

CARBON DIOXIDE CAPTURE METHOD AND SYSTEM

TECHNICAL FIELD

This disclosure relates to field of carbon capture from streams such as waste gases
5 or the ambient atmosphere.

BACKGROUND ART

The continued advancement of carbon capture and utilization technologies has led to the prospect of establishing an anthropogenic carbon cycle by capturing carbon dioxide and subsequently converting it into fuels and chemicals. Interest is growing
10 in technologies that attempt to capture carbon dioxide from various sources including the atmosphere and waste gas streams such as flue gases released from power plants. Direct air capture (DAC) is one such negative emission technology for direct extraction of carbon dioxide from the atmosphere that has gained significant interest as a sustainable source of carbon dioxide.

15 Adsorption-based DAC utilizing amine-grafted adsorbents is considered a highly promising technology owing to its ability to release carbon dioxide at relatively low temperatures. The amine-grafted adsorbents are able to capture very small amounts (400 ppm) of carbon dioxide from air. The captured carbon dioxide can be subsequently released to produce high-purity carbon dioxide and regenerate the
20 amine-grafted adsorbent. The driving force for desorption is created using a combination of heat and/or partial pressure. One of the ways to accomplish the release of carbon dioxide is through a temperature vacuum swing adsorption (TVSA) process in which the temperature of the amine-grafted adsorbent is increased together with the application of vacuum (which decreases the partial
25 pressure of carbon dioxide). Similarly, it is also possible to heat the adsorbent in a stream of carbon dioxide gas or contact the adsorbent with steam to release the captured carbon dioxide. However, these existing processes have disadvantages. For example, heating the adsorbent in a stream of carbon dioxide reduces the amount of carbon dioxide that can be desorbed and can result in degradation of

amine-grafted adsorbents through formation of urea. Similarly, the TVSA process requires the use of equipment that can create vacuum and provide heat. Often the provision of external thermal energy together with operation of other required equipment (such as vacuum pumps) can cause emission of more carbon dioxide
5 than is being captured.

Accordingly, there exists a need to address the above drawbacks or at least provide a useful alternative.

SUMMARY

The present invention is directed to methods and systems for extracting carbon
10 dioxide from a gas stream. These methods and systems utilise a moisture sorbent material to capture moisture, which can subsequently be used for steam generation. The generated steam is then used for regenerating the CO₂ adsorbent, enabling the carbon dioxide to be recovered.

A first aspect of the invention provides a method of extracting carbon dioxide from
15 a gas stream, the method comprising:

contacting a CO₂ adsorbent with a moist gas stream containing CO₂ to capture CO₂ from the moist gas stream in the presence of moisture;

capturing a portion of the water from the moist gas stream using a moisture sorbent material;

20 regenerating the CO₂ adsorbent to produce an output stream comprising steam and CO₂, the regenerating comprising:

heating the moisture sorbent material to release water captured by the moisture sorbent material as steam;

25 exposing the CO₂ adsorbent to the steam to liberate captured CO₂ from the CO₂ adsorbent and generate the output stream.

In some embodiments, the CO₂ adsorbent is contacted by the moist gas stream upstream of exposing the moisture sorbent material to the moist gas stream.

Regenerating the CO₂ adsorbent may be conducted at a temperature in the range of 40 °C – 150 °C. In some embodiments, regenerating the CO₂ adsorbent comprises applying a vacuum during the heating of the moisture sorbent material to promote formation of steam. In some embodiments, a reduced pressure or vacuum is applied
5 during regeneration so that the captured CO₂ is liberated at a lower temperature than when the CO₂ adsorbent is exposed to the steam at ambient pressure.

In some embodiments, after contacting the CO₂ adsorbent with the moist gas stream, the method comprises purging the atmosphere around the CO₂ adsorbent to remove oxygen from said atmosphere. Purging may comprise displacing oxygen
10 from the atmosphere around the CO₂ adsorbent using the steam.

The amount of carbon dioxide adsorbent and moisture sorbent material used will generally be selected based on the desired capacity of the system and the individual uptake capacities of the carbon dioxide adsorbent and moisture sorbent material so as to capture a suitable amount of carbon dioxide (with the carbon dioxide
15 adsorbent) and capture a suitable amount of moisture (with the moisture sorbent material) so that sufficient steam can be provided for the effective regeneration of the carbon dioxide adsorbent. In some embodiments, a molar ratio of water captured by the moisture sorbent material to CO₂ captured by the CO₂ adsorbent is at least 8, such as at least 11, for example above 14. That is, in some embodiments, the
20 amount of carbon dioxide adsorbent and moisture sorbent material used will be selected to provide a sufficient molar ratio of water captured by the moisture sorbent material to CO₂ captured by the CO₂ adsorbent. In some embodiments, a volume ratio of the carbon dioxide adsorbent to the moisture sorbent material is less than 7, such as less than 6, for example in the range of about 1 – 7 or in the range of about
25 4 – 5.25.

In some embodiments, the moisture sorbent material is chosen from a group comprising silica gel; aluminosilicate gel; sorbead; Sepiolite; Bentonite; Kaolin; metal organic frameworks comprising MIL-101, MIL-100, MOF-801, CAU-10, CAU-23, UIO-66, UIO-67, MOF-841, DUT-67, DUT-51, MOF-808, MOF-5, and
30 MOF-74; zeolite comprising small-pore zeolites comprising 3A, 4A, 5A, 13X, and

10X, zeolite frameworks comprising ZSM-5, Y, Beta, FAU, MOR, and AIPO, and molecular sieves comprising SAPO, ITQ-29, SSZ-13, MCM-41, KIT-6, TNU-9, B-ZSM-5, and UTD-1; carbon materials comprising activated carbon, biomass carbon, activated carbon fibres, carbon molecular sieves, and mesoporous carbon; salt-impregnated desiccants comprising one or more of LiCl, CaCl₂, CuCl₂, CuSO₄, MgSO₄, an ionic liquid or a mixture thereof impregnated into a porous material comprising activated carbon, silica, or clay; alumina; polymers comprising hydrophilic functional groups in their polymer chain units.

In some embodiments, the CO₂ adsorbent is an amine-based CO₂ adsorbent or a salt-impregnated CO₂ adsorbent. The CO₂ adsorbent may be or comprise a salt-impregnated CO₂ adsorbent formed by impregnating alkali carbonates, ionic liquids, or a mixture thereof into a porous material selected from the group consisting of: activated carbon, silica, clay, or combinations thereof. Alternatively or additionally, the CO₂ adsorbent may be or comprise an amine-based CO₂ adsorbent selected from the group consisting of: an impregnated amine-based adsorbent formed by the deposition of tetraethylenepentamine (TEPA), pentaethylenhexamine (PEHA), polyethylenimine (PEI), polyallylamine (PAA), monoethanolamine (MEA) impregnated into the pores or on a surface of a solid support, said solid support comprising carbon, silica, clay, zeolite, metal-organic framework, metal oxide, cellulose, polymer, or combinations thereof; a covalently bonded amine-based adsorbent formed using 3-aminopropyltriethoxysilane (APS), aminopropyl (APS) silanes or diethylenetriamine (DT) silanes to covalently bond amine groups to a surface of a porous material; polymers comprising amine groups incorporated from styrene-divinyl benzene co-polymer.

In some embodiments, the relative humidity level of the moist gas stream is between 15 – 95%.

In some embodiments, the method comprises separating CO₂ from the output stream to produce a CO₂-rich stream. Separating may comprise condensing steam from output stream to form a CO₂-rich stream. The CO₂-rich stream may be 97 to 99% CO₂. The output stream or the CO₂-rich stream may be collected for use, or

directed to, other processes that can utilise the CO₂-containing stream, such as carbon sequestration processes.

In the first aspect, a moist gas stream contacts the carbon dioxide adsorbent and moisture sorbent material. In some other embodiments, different streams may
5 contact each of the carbon dioxide adsorbent and moisture sorbent material. Thus, a second aspect of the invention provides a method of extracting carbon dioxide from a gas stream, the method comprising:

contacting a CO₂ adsorbent with a first gas stream containing carbon dioxide to capture carbon dioxide from the first stream;

10 capturing water from a second stream containing water using a moisture sorbent material;

regenerating the CO₂ adsorbent to produce an output stream comprising steam and carbon dioxide, the regenerating comprising:

15 heating the moisture sorbent material to release water captured by the moisture sorbent material as steam;

exposing the CO₂ adsorbent to the steam to liberate captured carbon dioxide from the CO₂ adsorbent and generate the output stream.

In some embodiments, the first gas stream is a moist gas stream. In some embodiments, the second stream is a vapor stream.

20 Embodiments of the second aspect may be generally performed in accordance with the first aspect, save for the use of first and second streams for contacting the carbon dioxide adsorbent and moisture sorbent material, respectively. Thus, in some embodiments, regenerating the CO₂ adsorbent is conducted at a temperature in the range of 40 °C – 150 °C

25 In some embodiments, regenerating the CO₂ adsorbent comprises applying a vacuum during the heating of the moisture sorbent material to promote formation of steam. In some embodiments, a reduced pressure or vacuum is applied during

regeneration so that the captured CO₂ is liberated at a lower temperature than when the CO₂ adsorbent is exposed to the steam at ambient pressure.

In some embodiments, after contacting the CO₂ adsorbent with the first stream, the method comprises purging the atmosphere around the CO₂ adsorbent to remove oxygen from said atmosphere. Purging may comprise displacing oxygen from the atmosphere around the CO₂ adsorbent using the steam.

