US 20120058032A1

(19) United States

(12) Patent Application Publication

(10) Pub. No.: US 2012/0058032 A1

(43) Pub. Date: Mar. 8, 2012

Lackner et al.

(54) REMOVAL OF CARBON DIOXIDE FROM AIR

(76) Inventors: **Klaus S. Lackner**, Dobbs Ferry, NY (US); **Allen B. Wright**, Tucson, AZ (US)

(21) Appl. No.: **13/295,950**

(22) Filed: **Nov. 14, 2011**

Related U.S. Application Data

(63) Continuation of application No. 12/265,556, filed on Nov. 5, 2008.

(60) Provisional application No. 60/985,586, filed on Nov. 5, 2007.

Publication Classification

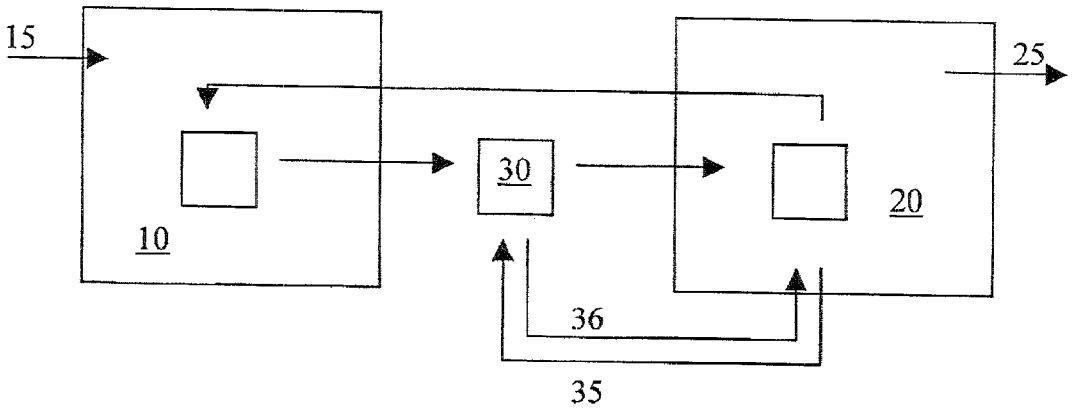
(51) **Int. Cl.**

B01D 53/62	(2006.01)
B01D 53/14	(2006.01)
B01J 19/00	(2006.01)
C01B 31/20	(2006.01)

(52) **U.S. Cl.** **423/228**; 423/220; 423/234; 423/232; 423/230; 423/231; 423/437.1; 422/198

(57) **ABSTRACT**

The present invention provides a method and apparatus for removing a contaminant, such as carbon dioxide, from a gas stream, such as ambient air. The contaminant is removed from the gas stream by a sorbent which may be regenerated using a humidity swing, a thermal swing, or a combination thereof. The sorbent may comprise a substrate having embedded positive ions and individually mobile negative ions wherein the positive ions are sufficiently spaced to prevent interactions between the negative ions. Where a thermal swing is used, heat may be conserved by employing a heat exchanger to transfer heat from the regenerated sorbent to an amount of sorbent that is loaded with the contaminant prior to regeneration.



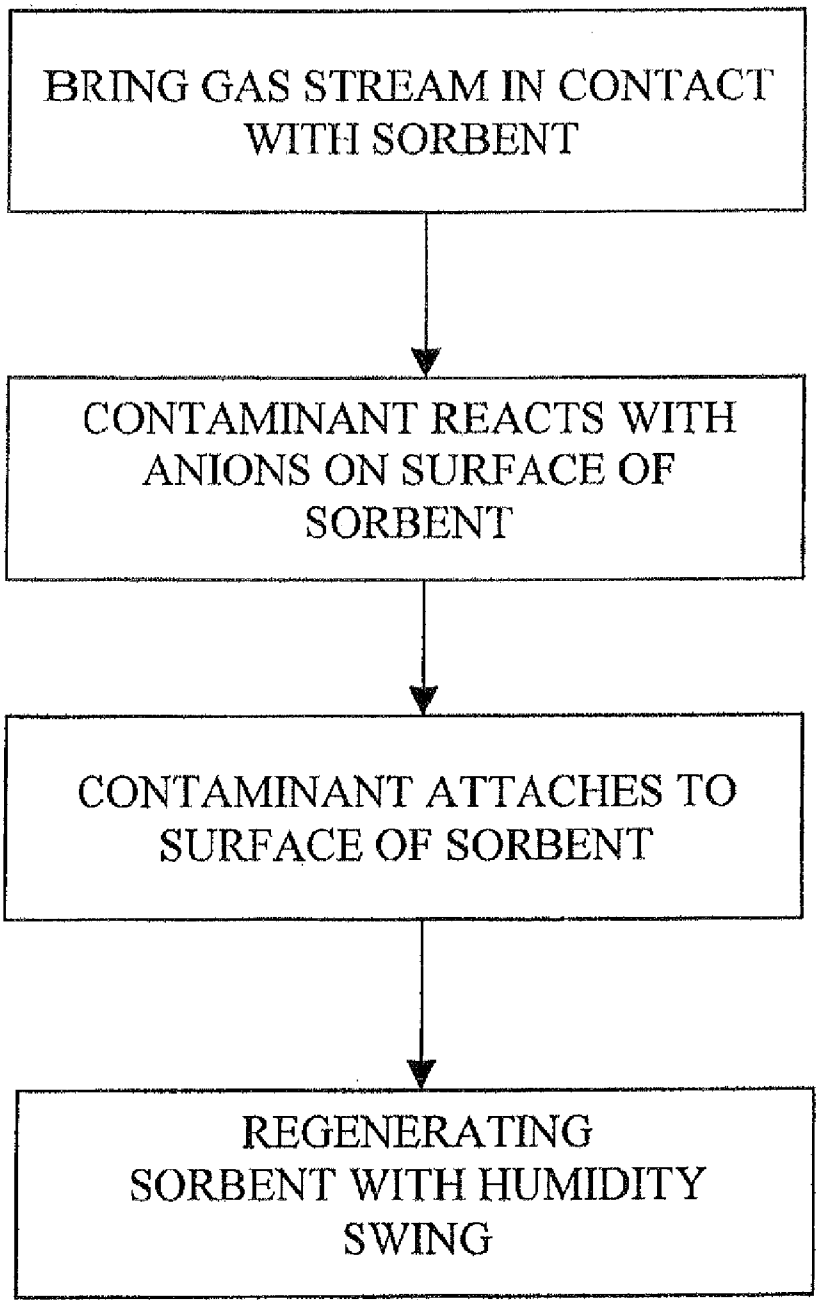

BRING GAS STREAM IN CONTACT WITH SORBENT
CONTAMINANT REACTS WITH ANIONS ON SURFACE OF SORBENT
CONTAMINANT ATTACHES TO SURFACE OF SORBENT
REGENERATING SORBENT WITH HUMIDITY SWING

