<sub>3</sub><sup>-</sup> from NaHCO<sub>3</sub> into the ion exchange resin by releasing OH<sup>-</sup> ions into solution, therein creating Na<sub>2</sub>CO<sub>3</sub>. The solution that had passed through the resin was then titrated  
15 to measure the quantity of Na<sub>2</sub>CO<sub>3</sub> produced from the ion exchange. The resin was then thoroughly washed until there was no NaHCO<sub>3</sub> or Na<sub>2</sub>CO<sub>3</sub> left in the resin. The washed resin was then divided into two equal parts by volume and each part was contacted with a liquid amine solution, one was contacted with a primary, the other with a tertiary amine. The primary amine (MEA) and the tertiary amine (MDEA) were each used to  
20 remove the CO<sub>2</sub> that was stored in the resin. The MEA solution showed a greater ability to cleave the carbonate from the resin, while the MDEA solution exhibited, similar, but slightly lower absorption ability. Each amine-CO<sub>2</sub> solution was then titrated to verify the presence of the CO<sub>2</sub> within the solution.

Yet another aspect of the invention is illustrated in FIG. 10 which provides an  
25 integrated system for CO<sub>2</sub> removal from ambient air on an ion exchange member (IEM) 502. The CO<sub>2</sub> removal from the air by an IEM is washed from the IEM by sodium hydroxide delivered from a sodium hydroxide supply tank 504, producing sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>) solution which is collected in collection tank 506. The sodium carbonate solution is electrolyzed in an electrolytic cell 508 wherein sodium hydroxide is  
30 recovered and returned to tank 504. A portion of the sodium carbonate solution is also passed to the tank 510 in which the sodium carbonate is passed to a reactor 512 wherein the sodium carbonate is reacted with acetic acid to produce sodium acetate which is passed to a electro dialysis stack 516 which regenerates sodium hydroxide and acetic acid from the sodium acetate salt feed. The acetic acid is returned to tank 514 where it is used

for subsequent mixing/reaction with the sodium carbonate from tank 510, while the sodium hydroxide is returned to tank 504. Oxygen and hydrogen are collected or vented at outlets 518, 520, while CO<sub>2</sub> is collected and disposed of, e.g. by deep well injection or other means at outlet 522.

5 Yet another aspect of the invention employs seawater, i.e. the ocean, as a collector for CO<sub>2</sub>. The mixed layer of the ocean, roughly the top hundred meters, are in chemical delayed equilibrium with the atmosphere and carbon dioxide in the air readily exchanges with dissolved inorganic carbon in this layer. The dissolved inorganic carbon is in equilibrium with the partial pressure of CO<sub>2</sub> in the air. Carbon dioxide will enter  
10 the water either if the carbon dioxide partial pressure in the air increases or, alternatively, if the alkalinity of the ocean water is increased. The concept of introducing alkalinity into seawater as a mechanism for capturing CO<sub>2</sub> from air is described in PCT/US2005/015453. The present invention provides improvements over this concept.

The alkalinity of seawater can be modified by either adding a base to the water or  
15 by removing an acid. In one case, alkalinity of seawater may be increased by extracting hydrochloric acid from the water. In another case, alkalinity may be increased by introducing a base that is obtained by splitting a salt, usually but not always sea salt, into an acid and a base. The base is added to seawater in a very dilute form, while the acid usually in a more concentrated form is retained for further processing and/or recovered  
20 for industrial use.

In order to reestablish equilibrium with the atmosphere, the water will absorb carbon dioxide from the air, until the CO<sub>2</sub> uptake has quantitatively matched the change in alkalinity.

Ocean water will absorb approximately one mole of carbon dioxide from the air  
25 for every mole of one-normal acid formed. A slight mismatch is due to the fact that inorganic dissolved carbon is not completely bicarbonate, but a small fraction that is present as carbonate ions. Thus the effective normality of carbonic acid in seawater is slightly higher than its molarity. Reestablishment of the carbonate equilibrium will occur on a short time scale of less than one year and thus will happen without human  
30 intervention, except in places where surface waters are rapidly sinking. Thus, nearly the entire ocean surface is suitable for this form of CO<sub>2</sub> management. An advantage of this aspect of the invention is that it obviates the need for air exchange apparatus to remove carbon dioxide from air. The actual act of carbon dioxide capture is performed spontaneously and without the need for a sorbent or physical collector installations.

As a result of this process, one is left with an acid other than carbonic acid, typically hydrochloric acid which is much stronger than carbonic acid, and therefore can more readily be neutralized by mineral based alkalinity. Thus, rather than trying to dispose of a weak acid like carbonic acid which is difficult to bind with mineral base, we  
5 generate a much stronger acid which is more readily neutralized by readily available minerals that have a low level of reactivity. Alternatively, the hydrochloric acid may be collected for industrial use.

The capture of carbon dioxide from the atmosphere by removing hydrochloric acid from ocean water could occur along the coast, or in the middle of the ocean on  
10 board a ship. The important thing is that the acid extraction is performed on seawater that is in the mixed surface layer and which therefore will be exposed to carbon dioxide in the air within weeks or months after it has been processed. Rather than bringing carbon dioxide to the disposal one removes hydrochloric acid from the ocean water. An important advantage of this approach is that it requires only minute modifications in  
15 alkalinity of a local area of the ocean, whereas addition of carbon dioxide without changes in the alkalinity greatly changes the carbonate chemistry of seawater. Furthermore, the CO<sub>2</sub> captured by excess alkalinity is stable and will not be released back into the air.

For such a sequestration method to become viable, it is necessary to dispose of  
20 the large volumes of hydrochloric acid that will be produced in this process. One possibility is to dispose of the hydrochloric acid by neutralizing it with readily available alkaline minerals such as basalt or serpentine rock. As an alternative, the hydrochloric acid can be injected underground into alkaline fluid reservoirs that can neutralize the acid. Yet another possibility is to use mined and ground up minerals that can be  
25 transformed with the acid. These processes all are known in the art and have been published in the literature. Here they are combined with a specific process for capturing carbon dioxide from the air to develop a method of carbon dioxide management that is distinct from other approaches to the problem.

In the case where magnesium and calcium chlorides are formed, if the minerals  
30 are clean, they may be reinjected into the ocean where they readily dissolve. Alternatively, the resulting brines could be injected underground.

In yet another aspect of this invention, an electro-dialysis device is used to extract hydrochloric acid from seawater. The result is to create concentrated hydrochloric acid which may be collected and used industrially, while barely changing the water chemistry



of the ocean water that is passed through the system. This is accomplished by flowing a large volume of seawater through the cells that collect the base, while running a small material flow through the cells that turn more acidic.

5 The input on the basic side is seawater, which is converted to seawater with a very small change in alkalinity. Ideally the change is so small that the local water chemistry is not much affected by the change. Since the total alkalinity in seawater is about 2 millimolar, changes could be kept much smaller than that. In practice, it may be useful, to have slightly larger changes and force dilution in the seawater stream at the exit of the system. On the other hand, in order to avoid fouling changes should still be  
10 kept as small as possible. Fouling could easily occur when solubility products in the mixture are changed by significant factors.

The input to the acidic side may be seawater or it could also be pure water, or any other brine that is available. Specifically, it is possible to have multiple stages in the creation of hydrochloric acid and thus the input of that least some of the cells could be a  
15 hydrochloric acid solution that upon its exit has been strengthened in its molarity. FIG. 11 shows an example of such a device. This design is based on a particular approach that eliminates the use of cationic membranes which are usually present in an electro dialysis stack.

There are two substantively different approaches. The first has a number of cells  
20 separated with anionic and bipolar membranes. The anionic and bipolar membranes alternate, with the stack completed on one end with an anode and at the other end with a cathode. Seawater in the larger cells will receive hydroxide ions from the bipolar membrane and lose chloride ions through the anionic membrane. The acid forms in the complementary compartments which receives protons from the bipolar membrane and  
25 chloride ions through the anionic membrane. Since the flow here is low the acid concentration will rise significantly, whereas the change in the seawater chemistry is kept small.

FIG. 11 is a sketch of a repeated section of an electro dialysis device for extracting hydrochloric acid from ocean water. The ocean compartments experience  
30 high flow in order to minimize the chemical change in the water. In contrast the flow rate in the acidic cell is very slow, so as to maximize the concentration of the resulting flow acid. It is possible to use the output of one HCl cell as inflow into the next one. As a result the pH step is not everywhere maximized.