As with the first aspect, the amount of carbon dioxide adsorbent and moisture sorbent material used will generally be selected based on the desired capacity of the system and the individual uptake capacities of the carbon dioxide adsorbent and moisture sorbent material, so as to capture a suitable amount of carbon dioxide (with the carbon dioxide adsorbent) and capture a suitable amount of moisture (with the moisture sorbent material) so that sufficient steam can be provided for the effective regeneration of the carbon dioxide adsorbent. In some embodiments, a molar ratio of water captured by the moisture sorbent material to CO₂ captured by the CO₂ adsorbent is at least 8, such as at least 11, for example above 14. That is, in some embodiments, the amount of carbon dioxide adsorbent and moisture sorbent material used will be selected to provide a sufficient molar ratio of water captured by the moisture sorbent material to CO₂ captured by the CO₂ adsorbent. In some embodiments, a volume ratio of the carbon dioxide adsorbent to the moisture sorbent material is less than 7, such as less than 6, for example in the range of about 4 – 5.25.

The moisture sorbent material noted above for the first aspect may also be selected for the second aspect. Similarly, the CO₂ adsorbent described above for the first aspect may also be used in the second aspect.

In some embodiments, the relative humidity level of the second stream is between 15 – 95%.

In some embodiments of the second aspect, the method comprises separating CO₂ from the output stream to produce a CO₂-rich stream. Separating may comprise

condensing steam from output stream to form a CO₂-rich stream. The CO₂-rich stream may be 97 to 99% CO₂.

- A third aspect of the invention provides a system for extracting carbon dioxide from a gas stream, the system comprising: a moisture capture zone and a CO₂ capture zone in fluid connection with the moisture capture zone, wherein the moisture capture zone has a moisture sorbent material configured to capture moisture from a moist gas stream and the CO₂ capture zone has a CO₂ adsorbent configured to capture CO₂ from the moist gas stream; and a regeneration means configured to produce an output stream comprising steam and CO₂, the regeneration means comprising a heating arrangement configured to heat the moisture sorbent material so that water captured by the moisture sorbent material is released as steam; wherein the moisture capture zone and a CO₂ capture zone are configured for exposing the CO₂ adsorbent to the steam to liberate captured CO₂ from the CO₂ adsorbent and generate the output stream.
- In some embodiments, the moisture capture zone and CO₂ capture zone are located adjacent each other in a single column reactor. Alternatively, in some embodiments, the moisture capture zone and CO₂ capture zone are located in separate reactors fluidly connected with one another. In some embodiments, the present invention provides a system configured for implementing the method of the second aspect.
- Thus, there is provided a system for extracting carbon dioxide from a gas stream, the system comprising: a moisture capture zone and a CO₂ capture zone, wherein the CO₂ capture zone has a CO₂ adsorbent configured to capture CO₂ from a first stream containing carbon dioxide and the moisture capture zone has a moisture sorbent material configured to capture moisture from a second stream containing water; and a regeneration means configured to produce an output stream comprising steam and CO₂, the regeneration means comprising a heating arrangement configured to heat the moisture sorbent material so that water captured by the moisture sorbent material is released as steam; wherein the moisture capture zone and a CO₂ capture zone are configured for exposing the CO₂ adsorbent to the steam to liberate captured CO₂ from the CO₂ adsorbent and generate the output stream.

In some embodiments of the system, the heating arrangement is powered by a heating coil, solar concentrator or a heat exchange arrangement configured to recover heat from an industrial process and provide the recovered heat to the moisture sorbent material. The solar concentrator may be a parabolic solar
5 concentrator.

In some embodiments, the heating arrangement further comprises a vacuum insulation layer that surrounds at least the moisture capture zone so as to prevent heat loss from the moisture capture zone. In some embodiments comprising a parabolic solar concentrator, the vacuum insulation layer is transparent to solar
10 radiation directed towards the moisture capture zone from the parabolic solar concentrator.

A fourth aspect of the invention provides a carbon dioxide capture plant for extracting CO₂ from a moist gas stream, the plant comprising a plurality of systems as described above. In some embodiments, the plant is a direct-air capture plant
15 configured to capture carbon dioxide from ambient atmosphere.

BRIEF DESCRIPTION OF THE DRAWINGS

Embodiments will now be described by way of example only, with reference to the accompanying drawings in which:

20 Figure 1 is a schematic view of illustrating an embodiment of the method disclosed herein used for DAC and including an adsorption step at ambient conditions, a preheating step for increasing temperatures, a desorption step for product collection, and a cooling step for the column to reach ambient conditions.

Figure 2 is a schematic view of one embodiment of a system according to the
25 present invention.

Figure 3 is a schematic diagram of a solar-powered DAC prototype of Example 1 during the regeneration step.

Figure 4A shows temperature change profiles of the adsorption column of Example 1 under 600 W/m^2 solar irradiation. Concentrated sunlight was generated by the parabolic concentrator.

Figure 4B shows heating powers of the photothermal system of Example 1 under natural sunlight and concentrated sunlight.

Figure 5A shows CO_2 loading and adsorbent temperature profiles of the three cases of Example 2 during the adsorption process (Case 1: 200 mL resin and 200 mL silica gel, at 40% RH and a GHSV of 6000 /h. Case 2: 320 mL resin and 80 mL silica gel, at 56% RH and a GHSV of 3750 /h. Case 3: 420 mL resin and 80 mL silica gel, at 57% RH and a GHSV of 3000 /h).

Figure 5B illustrates the performance of the proof-of-concept DAC system powered by solar energy of Example 2.

Figure 5C shows the adsorbent temperature, outlet air temperature and humidity during the cooling process of Case 1 of Example 2 after solar regeneration.

Figure 5D shows the energy consumptions and regeneration efficiencies of solar-powered VPD (Case 2) of Example 2, reported TVSA process and steam-assisted TVSA (STVSA) process using the same CO_2 adsorbent.

Figure 6 shows CO_2 adsorption isobars of VPOC 1065 (see Example 3).

Figure 7A illustrates the setup for the breakthrough experiments of Example 4.

Figure 7B are CO_2 breakthrough curves of VPOC 1065 using 28°C air with a gas hourly space velocity (GHSV) of 12000 /h, at varying levels of relative humidity. The inset shows atmospheric CO_2 adsorption capacities under dry and different humidity conditions.

Figure 7C are Fourier transform infrared spectroscopy (FTIR) spectra of VPOC 1065 pretreated using 25°C air with 30% RH.

Figure 7D are in-situ Fourier transform infrared spectroscopy (FTIR) spectra of VPOC 1065 after 0, 5, 10, 15, 20, 25 and 30 min treatment in flowing N₂ atmosphere at 100 °C. The sample was pretreated with 25 °C and 30% RH air for 12 hours.

- 5 Figure 7E shows cyclic CO₂ adsorption capacity of VPOC 1065 regenerated under (A) 120 °C and (B) 150 °C CO₂ flows. CO₂ adsorption was performed using 30 °C CO₂ and q_0 represented the CO₂ uptake of the first adsorption cycle.

Figure 7F shows CO₂-induced deactivation mechanism analysis. (A) In-situ FTIR spectra for VPOC 1065 after 0, 1, 2, 3 and 4 hours (bottom to top) treatment under
10 150 °C CO₂ stream. (B-C) Proposed mechanism for (B) open-chain ureas formation and (C) cyclic ureas formation.

Figure 8A shows water adsorption isotherms of VPOC 1065 at 25 °C, 35 °C and 45 °C.

Figure 8B shows water adsorption isotherms of silica gel at 25 °C, 35 °C and 45
15 °C.

Figure 9A illustrates the setup for adsorption-desorption cyclic experiments in Example 6.

Figure 9B is a schematic diagram of the column used for solar-powered DAC experiments, which has an adsorption column (1), a black coat (2), and a transparent
20 vacuum isolation layer (3).

Figure 9C shows CO₂ loading profiles during six adsorption-desorption cycles using 180 mL VPOC resin and 180 mL silica gel. Fresh air at 27 °C with RH ranged from 35 to 60% was used as the feed stream with a GHSV of 10000 /h.

Figure 9D shows working capacities of different cycles calculated from the CO₂
25 loading profiles.

Figure 9E shows desorption temperature profiles in the regeneration processes. The shaded areas indicated the variation of results from different cycles

Figure 9F shows normalized product volumes (ratios of collected product volume to final product volume) under different desorption temperatures.

- 5 Figure 9G shows real-time CO₂ purity and product volumes during the desorption stage.

Figure 10A shows cyclic CO₂ and water productivities under different relative humidities using 320 mL VPOC resin and 80 mL silica gel.

- 10 Figure 10B shows (A) the CO₂ loading profile in six adsorption-desorption cycles using 320 mL VPOC resin and 80 mL silica gel and (B) the temperature profile of the CO₂ adsorbent during a single desorption process.

Figure 10C shows the ¹H NMR spectra for the (A) deionized water and (B) water products. DMSO with 12 ppm concentration was employed as the reference.

- 15 Figure 10D shows the relationship between the molar ratio of adsorbed water to CO₂ ($n_{\text{water}}/n_{\text{CO}_2}$) and the required desorption temperature for Example 7.

Figure 11A shows the temperature profiles of the CO₂ adsorbent under different desorption pressures for Example 8.

Figure 11B shows the product volume profiles under different desorption pressures for Example 8.

- 20 Figure 12 is a schematic view of one embodiment of a system according to the present invention.