FIG. 1

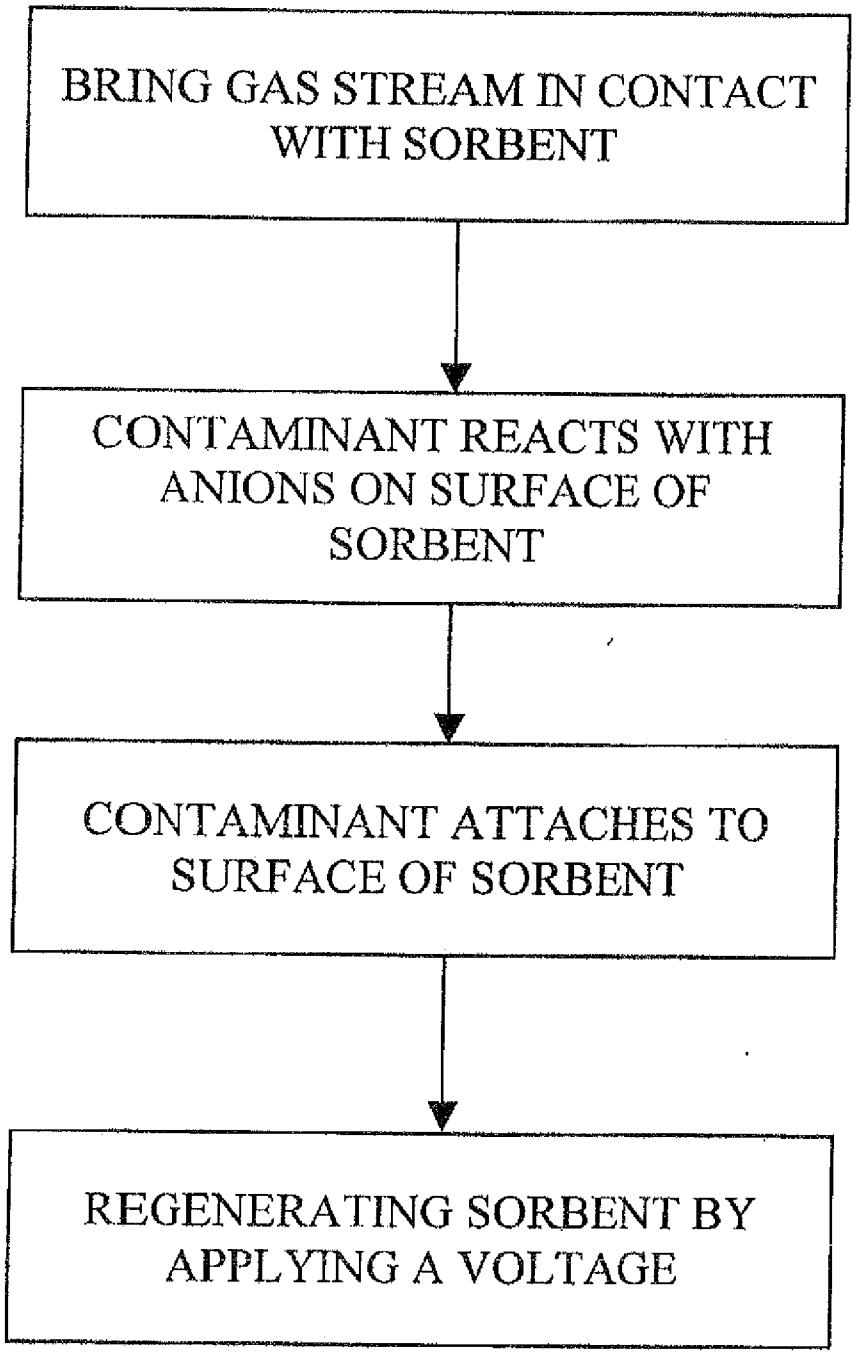

BRING GAS STREAM IN CONTACT WITH SORBENT
CONTAMINANT REACTS WITH ANIONS ON SURFACE OF SORBENT
CONTAMINANT ATTACHES TO SURFACE OF SORBENT
REGENERATING SORBENT BY APPLYING A VOLTAGE