Flow rates on the alkaline and acidic side of the cells may differ by orders of

magnitude. On the other hand, it is possible to achieve the same effect by reusing the acidic fluid multiple times before it is sent out as a product stream. In either design, the output streams are slightly modified ocean water and concentrated hydrochloric acid. With one mole of hydrochloric acid removed from the ocean water, the water will absorb  
5 from the atmosphere an amount of carbon dioxide that represents one mole of CO<sub>2</sub>. Since carbonic acid in seawater disassociates mainly into bicarbonate ions and protons, with a small contribution from carbonate ions, it requires approximately 1 mole of CO<sub>2</sub> to compensate for the amount of hydrochloric acid withdrawn.

It is possible to build an electro-dialytic device without cationic membranes  
10 because the concentration of chloride ions in the ocean water will always far exceed the concentration of hydroxide ions, as the pH is barely changed in the process. As a result the bipolar membrane separates two fluids where on both sides the dominant negative ion is a chloride ion. The complementary device which is built exclusively with cationic membranes alternating with bipolar membranes would not work well. In this case HCl  
15 would be formed by transferring sodium ions out of the HCl cell through the cationic membrane. Once HCl has started to form protons would compete with sodium in the transfer and thus create a large inefficiency.

It also is possible to design a conventional electro-dialysis device with three different membranes alternating in the design. In that case a salt is split into its anion  
20 and cation. The cation is added to an ocean water flow, the anion ends up in the acid compartment. If the reduction in alkalinity in the acid compartment starts with highly alkaline brine, that is never neutralized, then it is possible to eliminate the anionic membrane. In that case one in effect combines neutralization of the acid and production of the acid into a single step.

FIG. 12 is a sketch of an electro-dialytic device that alternates cationic, anionic  
25 and bipolar membranes. The cells are arranged to raise the alkalinity of seawater on one side of the bipolar membrane and create HCl on the other side of the bipolar membrane. The cell between the cationic and anionic membrane contains a salt solution, in this case seawater, which is diluted in its concentration.

A design shown in FIG. 12 allows the separation of seawater into a slightly  
30 diluted seawater stream, a slightly more alkaline stream and into a stream of separated acid. A preferred implementation might use the slightly diluted stream of seawater obtained from salt splitting and make it the input stream for the seawater that will leave with increased alkalinity. It is also possible to use a different salt in the cell from which

anions and cations are removed. A particular example would be the use of a sodium salt of a weak acid; in that case the acid produced in the last chamber would not be HCl but a different acid that again would be ready for disposal. See FIG. 13.

FIG. 13 illustrates an electro dialysis cell stack that utilizes a different salt with anion X, to raise the alkalinity of seawater while creating a separate acid HX ready for disposal. For illustrative purposes we assume that the salt is NaX, however, any cation that could be safely injected into ocean water could be used in the salt brine.

FIG. 14 illustrates a salt splitting cell without anionic membranes that immediately injects the produced acid into geological subsurface brine. The embodiment laid out in FIG. 14, combines electro dialysis with the disposal of the hydrochloric acid, while avoiding the need for anionic membranes. If the geological brine is more alkaline than seawater, it is possible, with appropriate membranes to have the system run without input of electricity, as it acts as a battery driven by the pH difference between the ocean water and the brine. Thermodynamics spontaneously will move toward reducing the pH difference between the two fluids. Since no cell operates at high acidity, it is possible to eliminate the anionic membrane which is used in the standard salt splitter.

Various changes made be made in the above without departing from the spirit and scope of the invention as described. By way of example, the air capture exchange membrane may be in the form of elongate threads, typically 0.1-10 mm wide, preferably 1-10 mm wide, forming a loose mat through which the air is flowed. The air capture exchange membrane also may be in the form of tubes, honeycomb structure or a foam structure. It is intended that all subject matter contained in the above description, as shown in the accompanying drawings or defined in the following claims to be interpreted as illustrative, and not in a limiting sense.

**CLAIMS**

We claim

1. A process for removing CO<sub>2</sub> from the air, comprising the steps of:
  - 5 (a) passing the air in contact with a first CO<sub>2</sub> sorbent to absorb CO<sub>2</sub> from the air;
  - (b) passing the CO<sub>2</sub> sorbent from step (a) in contact with an ion exchange resin to absorb CO<sub>2</sub> from the first CO<sub>2</sub> sorbent;
  - (c) contacting the ion exchange resin from step (b) with a second CO<sub>2</sub> sorbent to absorb CO<sub>2</sub> from the ion exchange resin; and
  - 10 (d) recovering the second CO<sub>2</sub> sorbent via thermal swing or pressure swing, or electrolytically.
2. The process of claim 1, wherein the first CO<sub>2</sub> sorbent comprises a carbonate brine.
3. The process of claim 2, wherein the carbonate brine comprises a sodium  
15 carbonate or potassium bicarbonate brine.
4. The process of any of claims 1-3, wherein the first CO<sub>2</sub> sorbent contains an hydroxide.
5. The process of any of claims 1-4, wherein the first and/or the second CO<sub>2</sub> sorbents contain chemicals for adjusting physical properties of the sorbents.
- 20 6. The process of any of claims 1-5, wherein the second CO<sub>2</sub> sorbent is different from the first CO<sub>2</sub> sorbent.
7. The process of claim 6, wherein the second CO<sub>2</sub> sorbent comprises an amine based ion exchange resin.
8. The process of any of claims 1-7, wherein the ion exchange resin comprises a  
25 solid anion exchange membrane.
9. The process of any of claims 1-7, wherein the ion exchange resin is coated on a polymer substrate.
10. The process of claim 8 or claim 9, wherein the polymer substrate comprises a polymer foam.
- 30 11. The process of claim 8 or claim 9, wherein the polymer substrate comprises a cellulose.
12. A process of claim 5, wherein the first and/or the second CO<sub>2</sub> sorbents contain chemicals to optimize water retention and/or viscosity.

13. An apparatus for recovering CO<sub>2</sub> from the air, comprising in combination:
- (a) a device in which the air is contacted with a first CO<sub>2</sub> sorbent whereupon CO<sub>2</sub> is absorbed from the air;
  - (b) a device in which the first CO<sub>2</sub> sorbent is contacted with an ion exchange resin whereupon CO<sub>2</sub> is absorbed from the first CO<sub>2</sub> sorbent;
  - (c) a device in which the ion exchange resin is contacted with a second CO<sub>2</sub> sorbent wherein CO<sub>2</sub> is absorbed from the ion exchange resin; and
  - (d) a device for recovering the second CO<sub>2</sub> sorbent via thermal swing or pressure swing, or electrolytically.
14. The apparatus of claim 13, wherein the ion exchange resin comprises a solid anion exchange membrane.
15. The apparatus of claim 14, wherein the polymer substrate comprises a polymer foam.
16. The apparatus of claim 15, wherein the polymer substrate comprises a cellulose.
17. The apparatus of any of claims 13-16, wherein the second CO<sub>2</sub> sorbent comprises an amine.
18. A method of enhancing flux of carbon dioxide from the atmosphere into seawater which comprises raising the alkalinity of the seawater by removing anions other than OH<sup>-</sup>, HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>=</sup> from the seawater.
19. The method of claim 18, wherein the anions removed comprise chloride ions.
20. The method of claim 18 or claim 19, wherein alkalinity is changed by less than a millimole per liter.
21. The method of claims 18-20, wherein alkalinity is raised by extracting acid from the seawater.
22. The method of claim 21, wherein an electrolytic device is used to extract acid.
23. The method of claim 22, wherein the electrolytic device includes alternating bipolar and cationic membranes.
24. A method of enhancing flux of carbon dioxide from the atmosphere to seawater which comprises raising the alkalinity of seawater by electrolytically splitting a salt into an acid/base pair with the resulting cations being added to the seawater.
25. The method of claim 24, wherein the salt comprises a sodium salt.
26. The method of claim 25, wherein the salt comprises sodium chloride.

27. An apparatus for practicing the process of claim 18, which comprises alternating cationic and bipolar membranes forming compartments therebetween, wherein the seawater receives  $\text{OH}^-$  ions from a bipolar membrane, and cations from an alkaline brine are passed through a compartment that receives protons from the bipolar membrane.