DETAILED DESCRIPTION

In the following detailed description, reference is made to accompanying drawings which form a part of the detailed description. The illustrative embodiments described in the detailed description, depicted in the drawings and defined in the claims, are not intended to be limiting. Other embodiments may be utilised and other changes may be made without departing from the spirit or scope of the subject matter presented. It will be readily understood that the aspects of the present disclosure, as generally described herein and illustrated in the drawings can be arranged, substituted, combined, separated and designed in a wide variety of different configurations, all of which are contemplated in this disclosure.

In one aspect, there is provided a method of extracting carbon dioxide from a gas stream, the method comprising:

- contacting a CO₂ adsorbent with a moist gas stream containing CO₂ to capture CO₂ from the moist gas stream in the presence of moisture;
- capturing a portion of the water from the moist gas stream using a moisture sorbent material; and
- regenerating the CO₂ adsorbent to produce an output stream comprising steam and CO₂, the regenerating comprising:
 - heating the moisture sorbent material to release water captured by the moisture sorbent material as steam; and
 - exposing the CO₂ adsorbent to the steam to liberate captured CO₂ from the CO₂ adsorbent and generate the output stream.

Such a method 10 is illustrated in Figure 1. As noted above, the method comprises contacting a carbon dioxide adsorbent 12 with a moist gas stream 14 containing carbon dioxide to capture carbon dioxide from the moist gas stream in the presence of moisture. In the illustrated embodiment, the moist gas stream 14 is air with a relative humidity of 40%. The method 10 comprises capturing a portion of water from the moist gas stream 14 using a moisture sorbent material 16. After contacting the moist gas stream 14 with the carbon dioxide adsorbent 12 and the moisture

sorbent material 16, a lean stream 15 is formed. In this embodiment, the lean stream 15 has a relative humidity of 20%.

The method further comprises regenerating the carbon dioxide adsorbent 12 to produce an output stream 18. That is, the method 10 includes a desorption stage in which the captured carbon dioxide is released, thereby regenerating the carbon dioxide adsorbent 12. In this embodiment, the output stream 18 is separated into a water-rich stream 20 and carbon dioxide-rich stream 22. The regenerating step comprises heating the moisture sorbent material 16 to release water captured by the moisture sorbent material 16 as steam. The regenerating step further comprises exposing the carbon dioxide adsorbent 12 to the steam to liberate the captured carbon dioxide from the carbon dioxide adsorbent 12 and generating the output stream 18.

In the illustrated embodiment of Figure 1, the method 10 includes preheating the carbon dioxide adsorbent 12 and the moisture sorbent material 16, in order to bring the carbon dioxide adsorbent 12 and moisture sorbent material 16 up to the temperature at which steam is released from the moisture sorbent material 16 and the regeneration of the carbon dioxide laden carbon dioxide adsorbent 12 commences. During preheating, gas from the interstitial spaces between the particles of carbon dioxide adsorbent 12 and the moisture sorbent material 16 is displaced, forming a stream 17 of gas (in this illustrated embodiment air, reflecting the nature of the initial input gas) that moves towards a direction where an open valve is located. In some embodiments, such as the embodiment illustrated in Figure 1, the open valve may be a valve located on a first side of the carbon dioxide adsorbent 12 (i.e. a side from where the moist gas stream enters a chamber/reactor in which the carbon dioxide adsorbent 12 is located). In this case, the displaced air will flow in a direction opposite to that of the initial input stream (i.e. it exits through a valve through which the moist gas stream 14 entered the chamber/reactor). In other embodiments, the open valve can be located on a second, opposite side of the carbon dioxide adsorbent. In this case, the displaced air will flow in the same direction as the moist gas stream. In some further embodiments, there may be two

open valves present on either side of the carbon dioxide adsorbent. In this case, the displaced air may flow in both directions and away from the carbon dioxide adsorbent. In some cases, a stream of displaced air may flow in the same direction as the initial input stream. In some other embodiments, the displaced gas may flow
5 in both directions.

After the carbon dioxide adsorbent 12 has been regenerated, the carbon dioxide adsorbent 12 and the moisture sorbent material 16 may be cooled. By cooling the carbon dioxide adsorbent 12 and the moisture sorbent material 16, they may be readied for a new adsorption and regeneration cycle. In the illustrated embodiment,
10 a cooling gas 19 is passed through the carbon dioxide adsorbent 12 and the moisture sorbent material 16. The cooling gas 19 may be around ambient temperature, such as about 25 °C, and a warmed gas stream 19' will be formed after passing the cooling gas through the carbon dioxide adsorbent 12 and the moisture sorbent material 16. In some embodiments, the warmed gas stream 19' may emerge at a
15 temperature of about 45 °C.

The cooling gas may have the same composition as the moist gas stream 14. In the illustrated embodiment, air is used. However, different gases or gas mixtures may be used as the cooling gas, such as nitrogen.

As discussed above, air can be used as a cooling gas 19, that is, an oxygen-containing gas mixture. At certain points in the method of the present invention, it may be undesirable for the carbon dioxide adsorbent material to be exposed to oxygen. It can be undesirable for the carbon dioxide adsorbent material to be exposed to oxygen at elevated temperatures. For example, an amine-based carbon dioxide adsorbent that comes into contact with air containing oxygen at elevated
20 temperatures can undergo oxidative degradation. The level of oxidative degradation can increase significantly with increasing time of contact between the amine-based carbon dioxide adsorbent and cooling air. Accordingly, it is desirable to limit the time of contact between the amine-based adsorbent with oxygen present in the air at the elevated temperatures to minimize oxidative degradation. Air may be used as
25 a cooling gas, as the cooling may occur quickly enough so that the CO₂ adsorbent
30

is not exposed to oxygen at an elevated temperature for an unacceptably long duration. In some embodiments, in addition to using the cooling gas, the cooling can be conducted to increase cooling rates. For example, it may be possible to reduce the temperature of the CO₂ adsorbent rapidly to less than 70 °C by using
5 evaporation of adsorbed water as a mechanism, as discussed further below.

In some other embodiments, to minimise the exposure of the CO₂ adsorbent to oxygen at elevated temperatures, the cooling gas may be a gas or gas mixture that is substantially oxygen-free. Use of a gas or gas mixture that is substantially oxygen-free may be desirable in cases where it may not be possible to bring down
10 the temperature of the carbon dioxide quickly enough,. For example, nitrogen may be used as the cooling gas 19. In general, nitrogen has lesser reactivity than oxygen at elevated temperatures. Thus, when using nitrogen, it may be possible to prolong the contact time between the cooling gas 19 and the carbon dioxide adsorbent 12 during the cooling phase. The cooling time can depend on the temperature of
15 regeneration, as well as the amount of adsorbent, the packing density of the CO₂ adsorbent, the configuration of the system in which the adsorbent has been placed (all of which can affect the flow of cooling gas through the system and the efficacy of cooling).

The present disclosure relates to carbon dioxide adsorbents that can be regenerated
20 through heating and/or steam stripping. A carbon dioxide adsorbent is capable of adsorbing, or releasably binding, carbon dioxide. The carbon dioxide adsorbent may be a solid carbon dioxide adsorbent. That is, it may comprise a substrate that has at its surface a carbon dioxide binding agent. The solid adsorbent may be a porous solid mass, so that there is a pathway for the moist gas stream to flow
25 therethrough and contact the surface. In some embodiments, the aspect ratio of the carbon dioxide adsorbent may be selected to maximise the surface area available for contacting the moist gas stream and, consequently, capturing carbon dioxide therefrom. The carbon dioxide adsorbent may be in the form of solid particles (e.g. a bed of particles) or may be a monolithic structure.

Solid carbon dioxide adsorbents and moisture sorbent materials are generally preferred for use with the method and system disclosed herein, compared to e.g. a liquid scrubber. The use of solid carbon dioxide adsorbents and moisture sorbent materials may avoid or minimise disadvantageous pressure changes during the process that affect efficiency.

The methods and systems disclosed herein may be particularly advantageous for use with amine-based carbon dioxide adsorbents. However, it will be appreciated that they are applicable to other carbon dioxide adsorbents. In some embodiments, the carbon dioxide adsorbent is a solid amine-based carbon dioxide adsorbent. The solid amine-based carbon dioxide adsorbent may be selected from the group including adsorbents based on porous supports impregnated with monomeric or polymeric amines, adsorbents based on amines that are covalently linked to a support and adsorbents based on porous supports on which aminopolymers are polymerized *in situ* starting from an amine containing monomer.

Carbon dioxide adsorbents typically have functional groups on their surface that trap the carbon dioxide. Amongst available carbon dioxide adsorbents, amine-based carbon dioxide adsorbents are known for their ability to form a strong bond with carbon dioxide allowing them to trap carbon dioxide from various sources. In particular, amines are capable of trapping very low amounts of carbon dioxide (in the order of 400 ppm) and releasing this trapped carbon dioxide at relatively low temperatures, thus making them suitable for carbon capture from direct air capture (DAC) and other gas streams containing low levels of carbon dioxide. However, effectively regenerating (i.e. releasing the captured carbon dioxide and making the adsorbent ready to take up more carbon dioxide in a subsequent cycle) amine-grafted adsorbents is challenging due to the large heat of adsorption (60-100 kJ/mol) for capturing atmospheric carbon dioxide. The regeneration process can subject amine-based adsorbents to excessive heat that will degrade the amine-based adsorbent when trying to release the adsorbed carbon dioxide. On the other hand, in some cases, only a limited fraction of the adsorbed carbon dioxide is released as final product, leading to increased capital and operational costs for DAC.