FIG. 2

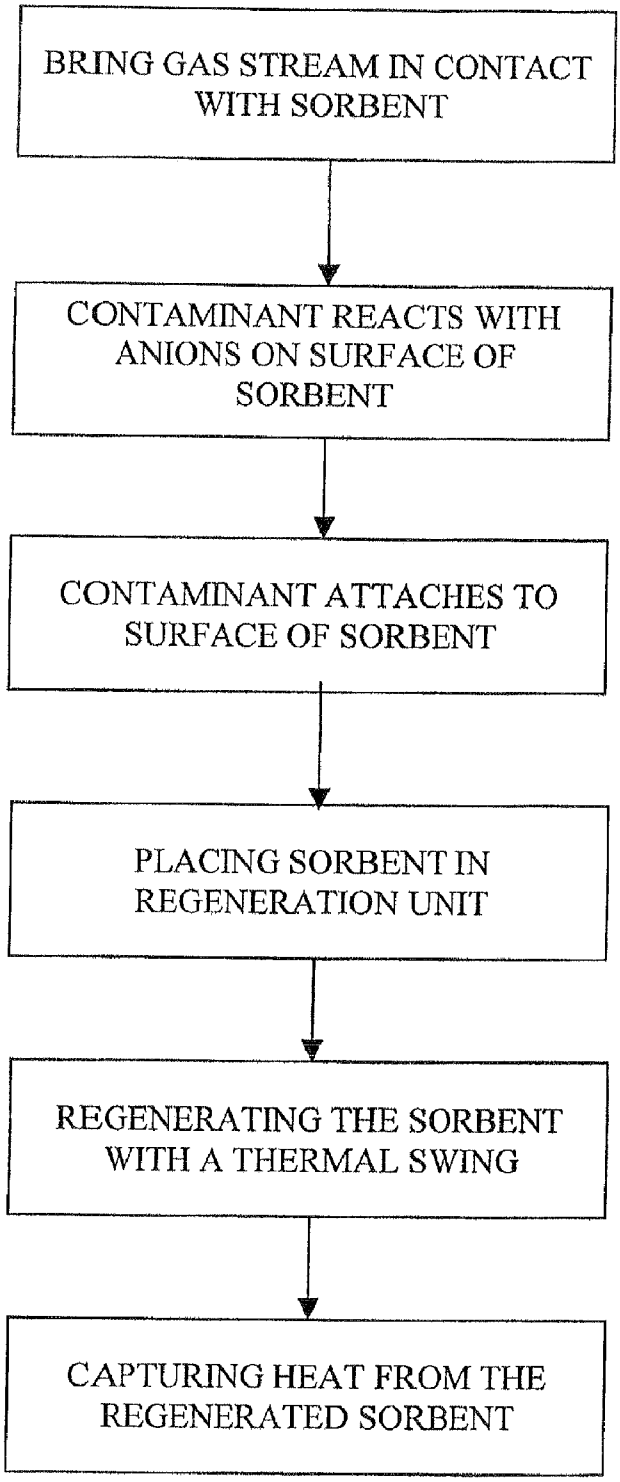

BRING GAS STREAM IN CONTACT WITH SORBENT
CONTAMINANT REACTS WITH ANIONS ON SURFACE OF SORBENT
CONTAMINANT ATTACHES TO SURFACE OF SORBENT
PLACING SORBENT IN REGENERATION UNIT
REGENERATING THE SORBENT WITH A THERMAL SWING
CAPTURING HEAT FROM THE REGENERATED SORBENT