28. The apparatus of claim 27, wherein the alkaline brine is derived from an underground geological reservoir, and including the step of reinjecting the brine back underground.

29. The apparatus of claim 27 or claim 28, wherein the alkaline brine has a pH higher than that of seawater.

30. The apparatus of claims 27-29, wherein the alkaline brine has a sodium concentration greater than that of seawater.

30. The apparatus of claims 27-30, wherein the membrane has a selectivity that allows for a spontaneous flow of protons and/or cations so as to result in an increase in alkalinity of the seawater driven at least in part by concentration gradients.

32. The apparatus of claims 27-31, comprising, in combination high flow cells for passing seawater from which chloride ions are removed, and low flow cells for containing an acidic brine that is enriched in hydrochloric acid.

33. The apparatus of claim 32, comprising a combination of high flow cells alternating with low flow cells.

34. The method of claim 23, wherein a brine is passed multiple times through an electrolytic device to raise a concentration of an acid in stages thereby minimizing the average voltage step between cells.

35. The method of claim 24, including the step of passing the acid multiple times through an electrolytic device.

36. The method of claim 35, wherein the electrolytic device includes alternating bipolar and cationic membranes.

37. The apparatus of claim 27, including a feed for pure water or seawater to selected compartments.

38. The method of claim 34, wherein the acid comprises hydrochloric acid.

39. The method of claim 24, wherein the salt comprises sodium chloride brine.

40. The method of claim 39, wherein the sodium chloride brine is derived from a source other than seawater.

41. The apparatus of claim 27, including feed of seawater to selected compartments.

42. The method of claim 24, wherein seawater from which ions have been removed is used as a feed for the electrolytic splitting.

5 43. The method of claim 24, including the step of using a concentrated brine obtained from seawater as a feed for the electrolytic splitting.

44. The method of claim 21, including the step of concentrating the extracted acid.

10 45. The method of claim 21, wherein the extracted acid is neutralized with an alkaline mineral.

46. The method of claim 21, wherein the extracted acid is neutralized and disposed of by injection into an underground alkaline rock formation.

47. The method of claim 21, wherein the extracted acid is neutralized by reaction with an alkaline mineral base material.

15 48. The method of claim 47, wherein the alkaline mineral base material is selected from the group consisting of serpentine, olivine, peridotite rock and clay.

49. The method of claim 47, wherein the alkaline mineral base material is selected from the group consisting of a mine tailing, waste asbestos, waste concrete, steel slag and other waste materials with high alkalinity.

20 50. The method of claim 24, including the step of releasing excess dissolved or neutralized brine back into the hydrological cycle and ultimately into the sea.

51. The method of claim 18, wherein compartments for seawater, salt brines and acid brines are sandwiched between bipolar, cationic, anionic and bipolar membranes, with the pattern repeated.

25 52. An apparatus for the capture of CO<sub>2</sub> from the atmosphere comprising an anionic membrane exposed to a flow of air.

53. The apparatus of claim 52, comprising a plurality of anionic membranes arranged in a series of flat plates with the air flow parallel to face surfaces of the membranes.

30 54. The apparatus of claim 53, comprising a plurality of anionic membranes spaced from one another with membrane spacings of from 1 - 25 mm, exposed to ambient air flow.

55. The apparatus of claim 53, comprising a plurality of anionic membranes spaced from one another, and further comprising a powered blower for moving air across surfaces of the membranes.

56. The apparatus of claim 52, wherein the membrane is arranged in a corrugated fashion to allow air flow through channels formed by the corrugations.

57. The apparatus of claims 52-56, wherein a flow path along the membrane has a length dictated by air flow velocity such that the air is not excessively depleted of CO<sub>2</sub>.

58. The apparatus of claim 52, comprising a plurality of membranes stacked in layers and forming "pie shaped" sections assembled into a wheel, rotating on an axle.

59. The apparatus of claims 52-58, further including a caustic solution wash for washing captured CO<sub>2</sub> from a surface of the membrane.

60. The apparatus of claim 59, wherein the wash comprises an amine or a carbonate solution.

61. The apparatus of claim 52, wherein the membrane comprises a continuous sheet which is moved in a serpentine pattern such that the membrane first is exposed to air flow, dipped in a caustic, amine, or carbonate solution, and then exposed to the air repeatedly.

62. The method for the capture of CO<sub>2</sub> from air which comprises exposing an anionic membrane to a flow of air.

63. The method of claim 62, wherein the membrane comprises a plurality of anionic membranes arranged in a series of flat plates, and the air is flowed substantially parallel to surfaces of the membranes.

64. The method of claim 63, wherein the membrane comprises a plurality of anionic membranes spaced from one another with membrane spacings of from 1 - 25 mm, and air is flowed past the membranes without auxiliary boost.

65. The method of claim 63, wherein the membrane comprises a plurality of anionic membranes spaced from one another, and a blower is used to power air flow across surfaces of the membranes.

66. The method of any of claims 62-65, wherein air flow and membrane surfaces are matched so that the air is not excessively depleted of CO<sub>2</sub>.

67. The method of claim 63, wherein the membrane comprises a plurality of membranes stacked in layers and forming "pie shaped" sections that are assembled into a wheel, and including the step of rotating the periphery of the wheel through a CO<sub>2</sub> sorbent.



68. The method of any of claims 62-67, including the step of washing the membrane with a wash solution after exposure to the air so as to wash captured CO<sub>2</sub> from the surface of the membrane, so that the membrane can repeatedly act as a CO<sub>2</sub> absorber.

5           69. The method of claim 68, wherein the wash solution comprises an amine solution.

70. The method of claim 68, wherein the wash solution comprises a carbonate or bicarbonate solution.

10           71. The method of claim 62, wherein the membrane comprises a continuous sheet, and including the steps of moving the membrane in a serpentine pattern such that the membrane is first exposed to air flow, dipped in a wash solution, and then exposed to the air repeatedly.

72. The method of claim 71, wherein the wash solution comprises an amine solution.

15           73. The method of claim 71, wherein the wash solution comprises a carbonate or bicarbonate.

20           74. A method for enhancing contact between a trace gas in a gas stream and a liquid or solid sorbent in which sorbent covered surfaces are created in an open and/or reticulated cell foam with flow channels that are large relative to a pore size of the foam and that guide a majority of gas flow along low resistance pathways through layers of the foam, and wherein the open cell foam is filled predominantly with gas and wherein gas volumes inside the foam are interconnected with each other and are connected to the gas flow in the channels passing through the foam, and continuously or intermittently mixing the gas flow through the channels with gas flow that moves through the bulk volume of the foam.

25           75. The method of claim 74, wherein the sorbent is a liquid that is caught in the pores of the foam, and coats the foam structures or forms liquid droplets caught inside the foam structure.

30           76. The method of claim 74, wherein the sorbent is the foam material or is permanently affixed to the foam material.

77. The method of claim 74 or 75, wherein the sorbent is introduced as a suspension of solid sorbent particles and wherein the liquid remains in the foam together with the solid particles.

78. The method of claim 74 or 75, wherein the sorbent is introduced as a suspension of solid sorbent particles and where the liquid is evaporated from the foam prior to the use of the sorbent material.

79. The method of any of claims 74-78, wherein the foam is traversed by straight channels that can have various cross sectional shapes.

80. The method of claim 79, wherein the cross sections of the channels are cylindrical.

81. The method of any of claims 74-80, wherein the foam comprises a plurality of separate layers of foam.

82. The method of any of claims 74-81, wherein the foam is hydrophobic.

83. The method of any of claims 74-81, wherein the foam is hydrophilic.

84. The method of any of claims 74-81, wherein the foam is comprised of both hydrophilic and hydrophobic components.

85. The method of claim 78 or 79, wherein the sorbent particles are adhered to the foam structure.

86. The method of claim 78 or 79, wherein the sorbent particles are immobilized by a cage structure of the foam.

87. The method of claim 83, including the step of capturing particles of opposite water wettability to bulk foam on different surfaces of the foam structure.

88. The method of claim 84, wherein the components are washed into the foam as a suspension.

89. The method of claim 84, wherein the components are captured in the foaming process.

90. The method of any of claims 79-86, wherein a pore size of the foam is less than 1 mm and more than 0.1 mm.

91. The method of any of claims 79-86, wherein a pore size of the foam is such that excess sorbent liquid will drain under gravity from pore spaces therebetween.