Consequently, the capacity of the amine-based adsorbents is underutilized. The methods and systems in accordance with the invention facilitates the desorption process and may allow for a higher utilization of the adsorbent capacity.

It is known to use steam stripping to remove the adsorbed carbon dioxide. Steam stripping can facilitate lower temperature regeneration of the carbon dioxide absorbent by providing both a thermal desorption and a partial pressure induced desorption. However, existing methods required the steam to be generated externally and supplied to the capture system. This requires separate equipment and its maintenance, incurring energy and economic costs that are associated with operating such equipment. As a result, the capital and operational costs associated with existing carbon capture methods and systems can be significant.

In the present invention, moisture which may be present in the gas stream or ambient atmosphere is captured, through the use of a moisture sorbent material, for subsequent use in the regeneration process. Thus, the present invention provides a vapor promoted regeneration (desorption) process that recovers adsorbed CO₂ by utilising moisture that have been captured inline with the CO₂ adsorption. The steam generated using the moisture from the moisture sorbent material (that is water harvested from the air with the aid of desiccants) may be around 100 °C. Steam generated in accordance with the method of the present invention can lead to a reduction in the CO₂ partial pressure, thereby significantly promoting the regeneration process. In some embodiments, the generation of steam may purge other gases from the atmosphere around the carbon dioxide absorbent. In some case, this may mean that CO₂ is released into an atmosphere that is predominantly steam, such that the output stream is substantially steam and CO₂. This can facilitate separation of the output stream into so as to produce high-purity CO₂ and water. In some embodiments, the use of steam to purge other gases from the atmosphere around the carbon dioxide absorbent from ambient air may permit the method to be performed without the need for external purge gas and/or vacuum conditions during adsorbent regeneration. In this way, methods and systems in accordance with the

present invention may enable the efficient use of moisture in the regeneration process.

It is known that ambient atmosphere can have relative humidity values anywhere between 15 – 95% . Furthermore, in some embodiments, the method may offer an
5 advantage in that the moisture in the gas stream can also facilitate improved adsorption of carbon dioxide. In particular, moisture can facilitate adsorption of carbon dioxide on amine-based adsorbents.

Embodiments in accordance with the present invention may be used to capture carbon dioxide from a variety of carbon dioxide containing gas streams. For
10 example, the method could be employed at a power plant emitting carbon dioxide from its operations (e.g. in flue gases or waste gas stream). Likewise, it can also be implemented at any chosen location for DAC. The only relevant determining factor in the implementation of this method is providing a moist gas stream with suitable relative humidity levels. The moist gas stream may contain at least 15% relative
15 humidity. For example, in some embodiments, the moist gas stream may contain at least 30% relative humidity. In some embodiments, the moist gas stream may contain about 35 – 85% relative humidity. In some embodiments, the moist gas stream has up to about 95% relative humidity. In some embodiments, such moisture levels are intrinsic to the gas mixture from which the carbon dioxide is to be
20 captured. For example, air from the atmosphere can, depending on location and prevailing weather conditions, have sufficient moisture for use as a moist gas stream without augmenting the moisture levels of the gas mixture. Similarly, in some other embodiment, the gas mixture from an industrial process may have a suitable moisture content. In some of such embodiments, use of the present invention may
25 be advantageous as it enables both carbon dioxide and water recovery from a waste stream.

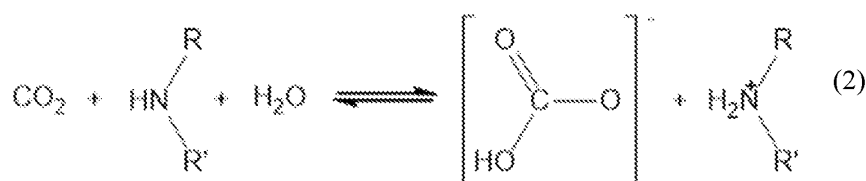
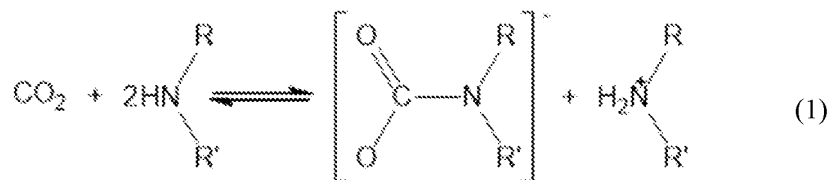
In some other embodiments, the moisture level in the gas stream may be adjusted prior to use in the process. That is, some embodiments of the method include adjusting the humidity of a gas stream to produce the moist gas stream, prior to
30 contacting a CO₂ adsorbent with the moist gas stream to capture CO₂ from the moist

gas stream in the presence of moisture. The moisture levels may be increased to produce the moist gas stream. Methods of increasing the moisture content of the gas stream to be treated can include conventional methods for adjusting the relative humidity of a gas stream. For example, the gas stream may be passed over a wet plate prior to contacting the carbon dioxide adsorbent to increase the moisture content.

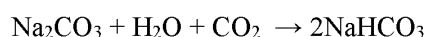
Referring to Figure 1, in the first step, a stream of moist gas 14 is passed over the carbon dioxide adsorbent 12 so as to contact the carbon dioxide adsorbent with the stream containing carbon dioxide to capture carbon dioxide from the moist gas stream in the presence of moisture. The term capture here is intended to refer to any process that assists with separation of the carbon dioxide from the stream and immobilizing it on/within the adsorbent. While majority of the capture is likely to occur through adsorption, it should be noted that other mechanisms such as absorption may also be occurring (albeit on a much smaller scale compared to adsorption). Accordingly, the term capture is intended to cover all such processes.

The time of exposure can be controlled to ensure that maximum uptake of carbon dioxide occurs on the carbon dioxide adsorbent. The residence time can be controlled by controlling the flow rate and flow path of the moist gas stream through the carbon dioxide adsorbent 12.

On contacting the carbon dioxide adsorbent 12, the moisture in the gas stream may facilitate uptake of carbon dioxide by the carbon dioxide adsorbent 12. For example, in an amine-based adsorbent, the reaction pathway for carbon dioxide adsorption may be altered in the presence of water (as shown Reactions (1) and (2) below).



Moisture can improve carbon dioxide uptake in other carbon dioxide adsorbent materials as well. For example, it is known that salt impregnated adsorbents can be used to capture carbon dioxide. One class of salt impregnated adsorbents include carbonates, such as sodium/potassium carbonate. It is known that carbonates can capture carbon dioxide in the presence of moisture through the following reaction (using sodium carbonate as an example carbonate):



Thus, the adsorption of carbon dioxide can be promoted by using salt adsorbents comprising carbonates impregnated in a solid in the presence of moisture through the above mechanism. The formed bicarbonate can be subsequently processed to recover the captured carbon dioxide and water. The carbon dioxide may be recovered in accordance with known methods for processing bicarbonates. For example, it is known that sodium bicarbonate can decompose at temperatures in the range of 80 – 100 °C to form sodium carbonate, carbon dioxide and water.

In one aspect of the present invention, the method includes capturing a portion of the moisture from the moist gas stream using a moisture sorbent material. This step can occur in parallel with the step of carbon dioxide adsorbent activation and capture of carbon dioxide. In the illustrated embodiment, the moisture sorbent

material 16 is located downstream from the carbon dioxide adsorbent 12. The moisture sorbent material 16 is configured to capture as much moisture as possible from the moist gas stream 14. The carbon dioxide adsorbent 12 does not typically take up as much moisture as the moisture sorbent material, and most of the moisture in the gas stream 14 will be taken up by the moisture sorbent material 16. The residence time of the moist gas stream 14 in contact with the moisture sorbent material 16 can be adjusted to absorb a suitable amount of moisture in the moisture sorbent material 16. The residence time can be controlled by controlling the flow rate and flow path of the moist gas stream through the moisture sorbent material 16. The moisture sorbent material 16 does not need to absorb so much moisture that it reaches saturation. Instead, the volume of moisture sorbent material 16 and the amount of moisture to be absorbed is determined based on the quantity of steam that will be required for regeneration. Again, as discussed above for the carbon dioxide adsorbent, the term capture reflects all processes that lead to the separation and immobilization of the moisture from the stream into/on the moisture sorbent material.

The capture of moisture by the moisture sorbent material 16 converts the moisture sorbent material 16 into a source of water for the vapor promoted regeneration. Heating of the moisture sorbent material will lead to conversion of this water into a source of steam that can be utilised as desired. As explained above, this may eliminate the need for an external water source for the release of carbon dioxide.

Ambient temperature and pressure can affect the kinetics of the capture of the carbon dioxide and moisture. These parameters may be controlled as desired to enhance or optimise performance.

Once the required moisture and carbon dioxide have been captured, the regeneration process can be initiated. The regeneration process involves two steps namely i) heating the moisture sorbent material 16 to convert water captured by the material to steam and ii) exposing the carbon dioxide adsorbent 12 to the generated steam.

In some embodiments, prior to regenerating the carbon dioxide adsorbent, oxygen may be purged from the atmosphere around the adsorbent. This may be advantageous when using an amine-based adsorbent. Purging oxygen from the atmosphere around the carbon dioxide adsorbent can reduce or prevent oxidative degradation of the adsorbent at high temperatures (i.e. the elevated temperatures encountered during regeneration), which may particularly affect amine-based adsorbents. In some cases, amine groups can undergo oxidation at temperatures above 70 °C, leading to a reduction in the carbon dioxide adsorption capacity. Therefore, in order to prevent the oxidation of amines, it can be imperative to limit their exposure to oxygen at elevated temperatures (e.g. temperatures above 70 °C).