FIG. 3

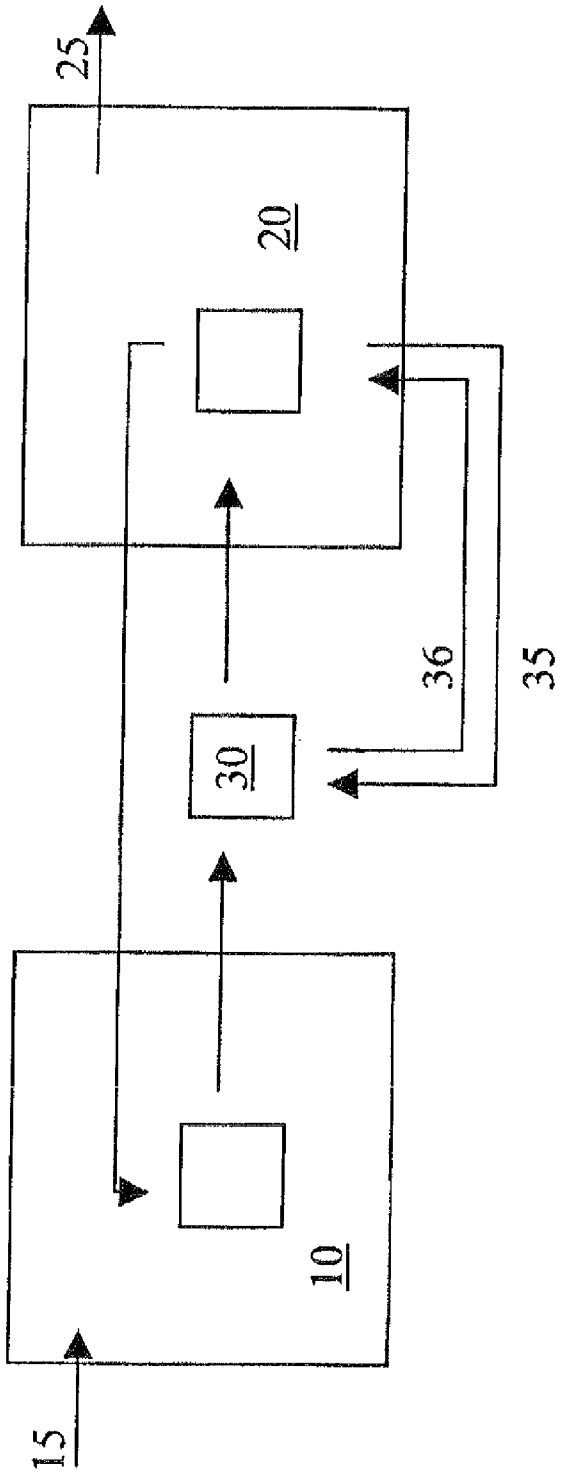


FIG. 4

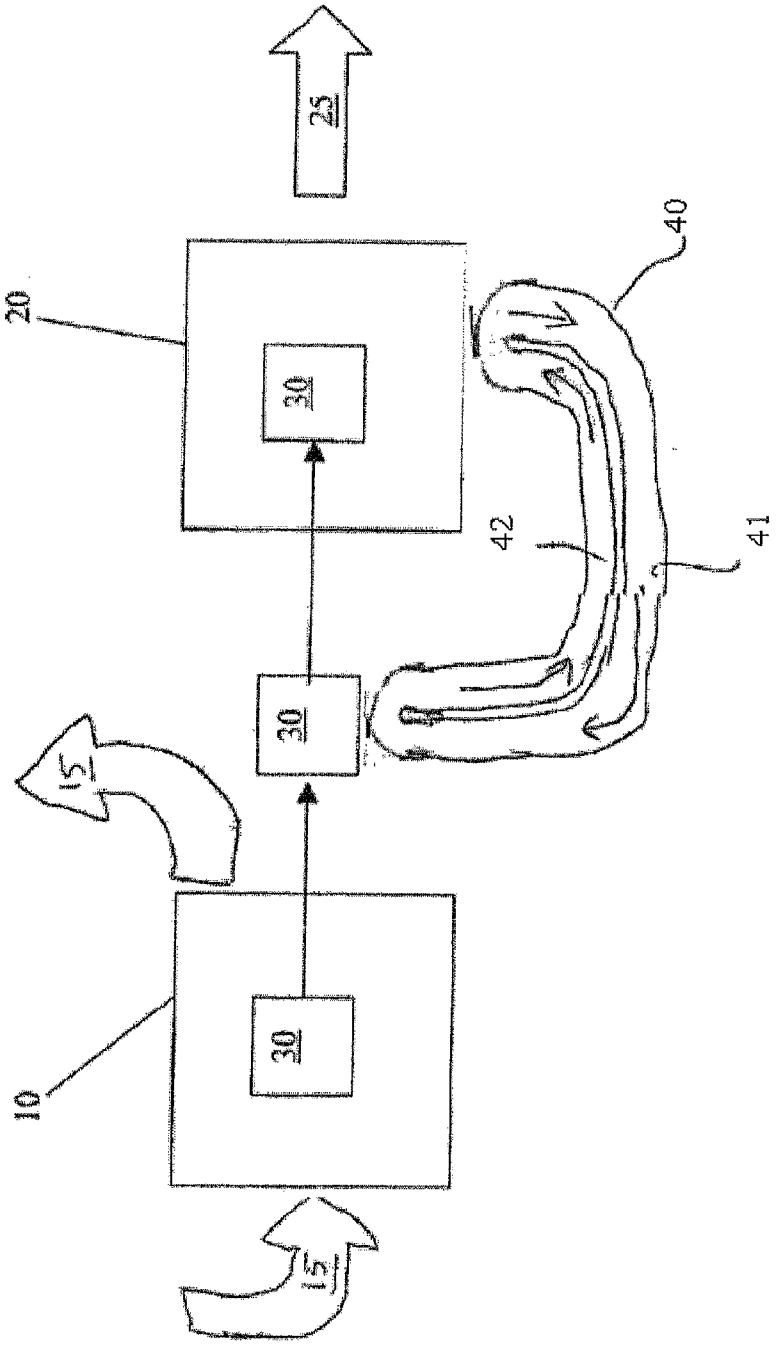


FIG. 5

REMOVAL OF CARBON DIOXIDE FROM AIR

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] The present application claims priority from U.S. Provisional Application Ser. No. 60/985,586, filed Nov. 5, 2007; the contents of which are incorporated herein by reference.

FIELD OF THE INVENTION

[0002] The present invention relates to removal of selected gases from air. The invention has particular utility for the extraction of carbon dioxide (CO_2) from air and will be described in connection with such utilities, although other utilities are contemplated.

BACKGROUND OF THE INVENTION

[0003] There is compelling evidence to suggest that there is a strong correlation between the sharply increasing levels of atmospheric CO_2 with a commensurate increase in global surface temperatures. This effect is commonly known as Global Warming. Of the various sources of the CO_2 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 CO_2 into the atmosphere. Combined, these major sources, as well as others, have lead to the creation of a sharply increasing rate of atmospheric CO_2 concentration. Until all emitters are corrected at their source, other technologies are required to capture the increasing, albeit relatively low, background levels of atmospheric CO_2. 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 CO_2. These efforts require methodologies to manage the resulting concentrated waste streams of CO_2 in such a manner as to prevent its reintroduction to the atmosphere.

[0004] The production of CO_2 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_2 gas, which at present is simply released to the atmosphere. However, as greenhouse gas concerns mount, CO_2 emissions from all sources will have to be curtailed. For mobile sources the best option is likely to be the collection of CO_2 directly from the air rather than from the mobile combustion device in a car or an airplane. The advantage of removing CO_2 from air is that it eliminates the need for storing CO_2 on the mobile device. Extracting carbon dioxide (CO_2) 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_2 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 CO_2 from air in order to compensate for equally sized emissions elsewhere and at different times.

[0005] The art has proposed various schemes for removal of CO_2 from combustion exhaust gases or directly from the air by subjecting the gases or air to a pressure swing or a thermal swing using a CO_2 adsorbent. These processes use pressure or temperature changes, respectively, to change the state of the sorbent material, whereby to release the CO_2. Different sorbent materials are disclosed, including zeolites, amines, and activated alumina. See, for example, 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; and co-pending U.S. application Ser. No. 11/683,824, the contents of which are incorporated herein by reference.

[0006] None of these references, however, provides a particularly efficient process for the removal of CO_2, primarily due to the amount of energy expended in CO_2 recovery and sorbent regeneration.

SUMMARY OF THE INVENTION

[0007] The present invention provides improvements over the prior art as described above. More particularly, the present invention provides a method and apparatus for removing a contaminant from a gas stream by utilizing a sorbent that that captures the contaminant, such as carbon dioxide (CO2) when it is sufficiently dry and releases the contaminant to a contained atmosphere when the sorbent is exposed to water or humidity. In an alternative embodiment, the sorbent may be regenerated by being placed in a regeneration unit maintained at a temperature higher than that of the gas stream and wherein the heat retained by the sorbent after regeneration is conserved by passing the sorbent through a heat exchanger. Finally, a combination of the humidity and thermal swings may be used to optimize the sorbent regeneration.

[0008] To conserve energy, the present invention may employ a heat exchanger using water as a refrigerant, wherein the water is evaporated in an evacuated space to draw heat from the regenerated sorbent and the water is then condensed on the sorbent loaded with the contaminant. The use of other fluids as refrigerants is also contemplated. Alternatively, the refrigerant may be isolated from the sorbent so as not to interfere with the thermal function of the sorbent.

[0009] In one aspect, the present invention provides a method for removing carbon dioxide from a gas stream by placing said gas stream in contact with a substrate having a surface in which cations are embedded and releasing the carbon dioxide from said substrate by use of a humidity swing. Anions that are individually mobile are initially included on the surface, wherein carbon dioxide from said gas stream becomes attached to the substrate by reacting with said anions. In a further embodiment, the carbon dioxide is captured by reacting with said anions to form bicarbonate.

[0010] In another aspect, the present invention provides a method for removing carbon dioxide from humid air, comprising placing the humid air in contact with a material having a surface on which hydroxide ions form, wherein carbon dioxide from the humid air becomes attached to the surface of the material by reacting with the hydroxide ions; and applying a bias voltage to the material which releases the hydroxide ions and the carbon dioxide. In yet another aspect, the present invention provides a method for extracting a contaminant from a gas stream, comprising the steps of:

[0011] a) bringing the gas stream in contact with a sorbent which captures the contaminant from the gas stream, so as to at least partially saturate the sorbent with contaminant;

[0012] b) placing the contaminant carrying sorbent in a regeneration unit for releasing the contaminant from the sorbent and regenerate the sorbent, wherein the regeneration unit is maintained at a temperature that is higher than the temperature of the gas stream; and

[0013] c) removing the regenerated sorbent from the regeneration unit; and

[0014] d) capturing heat from the regenerated sorbent as the sorbent is removed from the regeneration unit.

[0015] Finally, the present invention in another aspect provides an apparatus for extracting a contaminant from a gas stream using a sorbent employing a thermal swing, comprising: a sorbent for capturing the contaminant; a capture unit, wherein the sorbent is exposed to the gas stream and becomes at least partially saturated with the contaminant; a regeneration unit, wherein the sorbent is exposed to elevated temperatures thereby causing the sorbent to release the contaminant according to a thermal swing; and a heat exchanger for extracting heat retained from the sorbent in the regeneration unit.