92. The method of claim 91, wherein sorbent liquid is distributed on and in the foam by slowly rotating a periphery of the foam structure in contact with a supply of liquid sorbent whereupon excess liquid sorbent is drained from the foam by gravity.

93. The method of claim 92, wherein channels traverse the foam parallel to the axis of rotation.

94. The method of claims 91 or 93, wherein the liquid sorbent comprises an alkaline brine.

95. The method of claim 94, wherein the liquid sorbent supply is mixed with fluid returned from the foam after exposure to the sorbate gas and wherein external fluid processing maintains the fluid in the immersion reservoir in a fresh state.

5 96. The method of any of claims 92-94, wherein the foam structure is moved between a fresh sorbent tank and a spent sorbent tank.

97. The method of any of claims 74-90, wherein an elastic foam is used, and including the step of mixing sorbent liquid into the foam matrix by compressing the foam.

10 98. The method of claim 97, wherein the foam is compressed by one or more rollers that push against a surface of the foam.

99. The method of claim 98, wherein the rollers have structured surfaces.

100. The method of claim 99, wherein the rollers have ridges parallel to the roller axis.

15 101. The method of claim 99, wherein the rollers have ridges running in a circumferential direction.

102. The method of claim 99, wherein the rollers have indentations and protrusions of different shapes.

103. The method of any of claims 97-102, wherein pairs of rollers have surface patterns that are matched to maximize local compression.

20 104. The method of any of claims 97-103, wherein the rollers are held stationary, and foam pads are moved back and forth between the rollers.

105. The method of any of claims 97-103, wherein the rollers are moved along a side of a foam pad.

25 106. The method of any of claims 97-103, wherein the rollers push fluid through the foam as either the rollers move along the surface of the foam, or as the foam is moved through the rollers, and wherein spacing between the rollers or the rollers and the walls is adjusted to control an amount of fluid retained in the foam.

30 107. The method of claim 106, wherein the foam is alternatively subjected to relatively high compression strokes from the rollers to extract spent sorbent therefrom and to relatively low compression strokes to distribute fresh sorbent.

108. The method of claim 107, wherein fresh sorbent is applied when the rollers are at a top of the foam or in front of the moving rollers between the high compression and the low compression strokes.

109. The method of claim 107, wherein the high compression strokes are performed in a downward motion of the rollers or upward motion of the foam, and the low compression strokes are performed in an upward motion of the rollers or downward motion of the foam.

5 110. The method of claim 107, wherein the rolling compression strokes are performed in a downward motion of the rollers, and the rollers are returned to an up-position without substantively compressing the foam.

10 111. The method of any of claims 97-110, wherein a continuous loop of foam is stretched over two opposing rollers with one end of the loop immersed in a liquid sorbent bath, and driving the rollers to drive the foam loop through the liquid sorbent bath.

112. The method of any of claims 74-111, wherein a surfactant is added to the sorbent fluid.

113. The method of any of claims 74-112, wherein the gas stream comprises air, and the trace gas comprises CO<sub>2</sub>.

15 114. The apparatus of claim 14 or claim 52, wherein the air capture exchange membrane comprises a loose mat of threads or tubes.

115. The apparatus of claim 14 or claim 52, wherein the air capture exchange membrane comprises a honeycomb structure or a foam structure.

20

FIG. 1 (a)

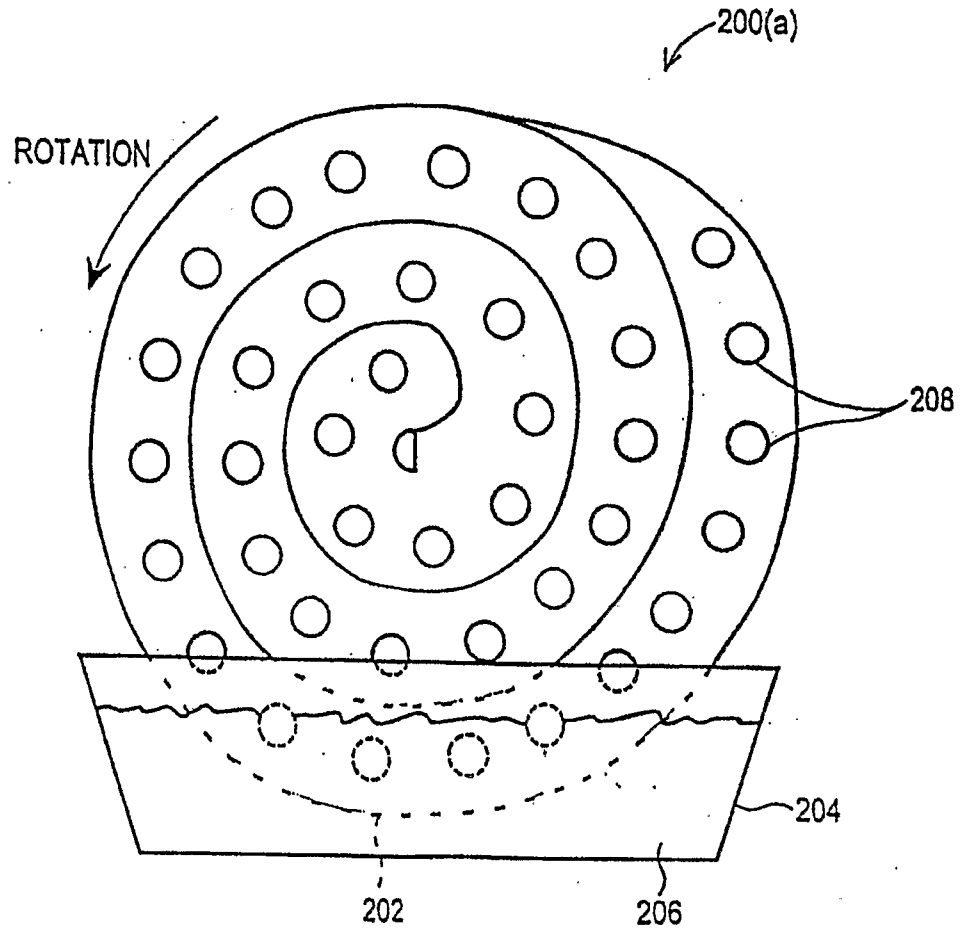


FIG. 1 (b)

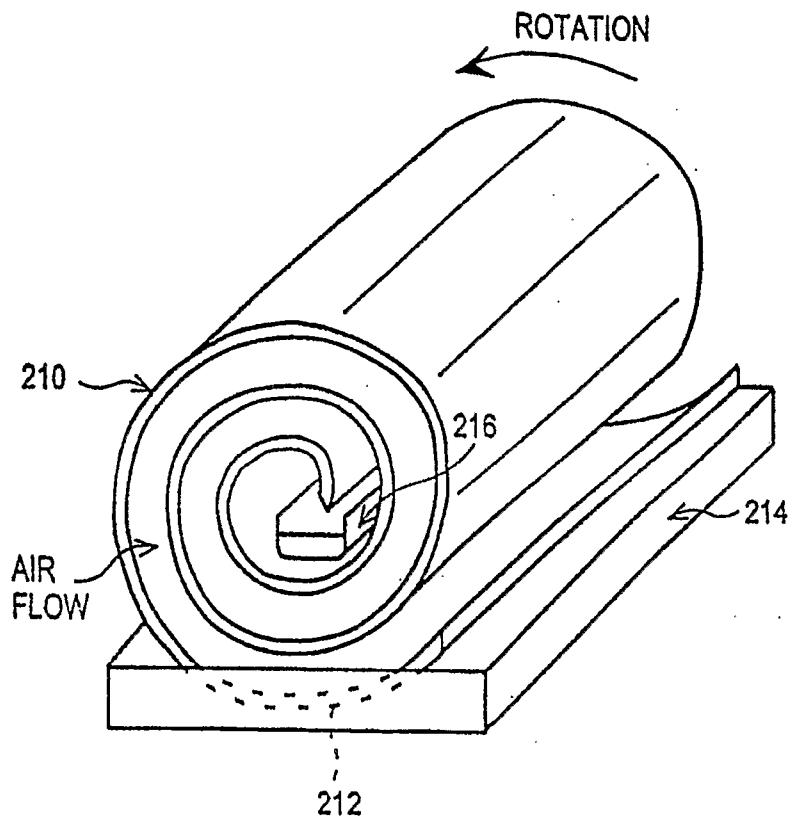


FIG. 2(a)