Purging oxygen from the atmosphere around the carbon dioxide adsorbent can be accomplished in various ways. In the preferred embodiment, purging is achieved by steam purging during the initial stages of heating in the regeneration step. More specifically, once the capture of carbon dioxide and moisture is completed, the supply of moist gas stream is turned off and heating of the moisture sorbent material 16 is commenced. This heating results in the release of moisture from the moisture sorbent material 16. The resulting steam drives out the atmosphere around the carbon dioxide adsorbent 12 (e.g. air). That is, the gas surrounding the carbon dioxide adsorbent 12 at the start of the heating process may be displaced by the steam that is generated. In some embodiments, purging oxygen from the atmosphere can be accomplished through the application of a vacuum prior to or during regeneration.

Alternatively or additionally, purging may be performed using external gases to displace gasses from the atmosphere around the adsorbent. For example, nitrogen may be employed as a purging gas that displaces air from the atmosphere surrounding the carbon dioxide adsorbent. Purging of the atmosphere around the carbon dioxide adsorbent 12 and the moisture sorbent material 16 can be beneficial even in cases where the moist gas stream 14 does not include oxygen. Purging the atmosphere may assist in producing an output stream 18 with a more desirable composition. In particular, by displacing other gases with the steam before

desorption of the carbon dioxide, it may be possible to provide an output stream comprising substantially only steam and carbon dioxide. This is discussed further below.

In the regeneration process, both the moisture sorbent material 16 and the carbon dioxide adsorbent 12 may be subjected to heating so as to increase their temperature. In some embodiments, the moisture sorbent material 16 may be heated by a heating arrangement to generate steam, and then this steam may be used to heat the carbon dioxide adsorbent 12 so that the carbon dioxide adsorbent 12 is regenerated. In some other embodiments, heat may be applied to the carbon dioxide adsorbent 12 to supplement the heat provided by the steam.

As noted above, the temperature of the moisture sorbent material 16 is increased to convert water captured on the moisture sorbent material 16 to steam. The increased amount of steam leads to a reduction in the partial pressure of carbon dioxide that is present around the carbon dioxide adsorbent 12. This reduction in partial pressure, in addition to the heating of the carbon dioxide adsorbent 12, creates a driving force for carbon dioxide captured on the carbon dioxide adsorbent 12 to be released. The temperature in this stage may be held at a desired level, or maintained within a desired temperature range, until the desired level of desorption has been achieved. The temperature applied during this stage can affect the stability of the carbon dioxide adsorbent.

Degradation of the carbon dioxide adsorbent is dependent on the nature of the carbon dioxide adsorbent, the temperature to which it is exposed and the surrounding atmosphere that is in contact with the adsorbent, amongst other factors. Ideally, regeneration is performed at a temperature that can promote regeneration at a desired rate while ensuring that the adsorbent does not degrade at this temperature. For example, in case of amine-based carbon dioxide adsorbents, exposure to high temperature, e.g. temperatures above 150 °C in the presence of carbon dioxide gas, may deactivate the carbon dioxide adsorbent. Similarly, exposure of the amine-based adsorbent to temperatures above 70 °C in the presence of oxygen can result in oxidative degradation of the adsorbent. Accordingly, it is

beneficial in some embodiments using amine-based carbon dioxide adsorbents to ensure that the temperature is maintained below 150 °C and that substantially no oxygen is present in the surrounding atmosphere when the amine-based adsorbent is at this temperature. Advantageously, in some embodiments, the temperature of the regenerating step may range from about 80 °C to 120 °C for amine-based carbon dioxide adsorbents. The use of steam in the regeneration process, can enable effective desorption at lower temperatures.

In case of salt-impregnated adsorbents, the regeneration step may be performed at temperatures of about 300 °C. Salt-impregnated materials are stable and do not deactivate at this temperature. Accordingly, it may be possible to utilize higher temperatures (e.g. more than 120 °C) to facilitate/expedite the desorption process. For example, temperatures in the range 100 – 150 °C may be applied during the regeneration step.

In some embodiment, a reduced pressure or vacuum may be applied when regenerating the CO₂ adsorbent. By reducing the pressure or applying a vacuum, the temperature at which desorption occurs may be reduced. For example, it may be possible to perform regeneration of the carbon dioxide adsorbents at temperatures as low as 40 °C to 80 °C under vacuum conditions.

In some embodiments, the temperature of the regenerating step ranges from about 80 – 120 °C.

In some embodiments, vacuum may be applied during the heating of the moisture sorbent material 16 to assist in the formation of steam. The benefit of this step is that the temperature required for formation of steam is reduced (depending on the extent of vacuum applied). In turn, this prevents the temperature of the carbon dioxide adsorbent from reaching its degradation temperature. In embodiments in which a vacuum is applied during the regeneration process, carbon dioxide desorption may be performed at adsorbent temperatures of between 40-80 °C.

In the illustrated embodiment (as shown in Figure 1), the moisture adsorbent 16 and the carbon dioxide adsorbent 12 are located adjacent to each other in a column.

Such a location facilitates the step of exposing the carbon dioxide adsorbent 12 to the produced steam (i.e. there may be better contact occurring between the steam and the carbon dioxide adsorbent). In addition, co-location of the moisture adsorbent 16 and the carbon dioxide adsorbent 12 may avoid pressure drops as the gas and vapor flows move through the process. However, it will be appreciated that these materials can be located separately and the steam produced can be transferred from the moisture sorbent material 12 to the carbon dioxide adsorbent 16 as well.

In embodiments in which the moisture adsorbent and the carbon dioxide adsorbent are located separately, the step of contacting of the carbon dioxide adsorbent and the moisture sorbent material may occur with separate gas streams. In some of these embodiments, second stream containing moisture may only contact the moisture sorbent material. Similarly, a first stream containing carbon dioxide contacts only the carbon dioxide adsorbent. In some embodiments using first and second streams, it may be advantageous to keep the first and second streams separate so that the first stream does not contact the moisture sorbent material and, optionally, so that the second stream does not contact the carbon dioxide adsorbent. In some embodiments, the first stream may have a low moisture content, such that contacting the moisture adsorbent with the second stream may remove captured moisture from the moisture sorbent material thus reducing the moisture available for steam generation. In some embodiments, the carbon dioxide adsorbent is not contacted by the second stream during the adsorption step as it may lead to removal of any adsorbed carbon dioxide. In some other embodiments, such as when adsorption in the presence of moisture may be advantageous, the first stream may be formed by combining the second stream with a carbon-dioxide containing steam to provide a first stream containing moisture. The second stream may be combined with a carbon-dioxide containing steam to provide a first stream with a predetermined or desired moisture content.

Accordingly, in a second aspect, the present invention provides method of extracting carbon dioxide from a gas stream, the method comprising: contacting a CO₂ adsorbent with a first gas stream containing carbon dioxide to capture carbon

dioxide from the first stream; capturing water from a second stream containing water using a moisture sorbent material; and regenerating the CO₂ adsorbent to produce an output stream comprising steam and carbon dioxide, the regenerating comprising: heating the moisture sorbent material to release water captured by the moisture sorbent material as steam; and exposing the CO₂ adsorbent to the steam to liberate captured carbon dioxide from the CO₂ adsorbent and generate the output stream.

The underlying mechanism and principles behind the second aspect are similar to those described for the first aspect in that moisture trapped from a gas stream is employed to facilitate the release of carbon dioxide trapped on the carbon dioxide adsorbent. However, the difference is that the moisture adsorbent material and the carbon dioxide adsorbent material are contacted by first and second stream. In some embodiments, the method may be implemented using a system in which the moisture adsorbent material and the carbon dioxide adsorbent material are separated in physically distinct reactors/chambers. Such embodiments may be used to treat two separate gas streams – one rich in carbon dioxide and the other rich in moisture using the method of the second aspect. Such a configuration allows a degree of flexibility in design.

In some embodiments of the second aspect, the first gas stream may include a moist gas stream. In these embodiments, it is possible to take advantage of the effect of moisture promotion carbon dioxide adsorption as discussed for the method of the first aspect. In some embodiments, the second gas stream may include a vapor stream.

As a result of the regeneration process, an output stream 18 comprising steam and carbon dioxide may be produced from the method of the first and second aspects of the present invention. In some embodiments, such as when there has been effective purging of the atmosphere around the moisture sorbent material 12 to the carbon dioxide adsorbent 16, the output stream may be substantially steam and carbon dioxide. In the preferred embodiment, the steam can be separated from the carbon dioxide using a condenser to provide a water-rich stream 20 and a carbon dioxide-

rich stream 22. The remaining carbon dioxide may have a high purity (97 – 99%). In other embodiments, other means of separation may be utilised such as membrane-based separation processes.

Following the release of the captured carbon dioxide from the carbon dioxide
5 adsorbent 12, the moisture sorbent material 16 and the carbon dioxide adsorbent 12 may be cooled. In the illustrated embodiment, a cooling gas 19 is passed through the carbon dioxide adsorbent 12 and the moisture sorbent material 16. The cooling gas 19 may be around ambient temperature, such as about 25 °C, and a warmed gas stream 19' will be formed after passing the cooling gas through the carbon dioxide
10 adsorbent 12 and the moisture sorbent material 16. In some embodiments, the warmed gas stream 19' may emerge at a temperature of about 45 °C.