BRIEF DESCRIPTION OF THE DRAWINGS

[0016] Further features and advantages of the present invention will be seen from the following detailed description, taken in conjunction with the accompanying drawings, wherein

[0017] FIG. **1** is a flowchart showing a method for removing a contaminant from a gas stream according to one aspect of the present invention;

[0018] FIG. **2** is a flowchart showing a method for removing a contaminant from a gas stream according to a second aspect of the present invention;

[0019] FIG. **3** is a flowchart showing a method for removing a contaminant from a gas stream according to a third aspect of the present invention;

[0020] FIG. **4** is a schematic of an apparatus for removing a contaminant from a gas stream according to the method shown in FIG. **3**; and

[0021] FIG. **5** is a schematic of an apparatus for removing a contaminant from a gas stream according to an alternative embodiment of the method shown in FIG. **3**.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

[0022] The present invention provides a method and apparatus for the extraction of a contaminant from a gas stream. The present invention is discussed in reference to a method and apparatus for capturing CO_2 from ambient air, but the technology is also applicable to exhaust air or other gas streams and may be used to capture hydrogen sulfide, ammonia, or other common contaminants from such gas streams.

[0023] In co-pending Patent Appln. Serial No. PCT/US07/84880, assigned to a common assignee and incorporated by reference herein, we discuss a CO_2 capture process that utilizes a humidity swing to regenerate a sorbent, releasing a mixture of CO_2 and water vapor. The water vapor may be removed from the mixture by compression or cooling, either of which will cause the water vapor to condense and precipitate out of the mixture.

[0024] A first aspect of the present invention provides an improved substrate that can hold cations embedded into its surface, thereby facilitating the capture and release of carbon dioxide using a humidity swing. See FIG. **1**. For a solid substrate to efficiently absorb CO_2, it must have a large surface area exposed to the gas stream and it needs to be able to temporarily hold on to CO_2 molecules by some mechanism. The mechanism used by the present invention is based on the binding energy between positive ions and negative ions and on the interplay between carbonate ions and bicarbonate ions. A matrix loaded with attached positive ions will hold on to negative ions even if the negative ions are individually mobile. In contrast to the positive ions, the negative ions are mobile in water. As these ions "dissolve" into the water, their dynamics will be similar to those of the same ions in a dissolved salt. However, the positive charge on the substrate must be neutralized by some negative ions.

[0025] The initial preparation of a substrate could use any negative ion to satisfy charge balance, but according to the present invention, it is useful to replace these negative ions with hydroxide ions. This is difficult for two reasons. One is that the substrate itself could be destroyed by hydroxide solutions; e.g., it may dissolve or chemically react with hydroxides. The second reason is that the hydroxide ion, once attached, is unstable in a dry environment. In that case, two hydroxide ions would react to form water and an oxide ion. This outcome becomes more likely where the positive ions are closely spaced. If they are sufficiently far apart this outcome is less likely.

[0026] Hydroxide ions attached to the surface can react with CO_2 to form bicarbonate ions. Two bicarbonate ions could then react to form water, CO_2, and a carbonate ion. In that case, energetics likely would favor the formation of carbonate over bicarbonate. Thus CO_2 loading would be limited to what can be achieved with carbonate. To optimize this process, the energetics has to be such that on a dry surface bicarbonates are favored over carbonates, Furthermore, the cations must not leach out in the presence of water. The energetic difference between carbonate and bicarbonate at this point can be engineered to control the balance between the two options. By optimizing the energy difference we can assure that a large change in loading of the substrate between carbonate loading (50% of maximum) to bicarbonate loading (100% of maximum) happens in partial pressures of CO_2 that are near those of ambient air.

[0027] When exposed to water, the above-described material will convert bicarbonate ions in water into carbonate ions, water, and carbon dioxide. Thus, when wetted, the material will release a large amount of carbon dioxide.

$$2HCO_3 \rightarrow H_2O + CO_2 + CO_3^{-2}$$

[0028] The water carrying capacity of the substrate should be minimized, limiting the amount of water that needs to be removed before the surface can once again pick up CO_2. However, the substrate material should be highly porous to maximize the surface area. Further, the surface should be covered with ions that attract polar molecules, such as water molecules. Since these last two features may conflict with the need to limit water carrying capacity, optimization is required.

[0029] A water swing will work with any substrate that has the properties laid out above. In the presence of water the ions that are dissolved into the water will achieve an equilibrium state that is similar to what one would expect in an aqueous solution that is in equilibrium with an atmosphere having a specific partial pressure of CO_2. In the absence of the water the energetic state of the carbonate ion is disfavored and thus the loading with CO_2 in the form of bicarbonate can increase. This is the case in conventional strong base quaternary amine resins and it appears to be true for all structures comprising ions fixed to a surface. By understanding the underlying

mechanism we can define a whole family of substrates that can collect CO_2 from the air and release it via a humidity swing.

[0030] Preventing the formation of carbonate ions in favor of bicarbonate ions can be achieved by spacing the cations embedded in the substrate sufficiently far apart so that a single doubly charged ion such as CO_3^{-2} does not cover two positive ions. Other configurations also may be feasible. In the dry state the cations may be neutralized by hydroxide ions. If the system in this form is not stabilized, however, the hydroxides would convert to oxides, and water would be released. In such a system, water would compete with CO_2 for the uptake on the surface.

[0031] Strong base quaternary resins such as Marathon A satisfy the above criteria. However, there are other substrates that could support such cations and have properties that are more efficient for the purpose of this invention. For example, one class of ionic substrates that meet these requirements are materials produced by ion implantations into material surfaces, where these ions have to be sputtered on. This introduces a wide class of materials that otherwise would be inaccessible for functionalizing the surface.

[0032] Other methods could include functionalization of minerals, or other inorganic materials where defects can be accommodated in the surface and made to be stable even in the presence of water. What is important is that the material formed is stabilized against the formation of carbonates and oxides. Presumably, the same spacing argument would make it possible to avoid the formation of an oxide that could negate two charges.

[0033] The two reactions that must be suppressed are;

$$2OH^- \rightarrow H_2O + O^{-2}$$

and

$$2HCO_3^- \rightarrow H_2O + CO_2 + CO_3^{-2}$$

[0034] In both cases this can be achieved by spacing the ions far enough apart for the bivalent negative ions to be unstable in the presence of two single positive charges.