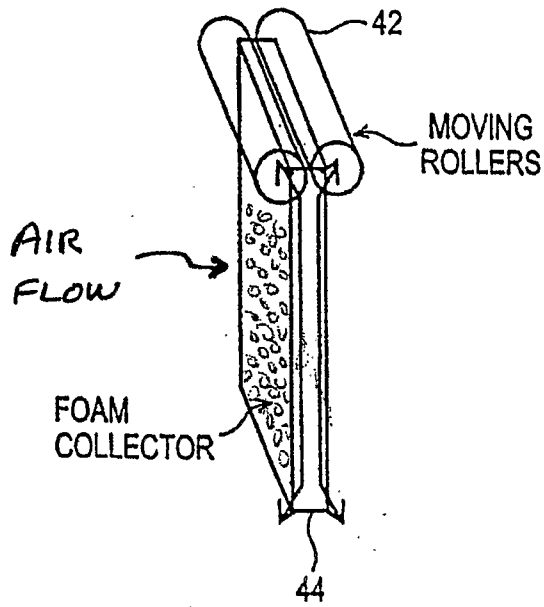


FIG. 2(b)

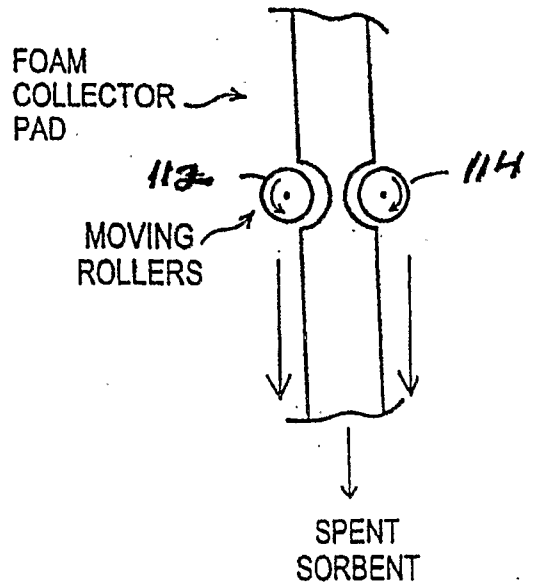


FIG. 2(c)

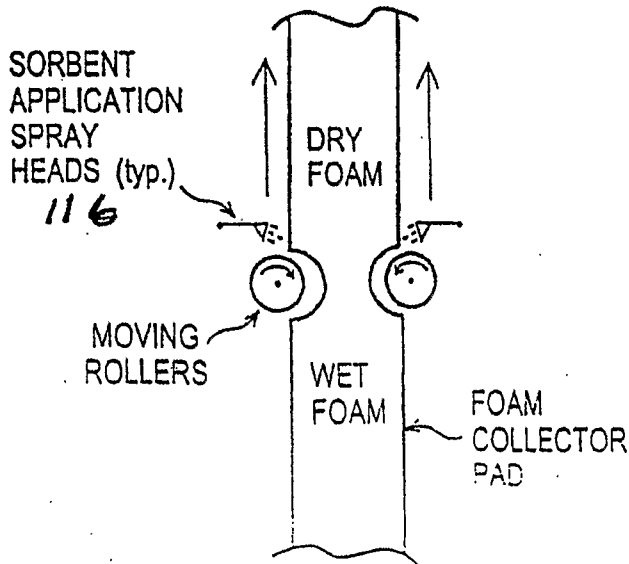


FIG. 3(a)

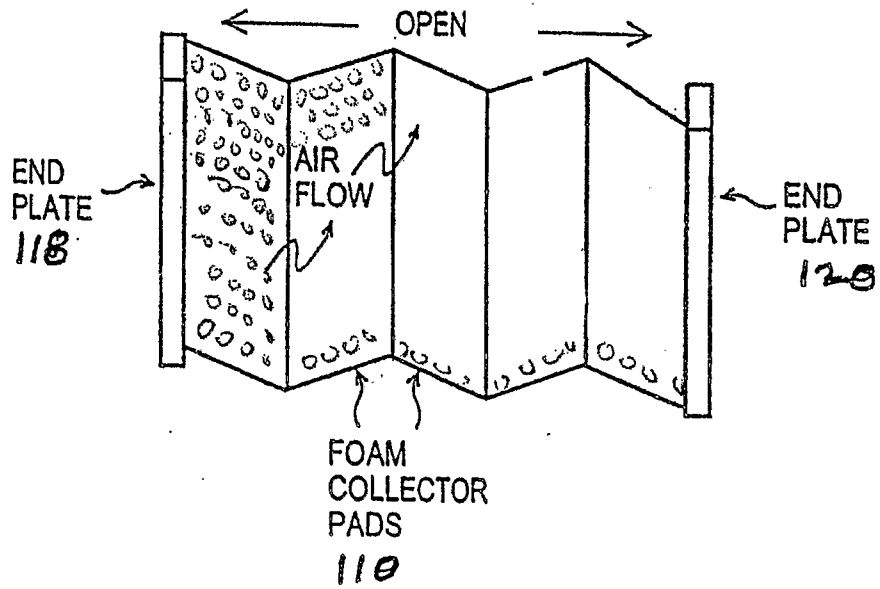


FIG. 3(b)

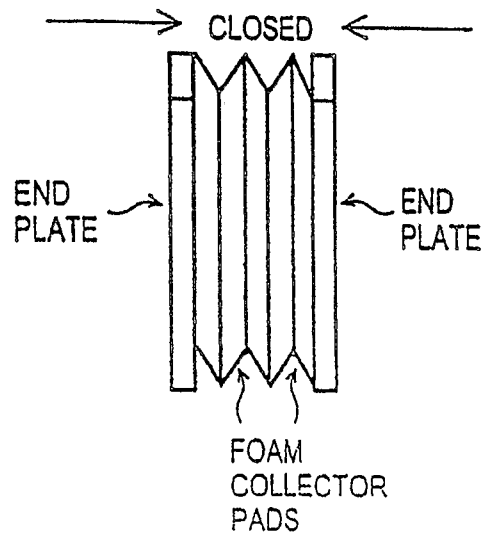




FIG. 4(a)

COLLECTOR "OPERATING"

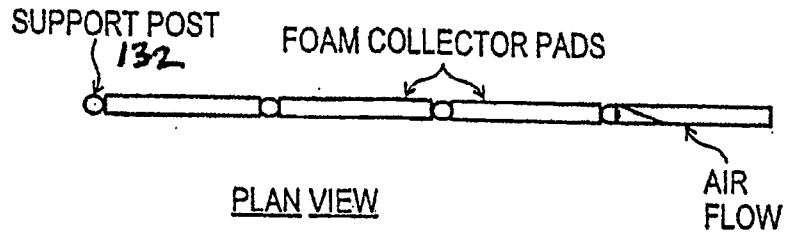


FIG. 4(b)

COLLECTOR "OPEN"

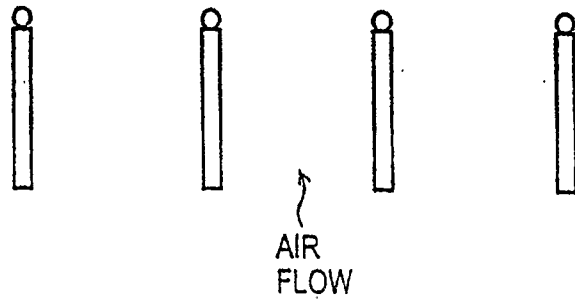
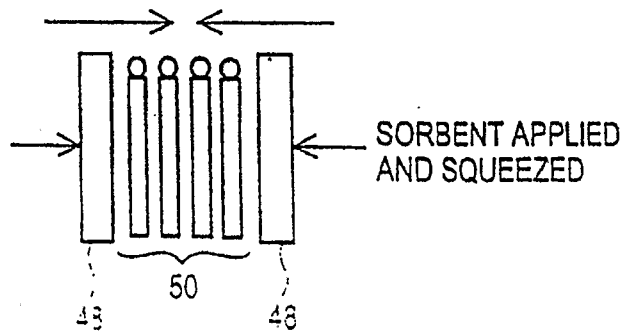