In some other embodiments, a heat exchanger 24 (see Figure 12) may be used for the cooling process. The heat exchanger may comprise a fluid jacket that surrounds the moisture sorbent material and the carbon dioxide adsorbent. Fluids can be made
15 to flow through this jacket so as to both increase and decrease temperature. For example, it is possible to introduce heating fluids during the heating phase and cooling fluids during the cooling phase. By controlling flow rates of these fluids, it is possible to control the heating/cooling rates and temperature of the moisture sorbent material and the carbon dioxide adsorbent.

20 Cooling brings down the temperature of the carbon dioxide adsorbent 12 and the moisture sorbent material 16 back to lower values suitable for adsorption (e.g. from 80 – 120 °C to around 25-30 °C). In some embodiments, the cooling effect may be accelerated due to the effect of water being removed from the moisture sorbent material 16. The temperature and humidity of the output stream 18 is higher
25 compared to the gas stream 14 being input.

The time required for the entire process starting from the adsorption step to the end of the cooling phase depends on several factors. At the minimum, this time is dictated by the time required for complete adsorption of the carbon dioxide on the carbon dioxide adsorbent and the time required for complete desorption of the
30 adsorbed carbon dioxide. Amongst other things, the time required for adsorption

can be affected by the temperature of the carbon dioxide adsorbent during the adsorption step. Thermodynamics dictates that some materials can undergo an exothermic adsorption process. In this regard, it should be noted that the capture of water by the moisture sorbent material may be an exothermic process (depending
5 on the moisture sorbent material used). As a result, heat may be generated during the capture of water by the moisture sorbent material. Similarly, heat may also be evolved on adsorption of the carbon dioxide on the carbon dioxide adsorbent. Again this depends on the nature of the adsorbent used. The evolution of heat will affect adsorption times and, depending on the configuration of the moisture sorbent
10 material and the carbon dioxide adsorbent, the temperature of one may affect the temperature of the other.

In some embodiments, such as in the illustrated embodiment of Figure 1, the carbon dioxide adsorbent 12 is contacted by the moist gas stream at a position upstream of the moisture sorbent material 16. In other words, the gas entering the system will
15 first contact the carbon dioxide adsorbent 12 before contacting the moisture sorbent material 16. This arrangement may have advantages in terms of process times. Specifically, this arrangement may reduce the effect of the heat of adsorption that arises from the process of water being captured by the moisture sorbent material 16 upon the adsorption process of carbon dioxide on the carbon dioxide adsorbent 12.
20 This is because the carbon dioxide present in the moist gas stream first comes into contact with the carbon dioxide adsorbent 12 before moisture present in the moisture stream can come into contact with the moisture sorbent material 16.

In some embodiments, the carbon dioxide adsorbent may be contacted by the moist gas stream at a position downstream of the moisture sorbent material. In other
25 words, the moist gas stream entering the system will first contact the moisture sorbent material before contacting the carbon dioxide adsorbent. As a result, the gas stream may be warmed as it passes through the moisture sorbent material, before contacting the carbon dioxide adsorbent material. As a result, heat from the moisture sorbent material may be transferred to the carbon dioxide adsorbent by the
30 flow of gas through them. In some embodiments, consequential increases in the

temperature of the carbon adsorbent material may lead to increased adsorption times. It may be desirable to place the moisture sorbent material away from the carbon dioxide adsorbent in this case to minimise effects of the heat. This may allow the temperature of the gas stream to cool before contacting the carbon dioxide
5 adsorbent. In addition, this may reduce the transfer of heat where the moisture sorbent material is adjacent to the carbon dioxide adsorbent.

In some embodiments, depending on the adsorbent selected, increases in the temperature of the carbon adsorbent material may lead to increased adsorption and/or reduced adsorption times. In other words, some degree of heating may be
10 beneficial to the adsorption process occurring on these adsorbents. For example, adsorbents comprising polyethylene imine (PEI) grafted materials may exhibit higher adsorption performance on heating to about temperatures of 30 – 60 °C. Specifically, the adsorption capacity and the adsorption kinetics can be improved by heating to these temperatures. This may translate to a larger amount of carbon
15 dioxide uptake in a shorter time period. Thus, in some embodiments using an adsorbent that benefits from a degree of heating, the moisture adsorbent material may be located upstream of the carbon dioxide adsorbent. As discussed above, with such a configuration the gas stream may be warmed as it passes through the moisture sorbent material, before contacting the carbon dioxide adsorbent material.

20 As a result, heat from the moisture sorbent material may be transferred to the carbon dioxide adsorbent by the flow of gas through them. In these embodiments, heat generated during the capture of water by the moisture sorbent material may be utilized to facilitate the adsorption of carbon dioxide on the carbon dioxide adsorbent.

25 In some embodiments, the system used to implement the method may be configured to permit reversing flow directions. Such a configuration may offer advantages in terms of the system design and implementation.

Moist-gas stream

As discussed above, the method disclosed herein in the first aspect and some embodiments of the second aspect involves contacting a carbon dioxide adsorbent with a moist gas stream. The moist gas may be a gas with some degree of humidity through to a gas stream saturated with liquid vapor. In some embodiments, the moist gas stream may be a multiphase stream comprising liquid and gas phases. In general, if the moist gas stream is a multiphase stream, the multiphase stream comprises a minor amount of liquid phase dispersed in the gas phase (i.e. a discontinuous phase of small liquid droplets). The liquid could be for example water and/or one or more other liquids. Such liquids may be introduced deliberately into the gas stream or alternatively be present inherently in the gas stream treated using the method disclosed herein. Ideally, the amount of liquid phase in the moist gas stream is as small as possible. Large amounts of liquid can lead to a pressure drop that affects the efficacy and efficiency of the method. The effect of pressure drops is discussed further below, and pressure drops as the gas stream passes through the system used to implement the method can increase the energy required to pump the moist gas stream through the carbon dioxide absorbent and moisture sorbent material. In some embodiments in which the moist gas stream is a multiphase stream, it may comprise at least 90% by volume of the gas phase, such as at least about 95% by volume of the gas phase.

The moist gas stream may be obtained from a number of sources. As an example, this stream could simply be ambient air. Alternatively, this stream can comprise waste gases generated at various facilities such as power plants, manufacturing industries, chemical treatment plants etc. The method may also be applied to dry streams by first adjusting the moisture content of the stream. For example, a gas stream to be treated comprising dry gas may be bubbled through a water column to increase the moisture content before undergoing the present method. As another example, the water that is obtained from condensation of the output stream can be recirculated back and added to the input gas stream to control its moisture.

Carbon dioxide adsorbents

The carbon dioxide adsorbents suitable for use in the invention are chemisorbents designed for carbon dioxide adsorption. The carbon dioxide adsorbent used in this method may be chosen from a variety of carbon dioxide adsorbents. The carbon
5 dioxide adsorbent may be a solid amine adsorbent or a salt-impregnated carbon dioxide adsorbent.

The solid amine adsorbent may be materials that have amine groups introduced into the porous support through surface modification. The amine groups can be primary, secondary, tertiary amines, or a mixture thereof. The corresponding surface
10 modification methods include, but are not limited to:

1. Physical impregnation, which comprises the deposition of amine-containing compounds, such as tetraethylenepentamine (TEPA), pentaethylenhexamine (PEHA), polyethylenimine (PEI), polyallylamine (PAA), monoethanolamine (MEA), preferably PEI, into the pores or on the
15 surface of a solid support. The solid support may be carbon, silica, clay, zeolite, metal-organic frameworks, metal oxides, cellulose, polymers, preferably a silica support.

2. Covalent bonding, where amines are covalently bonded to the walls of porous materials. Reagents such as 3-aminopropyltriethoxysilane (APS), aminopropyl (APS) silanes, diethylenetriamine (DT) silanes may be used to
20 introduce amine groups into porous supports such as silica. Alternatively, benzene-based polymers such as styrene-divinylbenzene copolymer can be utilized as starting materials to introduce amine groups into the polymer through amination reactions.

25 In some embodiments, the carbon dioxide adsorbent is an amine-based adsorbent comprising amine groups incorporated from styrene-divinyl benzene co-polymer. It may be a polystyrene-divinylbenzene resin covalently bonded with primary amine.

The salt-impregnated carbon dioxide adsorbent may include, but is not limited to, a material prepared by adding salts (such as alkali carbonates, ionic liquids, or a mixture thereof) into porous materials (such as activated carbon, silica, or clay). For example, sodium carbonate and/or potassium carbonate loaded on activated carbon
5 can function as carbon dioxide adsorbents.

In some embodiments, a single type of adsorbent will be used. In other embodiments, a combination of two or more adsorbents may be used. In some embodiments, the two adsorbents may be mixed together uniformly (i.e. as a homogenous mixture of two types of adsorbents). In other embodiments, the two
10 adsorbents may remain separated and arranged sequentially one after the other. In some embodiments, such as embodiments in which the moisture sorbent material and the carbon dioxide adsorbent are co-located in a single reactor, it may be desirable to position a more temperature tolerant carbon dioxide adsorbent material immediately adjacent to the moisture sorbent material to act as a buffer for the
15 second (and any further) carbon dioxide adsorbent against heat that may be generated by the moisture sorbent material as a result of moisture adsorption.

The amount of carbon dioxide adsorbent will be calculated based on the desired capacity of the system and the individual uptake capacities of the adsorbents.