[0035] Zeolites are another class of materials that meet the aforesaid criteria. While there already is some binding of CO_2 and H_2O to the surface, which may complicate matters, zeolites provide lots of surface area, another important factor.

[0036] Non-electroactive materials to which positive ions can be added also meet the aforesaid criteria of the present invention. Positive ions may also be substituted by introducing negative defects; i.e., a missing negative ion could act, in effect, like a net positive ion. Electroactive materials would screen out fixed charges. It is important that the positive net charge is fixed onto the substrate and cannot be dissolved away in the presence of water.

[0037] In a preferred embodiment, the present invention provides a strong-base resin in which hydroxide ions are gradually replaced with inorganic carbon ions. The stoichiometry is such that the final state tends to be a bicarbonate rather than a carbonate as there is essentially one positive charge per CO_2 molecule absorbed. The resin is hygroscopic, but more importantly the CO_2 partial pressure over the resin is not only a function of the CO_2 loading of the resin, but also a function of the water vapor in the gas. The response to changes in the humidity in the gas is very fast. The relevant factor appears to be the CO_2 vapor concentration in the air. In setting the equilibrium partial pressure of CO_2 over the system, however, the water loading of the resin is also a factor. Results indicate that the dependence on water vapor is driven more by absolute humidity than by relative humidity. Thus the system works equally well in hot dry climates and cool humid climates, as both will have a similar dew point temperature.

[0038] The advantage of the resin of the present invention over the ordinary metal oxides of the prior art is twofold: first it binds CO_2 more weakly than a typical metal oxide or hydroxide would; second it presents an unusually large amount of surface for absorption of CO_2. The loading can reach a concentration of nearly two mole of CO_2 per liter.

[0039] Rather than washing the resin in sodium hydroxide, we use sodium carbonate solutions to wash CO_2 off the resin. We have shown that this leads to a resin saturation with CO_2 of one carbon ion per two positive charges. Hence the resin in this state resembles a carbonate rather than a bicarbonate. A fully saturated sorbent, however, can drive the resulting carbonate/bicarbonate mixture to become almost entirely composed of bicarbonate. This is possible due to the amount of surface area available.

[0040] Another advantage of the resin is that the spacing between positive charges is optimized to discourage the deposition of carbonate ions on the resin in favor of bicarbonate ions. It appears that the resin can reach a state where it binds one carbon ion for every positive charge on the resin and it reaches this state at ambient conditions. Furthermore, there is no break in the reaction kinetics as the resin moves from a composition with less than one carbon ion per 2 positive charges to more than one carbon ion per 2 positive charges. This is possible because the distance between two positive charges is too large to be covered by one doubly charged carbonate ion. Instead the carbonate appears to split one water molecule and transforms into a bicarbonate ion and a hydroxide ion. The two ions independently neutralize each charge. When water is present, the large hydration cloud of the carbonate ion discourages this reaction. Thus as the water on the surface is removed, it leaves behind a system that absorbs additional bicarbonate from the air, as it exposes more hydroxide ions.

[0041] The equilibrium state of the resin is dramatically affected by the water vapor content of the air. For dry air the loading is far higher than it is for humid air. This forms the basis for the water vapor swing of the present invention.

[0042] For a sorbent to perform as described above, the sorbent should comprise positive ions embedded into the sorbent matrix in a way that allows the matrix to attract negative ions like OH^-, Cl^-, $CO_3^=$, and HCO_3^-. It is important for the positive charges to be substantially immobile. Also, the spacing between positive ions has to be such that a bicarbonate form is favored over that of carbonate. For a surface with little moisture residue, the carbonate ions will lack most of their hydration cloud and thus they are less stable than they would be in a dilute brine. As discussed above, it is believed that a water molecule is split by the $CO_3^=$ to form a HCO_3^- and an OH^-. These two ions will then bind to the positive sites. In such a system the CO_2 uptake capacity is maintained even if stoichiometrically there are is one carbonate for every two positive ions. The hydroxide is preformed and then absorbs a second CO_2 to form a second bicarbonate. It is possible that other mechanisms may be in play. Nevertheless the essential feature that the bicarbonate is stabilized in favor of the carbonate is undoubtedly correct. It is also clear that the bicarbonate is favored if the distance between the sites gets too large.

[0043] There are several strategies to improve this sorbent. The first category is to optimize the spacing of positive ions and other critical parameters in the current resin. The second category of improvements is to find a different material. One example is highly porous, high surface area (activated) metal oxides and metal hydroxides that could lend themselves to the same treatment as the resin. In particular, we are interested in oxides that are already partially carbonated and whether or not we can drive them to bicarbonate. High surface powders formed from Na_2CO_3, $Al(OH)_3$, $Mg(OH)_2$, Fe_2O_3 are a few examples. More specific examples include activated alumina, activated magnesia, and activated iron oxides.

[0044] An alternative embodiment comprises a metal that forms hydroxides in the presence of humid air. See FIG. **2**. In this situation we can consider the metal surface as an electrode that can be biased in voltage relative to the air. The hydroxylation reaction in the presence of an electric voltage is reversible. That is to say, it should be possible to reduce the metal on its surface and free water and oxygen according to the reaction:

$$2M^{++}(OH^-)_2 \Leftrightarrow 2M+4e^-+2H_2O+O_2,$$

[0045] By reversing the voltage, it is possible to reverse the reaction and form a hydroxide layer again. The reaction can be driven forward and back by changing the applied bias voltage. The hydroxide once formed could then be transformed into either a carbonate or a bicarbonate in the presence of CO_2. Whereas the bias voltage would destroy the hydroxide, the carbonate is unstable under voltage change and would thus come off. Thus, it is possible to drive off the CO_2 by a voltage switch. This switch would also produce water and oxygen from 4 hydroxide ions, but the energy expended here can be recovered in the immediate reversal, which will also recover the hydroxide.

[0046] This system may be viewed as analogous to a capacitor that is charged up; a chemical storage capacitance. The reversal of the voltage will recover most of the energy that was put into the system in the forward swing. Thus, we will look for low frequency oscillations (tied to the RC value of the circuit) that would allow us to drive CO_2 off the membrane. It is possible to clean the CO_2 off in a single swing but it may take more than one cycle. It is also possible to recover the CO_2 from the gas stream, while the water and oxygen have been retained within the system. This may be accomplished by having humid oxygen, water mixtures flow through the system, carrying CO_2 out of the system as it is freed from the surfaces. Since there is water and oxygen in the input stream, the reverse reaction will occur unimpeded, while the CO_2 is carried away by the gas stream.