FIG. 4(c)

COLLECTOR "CLOSED"



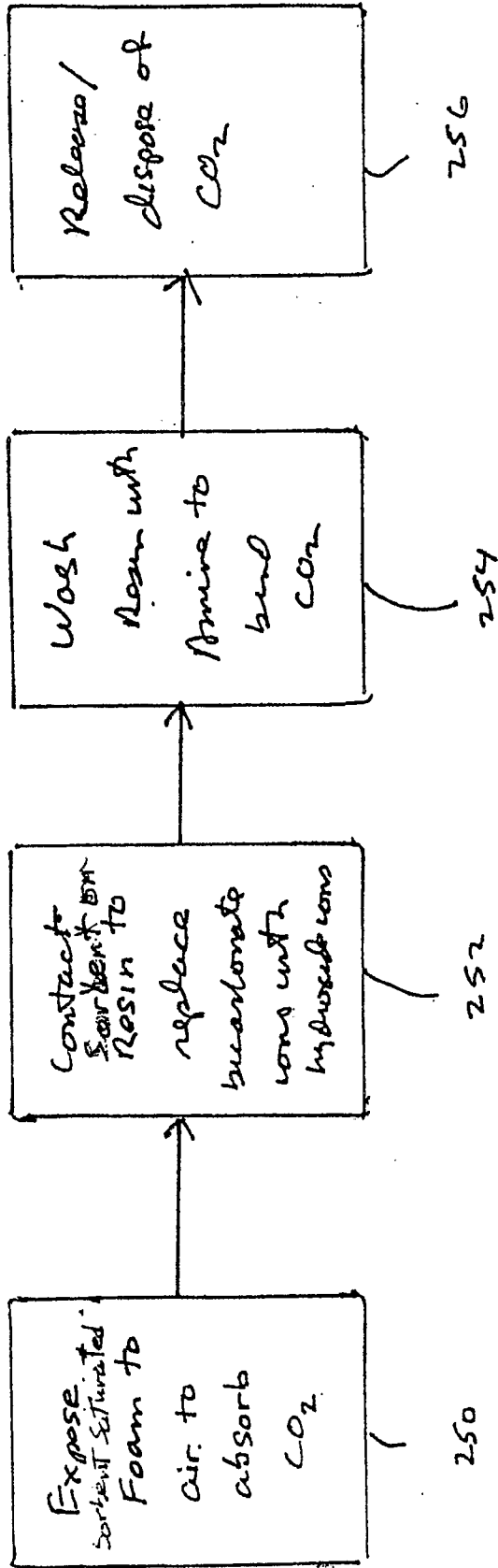


FIG. 5

4cm x 4cm Thick membrane in Large (128 L) Container Forced Ventilation over Sample, 1.0M NaOH Regen x 5 min, DI Wash Sep 28-29

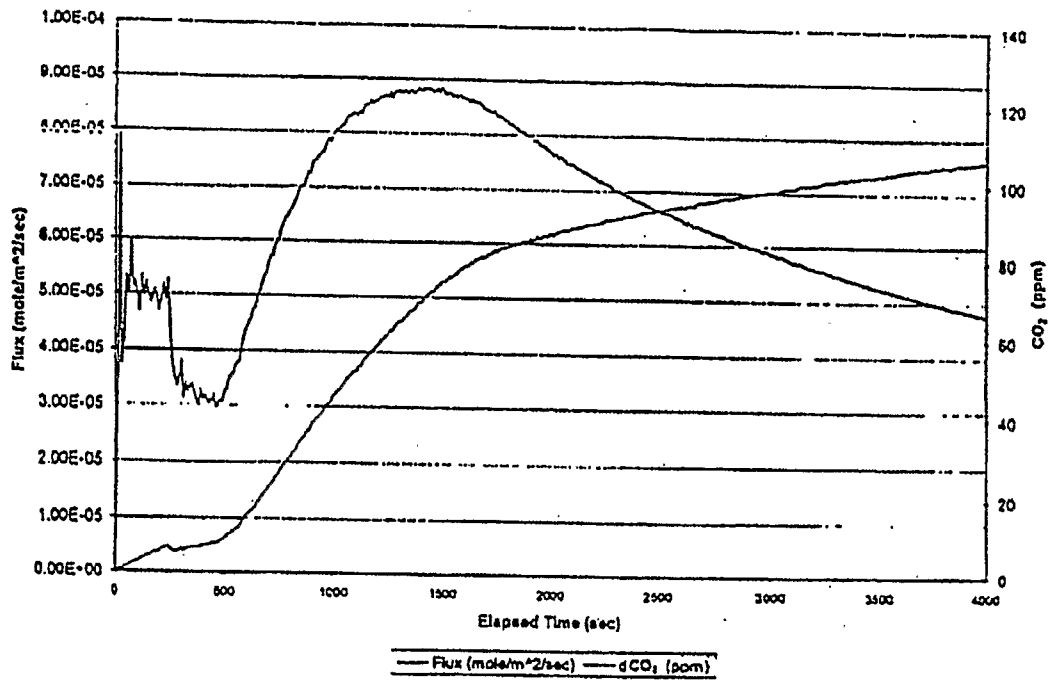


FIG. 6

FIG. 7

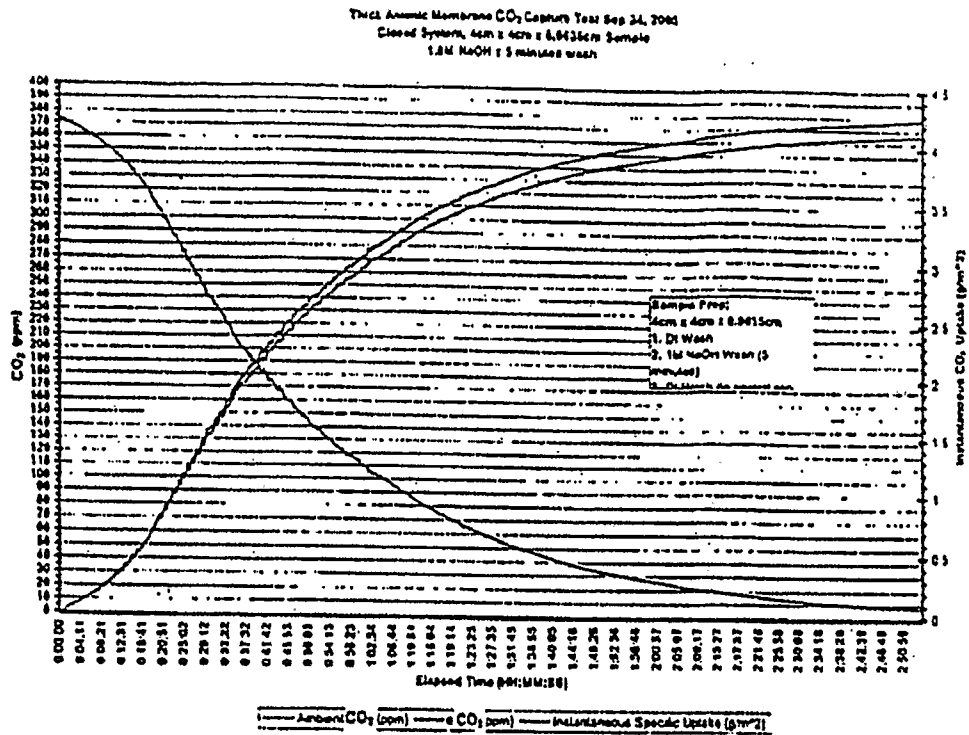
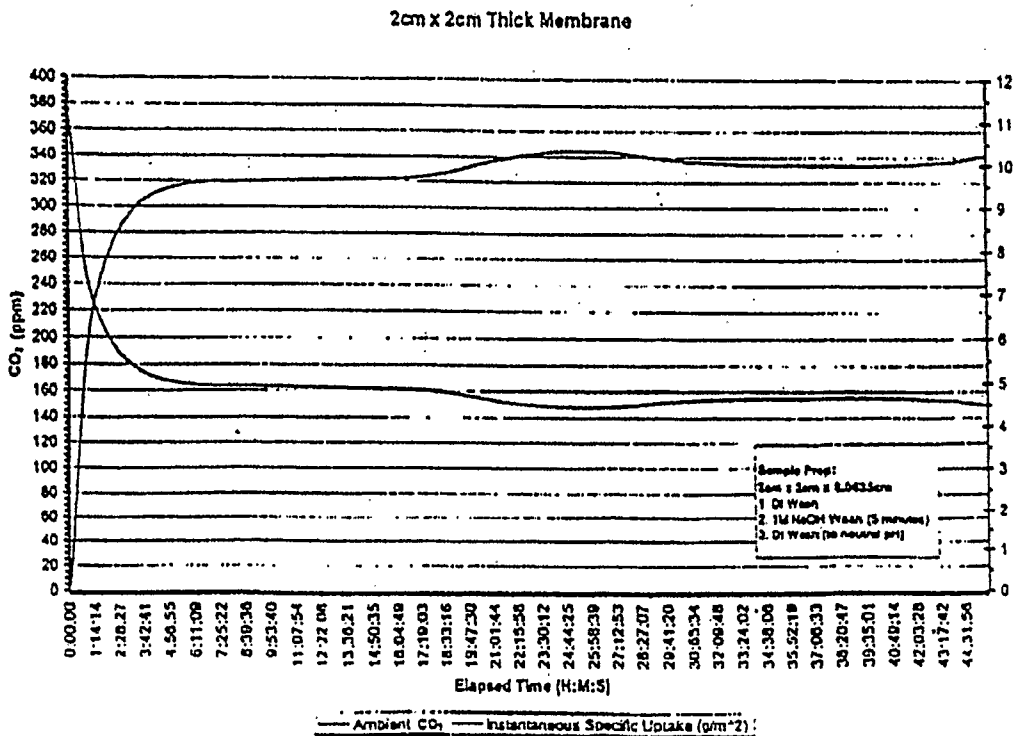