Moisture sorbent materials

20 The moisture sorbent material to be used for the method can be chosen from a variety of materials. A moisture sorbent material is capable of sorbing (e.g. adsorbing), or releasably binding, water, such as water from a humid gas stream or a vapor-containing stream. The moisture sorbent material may be a solid moisture sorbent material. That is, it may comprise a substrate that has at its surface a water
25 binding agent. The solid adsorbent may be a porous solid mass, so that there is a pathway for the moist gas stream to flow therethrough and contact the surface. In some embodiments, the aspect ratio of the moisture sorbent material may be selected to maximise the surface area available for contacting the moist gas stream and, consequently, capturing moisture therefrom. The moisture sorbent material

may be in the form of solid particles (e.g. a bed of particles) or may be a monolithic structure.

In some embodiments, the adsorbent may be a silica gel. In other embodiments, the moisture sorbent material can be chosen from a group comprising:

- 5 - silica gel;
- aluminosilicate gel;
- clay, such as one or more of Sepiolite, Bentonite, and Kaolin;
- metal organic frameworks, for example metal organic frameworks
 comprising MIL-101, MIL-100, MOF-801, CAU-10, CAU-23, UIO-66,
10 UIO-67, MOF-841, DUT-67, DUT-51, MOF-808, MOF-5, MOF-74;
- zeolites, such as: small-pore zeolites e.g. comprising one or more of 3A,
 4A, 5A, 13X, 10X; zeolite frameworks e.g. comprising one or more of
 ZSM-5, Y, Beta, FAU, MOR, AlPO; and molecular sieves e.g. comprising
 one or more of SAPO, ITQ-29, SSZ-13, MCM-41, KIT-6, TNU-9, B-ZSM-
15 5, UTD-1;
- Carbon-based materials, such as sorbents comprising one or more of
 activated carbon, biomass carbon, activated carbon fibers, carbon
 molecular sieves, and mesoporous carbon;
- salt-impregnated desiccants, such as salt-impregnated desiccants
20 comprising one or more of LiCl, CaCl₂, CuCl₂, CuSO₄, MgSO₄, or
 desiccants formed by an ionic liquid impregnated into porous materials
 comprising activated carbon, silica, or clay;
- alumina; and/or
- polymers comprising hydrophilic functional groups in their polymer chain
25 units.

The amount of moisture sorbent material to be employed will be calculated based on the amount of moisture that is required for the method to be implemented in a

successful manner. This includes consideration of factors such as amount of carbon dioxide to be adsorbed, and the amount of steam required to create the required partial pressure difference.

Carbon Capture System

- 5 The present invention provides a system for extracting carbon dioxide from a moist gas stream, the system comprising: a moisture capture zone and a CO₂ capture zone in fluid connection with the moisture capture zone, wherein the moisture capture zone has a moisture sorbent material configured to capture moisture from a moist gas stream and the CO₂ capture zone has a CO₂ adsorbent configured to capture
- 10 CO₂ from the moist gas stream; a regeneration means configured to produce an output stream comprising steam and CO₂, the regeneration means comprising a heating arrangement configured to heat the moisture sorbent material so that water captured by the moisture sorbent material is released as steam; wherein the moisture capture zone and a CO₂ capture zone are configured for exposing the CO₂ adsorbent
- 15 to the steam to liberate captured CO₂ from the CO₂ adsorbent and generate the output stream.

- The present invention may provide a system for extracting carbon dioxide from a gas stream, the system comprising: a moisture sorbent structure and a CO₂ adsorber in fluid connection with the moisture sorbent structure, wherein the moisture
- 20 sorbent structure has a moisture sorbent material configured to capture moisture from a moist gas stream and the CO₂ adsorber has a CO₂ adsorbent configured to capture CO₂ from the moist gas stream; and a regeneration means configured to produce an output stream comprising steam and CO₂, the regeneration means comprising a heating arrangement configured to heat the moisture sorbent material
- 25 so that water captured by the moisture sorbent material is released as steam; wherein the moisture sorbent structure and a CO₂ absorber are configured for exposing the CO₂ adsorbent to the steam to liberate captured CO₂ from the CO₂ adsorbent and generate the output stream.

In some embodiments, the present invention provides a system configured for implementing the method of the second aspect. Thus, there is provided a system for extracting carbon dioxide from a gas stream, the system comprising: a moisture capture zone and a CO₂ capture zone, wherein the CO₂ capture zone has a CO₂ adsorbent configured to capture CO₂ from a first stream containing carbon dioxide and the moisture capture zone has a moisture sorbent material configured to capture moisture from a second stream containing water; and a regeneration means configured to produce an output stream comprising steam and CO₂, the regeneration means comprising a heating arrangement configured to heat the moisture sorbent material so that water captured by the moisture sorbent material is released as steam; wherein the moisture capture zone and a CO₂ capture zone are configured for exposing the CO₂ adsorbent to the steam to liberate captured CO₂ from the CO₂ adsorbent and generate the output stream. That is, the system may comprise: a moisture sorbent structure and a CO₂ adsorber, wherein the CO₂ adsorber has a CO₂ adsorbent configured to capture CO₂ from a first stream containing carbon dioxide and the moisture sorbent structure has a moisture sorbent material configured to capture moisture from a second stream containing water; and a regeneration means configured to produce an output stream comprising steam and CO₂, the regeneration means comprising a heating arrangement configured to heat the moisture sorbent material so that water captured by the moisture sorbent material is released as steam; wherein the moisture sorbent structure and a CO₂ absorber are configured (e.g. fluidly connected to permit the passage of the steam) for exposing the CO₂ adsorbent to the steam to liberate captured CO₂ from the CO₂ adsorbent and generate the output stream.

25 In general, systems for carbon capture are driven by compressors and blowers. These blowers/compressors drive the stream(s) of gases through the column(s) containing the moisture sorbent material and the CO₂ adsorbent thereby facilitating the required capture of carbon dioxide and water. As the gas streams are forced through the column(s), they can experience a pressure drop across the (or each) column. This pressure drop is a result of the various obstacles the gas streams face

upon entering the system. For example, the gas stream interacts with the moisture sorbent material and carbon dioxide adsorbent in the respective zones of the system.

Solid carbon dioxide adsorbents and moisture sorbent materials are generally preferred for use with the method and system disclosed herein, compared to e.g. a liquid scrubber. The carbon dioxide adsorbent and moisture sorbent material may be a bed of particles. In such embodiments, the flow of the gas is impaired by these particles. If the pressure created by the blower/compressor is insufficient, the gas stream may for example not interact with all the carbon dioxide adsorbent and/or moisture sorbent material located in the system.

Ideally, the system is configured to minimise pressure drops as the gas stream flows through the system. In some embodiments, the carbon dioxide adsorbent and moisture sorbent material are co-located in a single column to provide a continuous bed of particles, with the carbon dioxide adsorbent and moisture sorbent material located adjacent to each other in order to minimise the pressure drop across the CO₂ capture zone and the moisture capture zone. In some other embodiments, the connection between the CO₂ capture zone in fluid connection with the moisture capture zone is configured to minimise or reduce the pressure drop. It may be desirable to minimise any “dead space” along the system.

The length of the column as well as the packing density of the column can affect the pressure drop occurring in the system. A longer column can result in a larger pressure drop (as the gas stream is forced to travel a longer flow path). Accordingly, a higher pressure may be required to force the gas stream to interact with all parts of the column. Similarly, a densely packed column will also result in a significant pressure drop thereby increasing the risk that the gas stream is not interacting with material located far away from the entry point of the gas stream into the system. In some embodiments, the particle size and packing density of each of the carbon dioxide adsorbent and moisture sorbent material may be selected to be as similar as possible to minimise pressure changes as the gas flows through system.

The heating and cooling requirements of the system may also depend on the carbon dioxide adsorbent and moisture sorbent material selected, including how effectively

a cooling medium (e.g. a cooling gas) can flow through the carbon dioxide adsorbent and moisture sorbent material, if used. Similarly, the dimensions and configuration of the the CO₂ capture zone and the moisture capture zone also affect the heating and cooling requirements. Various heating/cooling modes can be used

5 in embodiments of the system. For example, a reactor can be heated electrically using coils wound on the outside. In such cases, the heat generated must pass through the walls of the reactor and any void space in the reactor to reach the adsorbent material. Depending on the configuration of the remainder of the system, the dominant mode of heat transfer may be conduction, convection or radiation etc.

10 The heat transfer can be affected by the diameter of the column. A larger diameter column with greater thickness will result in a slower heat transfer compared to a smaller diameter column with smaller thickness when heated or cooled externally, such as by using a heating or cooling jacket. In some embodiments, a combination of heating and cooling methods may be used.

15 Referring now to Figure 2, disclosed herein is a system 100 suitable for implementing the method described above. The system 100 for extracting carbon dioxide from a moist gas stream comprises a moisture capture zone 116, and a carbon dioxide capture zone 112 that is in fluid connection with the moisture capture zone 116. The moisture capture zone 116 is the region in which the moisture

20 sorbent material 16 described above is located. The carbon dioxide capture zone 112 is the region in which the carbon dioxide adsorbent 12 described above is located. The moisture sorbent material 16 and the carbon dioxide adsorbent 12 may be packed into a contiguous chamber or column to define the moisture capture zone 116 and the carbon dioxide capture zone 112, respectively, as shown in the

25 illustrated embodiment. Alternatively, the chamber(s) or column(s) may be configured to define distinct regions in which each of the moisture sorbent material and the carbon dioxide adsorbent may be housed. For example, separate, fluidly connected chambers or columns may be provided for each of the moisture sorbent material and the carbon dioxide adsorbent.