[0047] The affinity of bicarbonate and carbonate to this surface will depend on the bias voltage applied. Thus we can tailor the binding strength of the sorbent with a bias voltage that is chosen for optimal conditions. It is then possible to change the equilibrium partial pressure of CO_2 simply by changing the bias voltage in a regime where no oxygen is formed. This would provide another mechanism for recovering CO_2. In this regime the voltage switch is insufficient to drive the hydroxide off, but it is sufficient to change the CO_2 partial pressure.

[0048] If the voltage is switched back and forth very rapidly then the energy expended in producing oxygen will be returned immediately in recovering the hydroxide. It is well known that the CO_2 uptake rate is slow, so once the CO_2 has been forced off, the CO_2 may be recovered before it has a chance to be returned to the matrix. The metal sponge would make it possible to create a large amount of surface and control the chemical behavior with a bias voltage. The bias voltage may be manipulated to assure that electric contact to all parts of the electrode material is maintained. It will be necessary to manage hydroxide formation, however, as the presence of too much hydroxide could inhibit conductivity.

[0049] It may be more favorable in terms of energy expended to operate between carbonate and bicarbonate rather than between carbonate and hydroxide. On the other hand, by using a voltage bias that will keep the hydroxide layer intact or a material where the spacing between the positive charges is such that the formation of carbonates is energetically suppressed will result in an apparatus that operates between hydroxide and bicarbonate, without the production of carbonate as an intermediary. This would likely require materials with a larger than normal spacing between positive charges. This spacing is larger than is typically feasible with simple hydroxide crystals. There are several ways to produce such materials. One would be to embed the positive ions in a noble or semi-noble metal, such as tin-copper, aluminum-copper, magnesium-aluminum, magnesium-copper or iron-copper alloys. Also useful are alloys with elements that prefer to go to an oxidation state of 1, e.g., sodium, potassium, Li alloys with copper or other more noble elements including silver. It could also be carbon matrix that is used to separate the fixed positive ions from each other. This strategy could lead to ion-implantation, perhaps by particle beams into activated carbon surfaces or other metallic surfaces.

[0050] Another alternative embodiment would use a semiconductor, e.g., phosphor doped Si. The phosphor atoms will act as positive charges embedded into a neutral matrix. The phosphor atoms, will attract hydroxides if the bias voltage is sufficiently positive, and thus could act as spaced hydroxides. Again, by changing the bias voltage it becomes possible to first manipulate the equilibrium partial pressure of CO_2 over a partially loaded surface, and in the extreme of driving off the hydroxide remove virtually all CO_2 from the surface.

[0051] These hydroxides in turn bind carbonates or bicarbonates. These materials may be optimized to create just the right binding energy. Ideally we eliminate the binding of carbonate, so that the dominant binding is to bicarbonate ions. By creating a nanoporous material we can create large numbers of binding sites. Then, by swinging the voltage we can bias the binding energy of the CO_2 and thus drive CO_2 from the substrate. We may also drive the voltage so high that the water will come off as well. This requires a fast swing, so that the energy of the oxygen formation is recovered immediately in the swing back to hydroxide.

[0052] Further embodiments are also possible without departing from the spirit and scope of the invention as described above. For example, an improved substrate may be composed of or include: sodium silicates, wherein hydrophobic resins with embedded ions are used; activated alumina; foam materials including aerogels; functionalized aquafoams or other foams; or large complex cations such as copper complexes. In addition, the substrate may be modified by using different bonding agents or by reshaping the resin.

[0053] In another aspect of the present invention, a heat exchanger is used to further improve the embodiments outlined above. See FIG. **3**. To perform the humidity swing, it 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 depends strongly on the temperature. To that end, the 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.

[0054] 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 also can be derived from the condensation of water that has been allowed to evaporate at ambient conditions. The present invention employs heat transfer methods increase the efficiency of the capture process.

[0055] Referring to FIG. **4**, the process employs an apparatus including a capture unit **10** and a regeneration unit **20**, having a sorbent material **30** that can be moved from one unit to the other. The gas stream **15** enters the capture unit **10** and the contaminant (in this instance, CO2) is captured by the sorbent **30**. The sorbent is then transferred to the regeneration unit **20**, where the contaminant is released in off stream **25**. This process is aided by using water as a means for transferring heat from the regenerated sorbent to the loaded sorbent.

[0056] For the purposes of this aspect of the present invention, the sorbent material may be a liquid that can absorb CO_2, such as for example, a sodium hydroxide solution, a sodium carbonate solution, or an amine solution; or may be a solid, such as for example, solid amine resins or other ion exchange resins.

[0057] In a primary embodiment, the capture unit is open to ambient air. The regeneration unit is assumed to be at a temperature T_1, where T_1 is greater than T_a, wherein T_a is the ambient air temperature. For example, T_1 preferably is at least 20° C. above T_a. The sorbent material in the capture unit must be brought into the regeneration unit to release the CO_2. The regeneration unit raises the temperature of the sorbent to release the CO_2. Then the sorbent material is returned to the capture unit. This thermal swing may be, for example, a rise of up to about 100° C. above ambient temperatures. The heat required to maintain the regeneration unit at temperature T_1 may be supplied by a heat reservoir **40**, such as the ground or a water reservoir, or may be provided from other sources, including but not limited to solar energy, geothermal energy, or waste heat from other processes such as for example power plants, steel mills, cement plants.

[0058] Referring again to FIG. **4**, the water absorbs heat from the regenerated sorbent and is evaporated, the evaporated water is transferred to the loaded sorbent along path **35**, where it condenses. The condensed water is then returned to the regeneration unit along path **36**. In order to avoid any unnecessary losses, heat from the sorbent can be returned to the regeneration unit before the sorbent is again exposed to ambient air, thus conserving energy. This may be done, for example, by evaporating water into an evacuated space. The water vapor contains the latent heat of evaporation, and if the water is compressed at a higher temperature it will release its heat content at the higher temperature. One way to bring about this transition is to let the water condense onto the surfaces of the sorbent. This may be counter-productive in some instances, however, as the presence of water may interfere with the CO_2 release of some sorbents.