FIG. 8



# Carbonate Recovery and Amine-Carbon Dioxide Separation

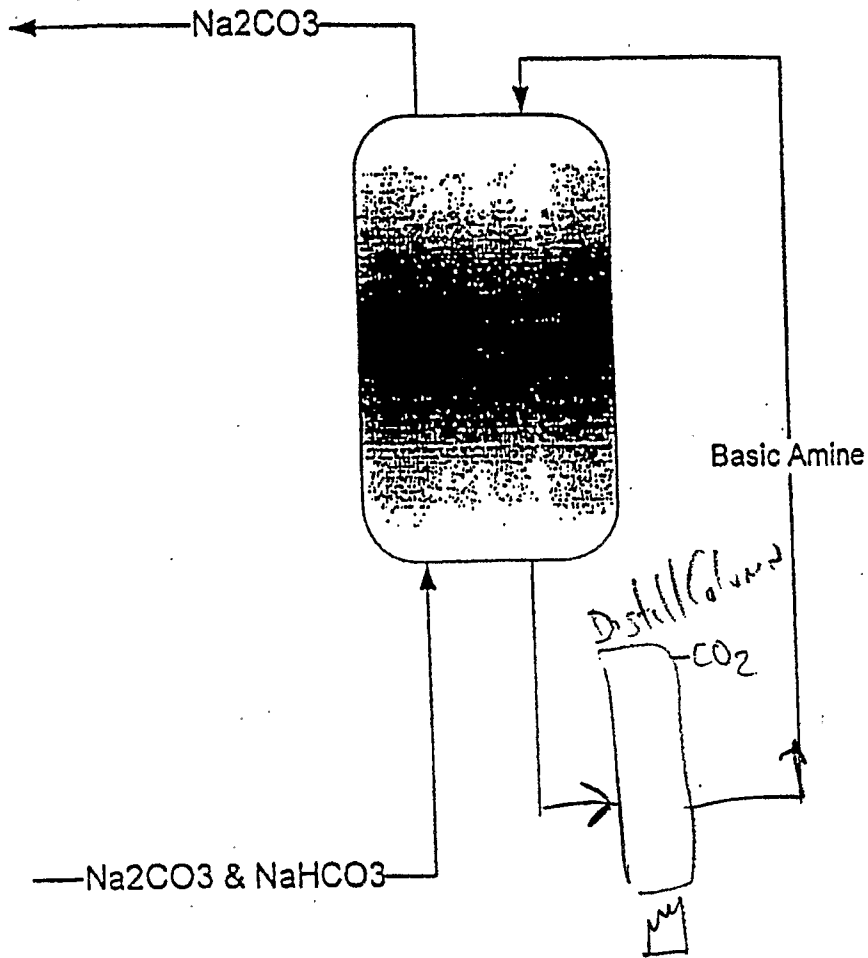


FIG-9

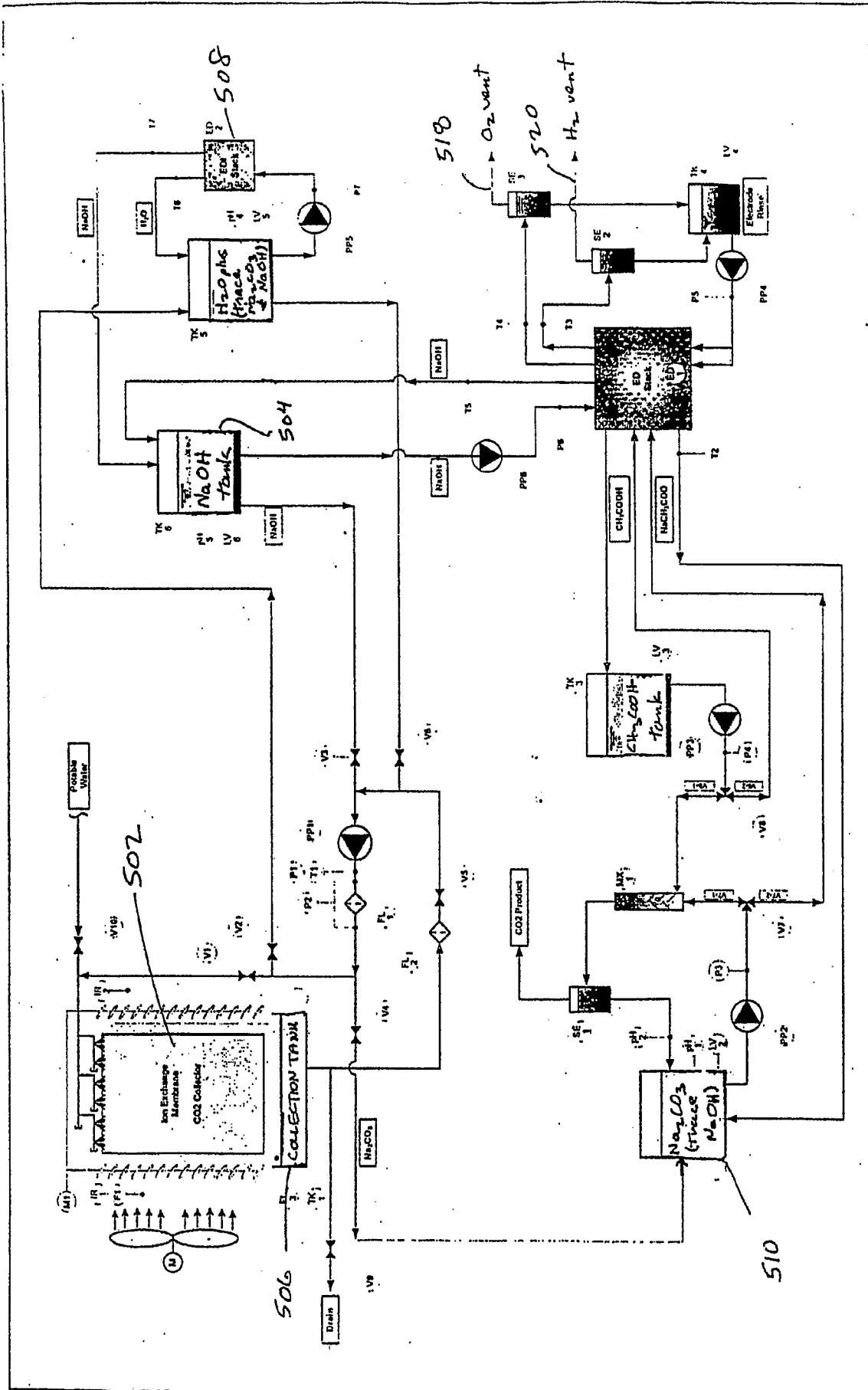


FIG. 10