[0059] For sorbents where contact with water is unacceptable, there may be other working fluids that could be deployed in a similar manner. In such case, it is important that the working fluid itself does not interfere with the release of CO_2 from the sorbent, and that it can readily be separated from the released CO_2. Water is a good choice for most sorbents because the water will condense out under compression and thus is easily separated from CO_2. CO_2 as a working fluid would not require a separation from the product CO_2, but it would of course interfere to some extent with the process of releasing CO_2 from the sorbent. Nevertheless, it is possible to remove the bulk of the compressed CO_2 at high pressure, and reduce the volume of residual CO_2 so much that the subsequent expansion does not provide enough heat mass for the resulting temperature drop to effectively cool the chamber or the sorbent material inside of it.

[0060] Referring to FIG. **5**, it also is possible to isolate the working fluid from the sorbent **30** in a heat exchanger **40**, in which case the working fluid may be used to transfer heat from the ambient conditions, or from the elevated temperature of the regeneration unit to the CO_2-loaded sorbent material that is about to enter the regeneration unit along path **41**. It also is possible to effectuate some of the transition by transferring directly heat from warm regenerated sorbent down a natural temperature gradient to cold, CO_2-loaded sorbent. Further, where the working fluid is isolated from the sorbent **30**, the choice of an optimal working fluid is not limited to water. It could, for example, be CO_2 which in near ambient conditions has been identified as a good choice of a refrigerant. Other refrigerants, such as R-12 or R-22, are also viable in this arrangement.

[0061] The present invention therefore provides a sorbent that absorbs a gas, such as CO_2, under controlled temperatures, and will load itself fully or partially with the gas it is absorbing. At the time the sorbent enters into the recycle loop we refer to it as the loaded sorbent, even if the loading does not reach the maximum level that is achievable. The sorbent is recovered at an elevated temperature, the goal of this invention being to provide the heat necessary to drive the sorbent to the higher temperature. It is implicitly assumed that the heat required to release the gas is also provided but that in the typical case this is small compared to the heat required to warm the sorbent. Whether or not this amount of heat can be considered small, in heating up the sorbent, it is understood that this heat is provided as well.

[0062] 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 without departing from the spirit and scope of the invention. All these and other such modifications and variations are intended to be included herein within the scope of this disclosure and protected by the following claims. Therefore the scope of the invention is not intended to be limited except as indicated in the appended claims.

1-18. (canceled)

19. A method for extracting a contaminant from a gas stream, comprising the steps of:

a) bringing the gas stream in contact with a sorbent which captures the contaminant from the gas stream, so as to at least partially saturate the sorbent with contaminant;

b) placing the contaminant carrying sorbent in a regeneration unit for releasing the contaminant from the sorbent

and regenerate the sorbent, wherein the regeneration unit is maintained at a temperature that is higher than the temperature of the gas stream;

c) removing the regenerated sorbent from the regeneration unit; and

d) capturing heat from the regenerated sorbent as the sorbent is removed from the regeneration unit.

20. The method of claim **19**, wherein the heat captured from the sorbent regeneration is used to raise the temperature of the contaminant carrying sorbent prior to the step (b) of placing the sorbent in the regeneration unit.

21. The method of claim **19**, wherein the contaminant is carbon dioxide.

22. The method of claim **19**, wherein the gas stream is an exhaust stream or ambient air.

24. The method of claim **19**, wherein the sorbent is a liquid or a solid.

25. (canceled)

26. The method of claim **19**, wherein heat is captured from the regenerated sorbent using a heat exchanger in a refrigeration cycle, wherein water preferably is employed as refrigerant in the refrigeration cycle, the refrigerant water optionally is evaporated using heat exchanged from the regenerate, and the evaporated water optionally is condensed on the contaminant carrying sorbent.

27-29. (canceled)

30. The method of claim **26**, wherein the heat exchanger uses carbon dioxide as a refrigerant.

31. The method of claim **26**, wherein the heat exchanger utilizes a refrigerant that is isolated from having contact with the sorbent.

32. The method of claim **19**, wherein the regeneration unit is maintained at an elevated temperature using heat from a source that is one from a group consisting of: solar energy, geothermal energy, and waste heat from an industrial process.

33. An apparatus for extracting a contaminant from a gas stream using a sorbent employing a thermal swing, comprising:

a sorbent for capturing the contaminant;

a capture unit, wherein the sorbent is exposed to the gas stream and becomes at least partially saturated with the contaminant;

a regeneration unit, wherein the sorbent is exposed to elevated temperatures thereby causing the sorbent to release the contaminant according to a thermal swing; and

a heat exchanger for extracting heat retained from the sorbent in the regeneration unit.

34. The apparatus of claim **33**, wherein heat extracted by the heat exchanger is used to raise the temperature of the at least partially saturated sorbent prior to placing the at least partially saturated sorbent in the regeneration unit.

35. The apparatus of claim **33**, wherein the contaminant is carbon dioxide or ambient air.

36. (canceled)

37. The apparatus of claim **33**, wherein the sorbent is a liquid or a solid.

38. (canceled)

39. The apparatus of claim **33**, (a) wherein the heat exchanger uses water or carbon dioxide as a refrigerant, and/or (b) wherein the heat exchanger utilizes a refrigerant that is isolated from having contact with the sorbent.

40-41. (canceled)

42. A method for extracting CO_2 from a gas stream comprising the steps of:

(a) bringing a sorbent in contact with said gas stream, so as to at least partially saturate said sorbent with CO_2;

(b) releasing CO_2 from said sorbent at a temperature that is higher than the temperature of said gas stream, thereby regenerating said sorbent;

(c) capturing heat retained by said sorbent using a working fluid; and

(d) recycling captured heat for use in step (b).

43. The method of claim **42**, wherein said gas stream is ambient air.

44. The method of claim **42**, wherein said sorbent is selected from the group consisting of: a sodium hydroxide solution, a sodium carbonate solution, an amine solution, a solid amine resin, an ion exchange resin, a functionalized mineral, a functionalized inorganic matter, a zeolite, a metal oxide, a metal hydroxide, a high surface powder, a sodium silicate, a foam material, and a functionalized foam.

45. The method of claim **44**, wherein said high surface power is formed from sodium carbonate, aluminum hydroxide, magnesium hydroxide, iron(III) oxide, activated alumina, activated magnesia, and activated iron oxide.

46. The method of claim **42**, characterized by one or more of the following features:

(a) wherein said working fluid is water, CO_2, R-12, or R-22;

(b) said working fluid contacts said sorbent; and

(c) said working fluid is isolated from said sorbent.

47. The method of claim **46**, wherein CO_2 released from said sorbent is collected in a vessel.

* * * * *