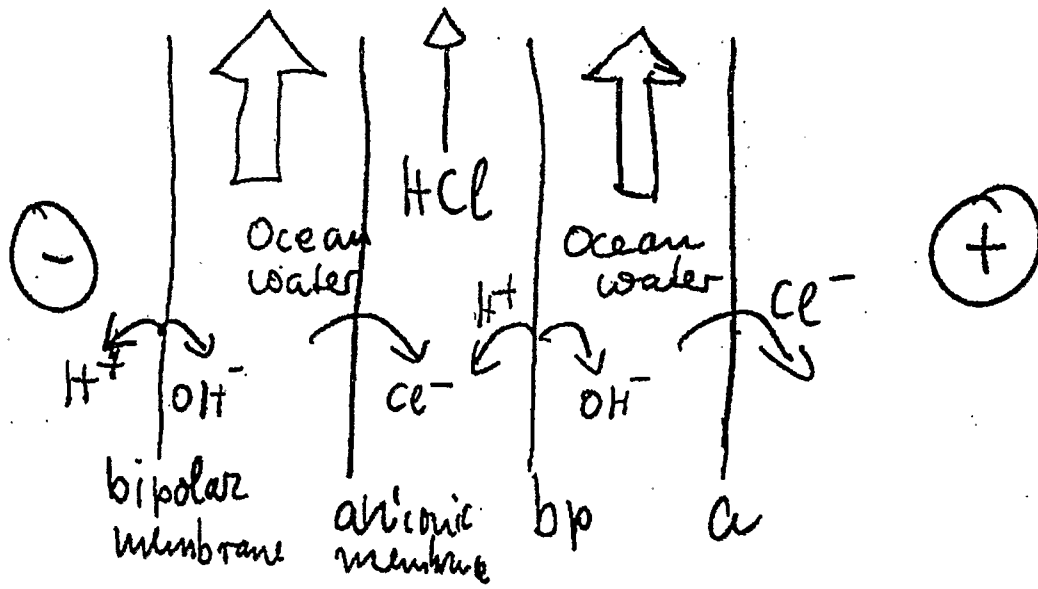


FIG. 11

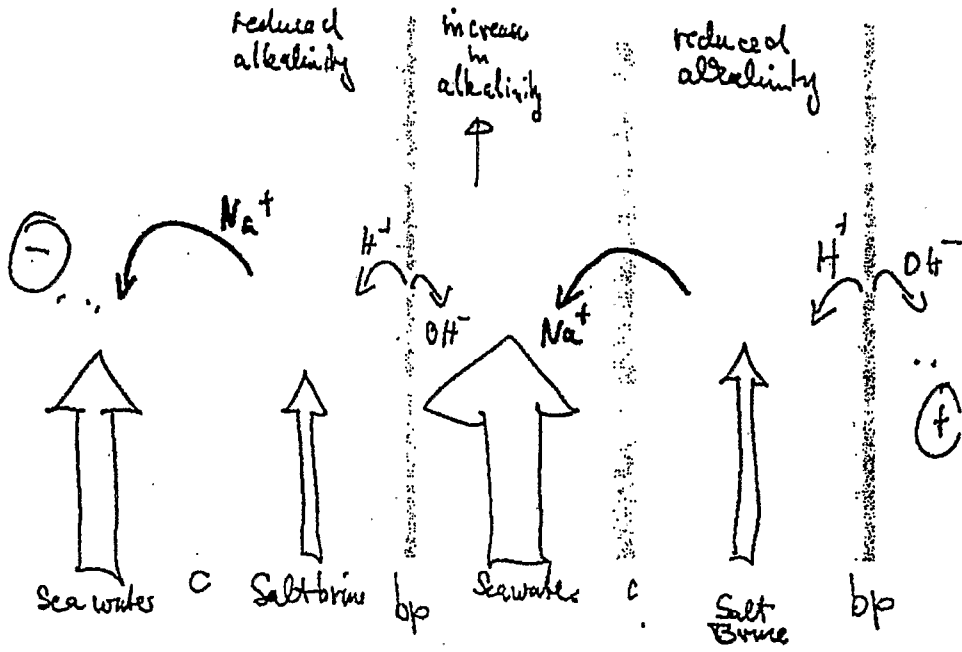


FIG. 12



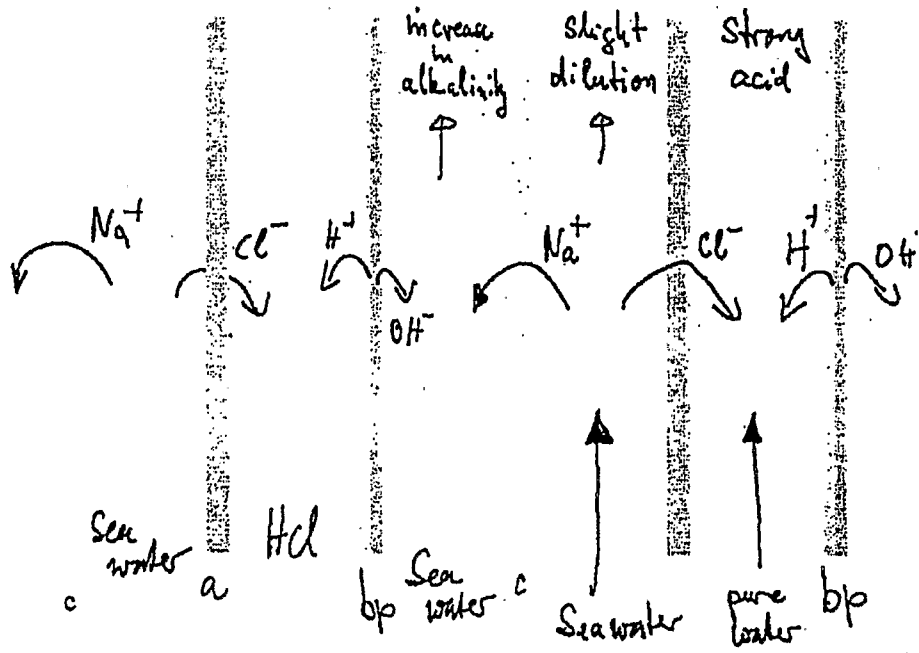


FIG. 13

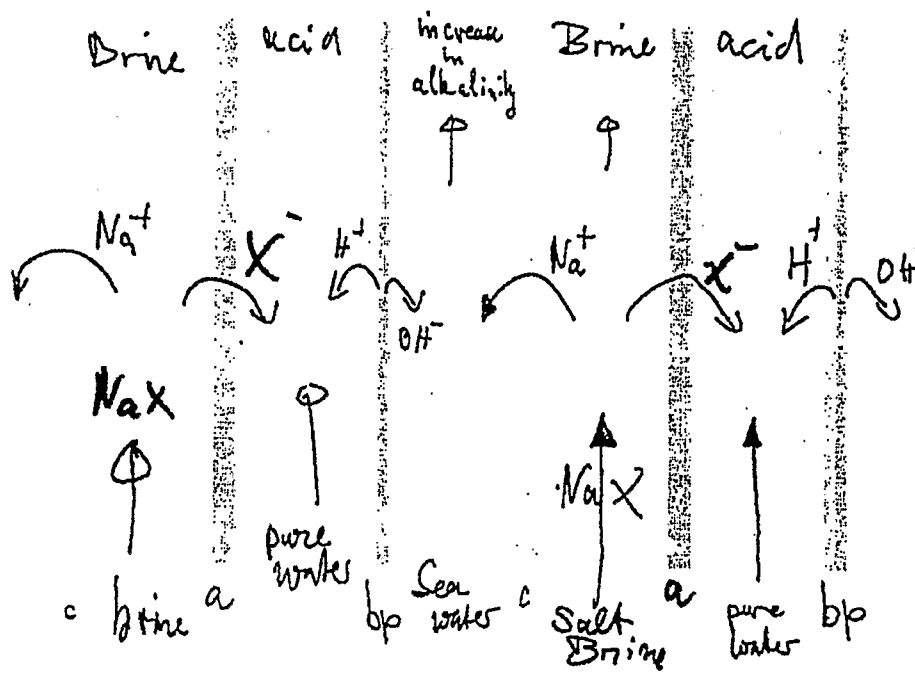


FIG. 14