The system 100 further comprises a regeneration means 150 configured to produce an output stream comprising steam and carbon dioxide. The regeneration means 150 comprises a heating arrangement 152 that is configured to heat the moisture sorbent material 16 so that water captured by the moisture sorbent material 16 is released as steam. The moisture capture zone 116 and the carbon dioxide capture zone 112 are configured for exposing the carbon dioxide adsorbent to the steam to liberate captured carbon dioxide from the carbon dioxide adsorbent 12 and generate the output stream 18.

In some embodiments, the regeneration means comprises a vacuum generation sub-system (not illustrated) that is configured to apply a vacuum to at least the carbon dioxide capture zone 112. The vacuum generation sub-system may be configured to apply a vacuum to the moisture capture zone 116 and the carbon dioxide capture zone 112 so as to purge the atmosphere in at least the carbon dioxide capture zone 112 and/or provide a reduced pressure to promote release of steam, as described above.

The zones 116 and 112 are configured to provide a suitable (e.g. predetermined and calculated) amount of moisture sorbent material 16 and the carbon dioxide adsorbent 12 for a specific treatment process.

In the illustrated embodiment, zones 116 and 112 are located within a single column reactor and are located adjacent to each other. Such an arrangement can ensure immediate and intimate contact of the steam generated during the regeneration step with the carbon dioxide adsorbent 116. In other embodiments, the zones 112 and 116 may be located in separate distinct reactors, chambers or columns. These zones 112 and 116 can be connected fluidly through appropriate tubing to allow passage of gases between the reactors.

In the preferred embodiment, the moisture capture zone 116 is located downstream of the carbon dioxide capture zone 112. As previously described, this may have the benefit of avoiding the undesirable effects of heat generated during capture of water by the moisture sorbent material 16.

The zones 116 and 112 are located proximal to ends 102 and 104 which can act as inlet/outlets to the reactor. In the illustrated embodiment, the moist gas stream 14 enters the single column reactor at the end 102 and the output stream 18 exits the system at the same end 102. The end 104 is utilized to enable a flow of the moist
5 gas stream 14 through the system 100. In addition, it may also be used during the final method step of cooling the reactor in order to enable a flow of cooling air through the system 100. In other embodiments, the moist gas stream 14 may enter the single column reactor at the end 104 while the output stream 18 may exit the reactor at end 102. Typically, the direction of flow of the output stream is such that
10 the moisture capture zone 116 is located downstream of the carbon dioxide capture zone 112 so that steam can flow from the moisture capture zone 116 to the carbon dioxide capture zone 112.

In some embodiments, the single column reactor may be fabricated from a stainless steel, carbon steel, galvanized steel and polymers such as polypropylene. The
15 reactor can be in the form of a cylindrical tube of dimensions 300 – 3000 mm in length and 10 – 300 mm in diameter. In other forms, the reactor may also be in the form of rectangular/square shaped tubes. The dimensions are chosen so as to accommodate the desired volume of the moisture sorbent material 16 and carbon dioxide adsorbent 12. As discussed above, the dimensions selected may have an
20 impact on the pressure drop, as well as heat transfer that occur in the system. Accordingly, these considerations will also be factored into the selection of dimensions for the reactor.

In some embodiments, the heating arrangement 152 of the regeneration means 150 surrounds both the zones 112 and 116. The heating arrangement 152 enables control
25 of temperature in these zones and thus enabling control of the regeneration process in these zones. In some embodiments, the temperature in the zones 112 and 116 can be independently controlled so as to obtain differential heating rates in the two zones. For example, the heating arrangement may be configured for providing different temperatures for the moisture sorbent material 16 and the carbon dioxide

material 12. This can assist in controlling the temperature of the carbon dioxide adsorbent and mitigating against the risk of temperature-induced deactivation.

The heating arrangement 152 can be powered by a heating coil such as a resistive heating coil. The resistive coils can be wound around the zones 112 and 116 so as to provide uniform heating all around the zone. Alternatively, two or more resistive coils can be used to separately control the temperature of zones 112 and 116. In some other embodiments, the heating arrangement can comprise a solar concentrator that focuses sunlight on to the moisture capture zone 116 and/or the carbon capture zone 112. The solar concentrator may be a parabolic solar concentrator comprising a convex mirror configured to focus sunlight on the desired zone.

In some embodiments, the heating arrangement includes a heat exchanger 24 configured to transfer heat recovered from one or more industrial processes to the system. Components of the system that are substantially the same as those in Figure 2 are shown with the same reference numerals in Figure 12. The heat exchanger 24 may comprise a fluid jacket that substantially surrounds the the zones 112 and 116. Fluids can be made to flow through this jacket so as to both increase and decrease temperature. For example, it is possible to introduce heating fluids during the heating phase and cooling fluids during the cooling phase. By controlling flow rates of these fluids, it is possible to control the heating/cooling rates and temperature. Such an embodiment is shown in Figure 12.

The heating arrangement may comprise a heat exchange arrangement configured to recover heat from an industrial process and provide the recovered heat to the moisture sorbent material.

In some embodiments, the reactor may comprise a vacuum insulation layer that at least surrounds the moisture capture zone 116. The vacuum insulation layer may be configured to reduce or prevent heat loss from the moisture capture zone 116 and thus reduce the energy required to maintain the temperature. This may enhance the energy efficiency of the system. The vacuum insulation layer may be configured

to reduce temperature variations in, or ensure there is a substantially consistent temperature in, the moisture capture zone 116.

In case of the heating arrangement being powered by a solar concentrator, the vacuum insulation may be formed from a transparent layer (for example, made from glass) so as to allow the passage of the solar radiation directed towards the moisture capture zone from the parabolic solar concentrator.

Examples

Various embodiments will now be described with reference to the following non-limiting examples.

Example 1 - solar DAC system

A solar powered, vapor promoted desorption DAC system (solar DAC system) in accordance with the embodiment shown in Figure 3 can be prepared according to the example. Figure 3 illustrated a system including an adsorption column 1, a black coating 2, a transparent vacuum isolation layer 3, a parabolic concentrator 4, a valve 5 in the closed position, a second valve 6 in the open position, a condenser 7, and a gas collector 8. These components are further described below.

Adsorption column 1

The adsorption column 1 is fabricated from a stainless steel tube of length 60 cm and diameter 4 cm.. The adsorption column 1 is also provided with a black coating 2. The coating is prepared from a nickel/chromium composite oxide. Alternatively, other commercially available materials may also be used. For example, Pyromark 2500 - a silicone based high temperature paint can also be used. To minimize heat loss via convection and conduction, the adsorption column 1 is further sealed within a transparent vacuum isolation layer 3. This is achieved by sealing the adsorption column within a glass tube, evacuating the atmosphere surrounding the glass tube and sealing the tube.

The adsorption column 1 is loaded with Lewatit VP OC 1065 (Lanxess): a commercially available carbon dioxide adsorbent (not shown in Figure 3). The material is provided as particles, which range in diameter from 0.3-1.2 mm, and is a primary amine functionalized weakly basic anion exchange resin. The adsorption column is also filled with type A silica gel (Desicco) with a particle size of 3-5 mm that acts as the moisture adsorbent material (not shown in Figure 3). Prior to loading into the column, the silica gel and wet resin (i.e. as obtained VPOC) are subjected to pre-treatment at 110 °C and 80 °C under vacuum, respectively.

Parabolic concentrator 4

10 The system also comprises a parabolic solar concentrator 4 that is configured to focus the sunlight onto the adsorption column 1. The parabolic solar concentrator 4 boosts and accelerates the heating process.

Thermocouple

15 A thermocouple (not shown) is inserted into the adsorption column 1 such that it lies at the centre of the carbon dioxide adsorbent. The thermocouple is used to measure the temperature profile of the adsorption column 1 during the adsorption – regeneration (desorption) cycles.

Condenser 7

20 The system also comprises a condenser 7 in the form of coiled gas condenser connected to the adsorption column 1. The condenser 7 facilitates collection of the water from an output stream 18 comprising carbon dioxide and moisture to provide a water-rich stream 20 and a carbon dioxide-rich stream 22.

Gas collector 8

25 The carbon dioxide that is desorbed is accumulated in a gas collector in the form of a syringe. The gas collector 8 is connected to the condenser 7 such that carbon dioxide that is separated from the moisture in the condenser is collected in the syringe.

Computer and DAQ

The processes in the system are controlled by a computer and a data acquisition system (DAQ). The DAQ is used to collect and process data from sensors, instruments, or other devices. Specifically, the DAQ collects data on solar intensity, adsorbent temperature, product purity, humidity. The data collected is used to
5 calculate desired parameters and monitor and control processes.

The above components are assembled in the following manner:

- First, tube fittings are connected to one end of the adsorption column 1.
- Then the calculated amount of silica gel (based on the total volume of the adsorbents to be used) is first loaded into the column 1 followed by the
10 calculated amount of the Lewatit VPOC 1065.
- The thermocouple is then inserted into the adsorption column and positioned at the centre of the VPOC 1065 resin.
- Following this, tube fittings are connected to the other end of the adsorption column 1.
- 15 - Valves 5 and 6 are connected to the ends of the column 1.
- The condenser 7 is connected to valve 6 and the gas collector 8 is placed at the end of the condenser 7.
- All connections are subsequently tested to ensure that there are no leaks.

Finally, the parabolic concentrator is connected to the adsorption column to
20 commence heating as desired.

Photothermal performance and power generated by solar system

The photothermal performance of the system described above was evaluated and the photothermal efficiency was calculated from measurements of the temperature changes and solar intensities as shown in Figures 4A and 4B.

- 25 To calculate the photothermal efficiency, temperature increases of an empty solar-heating column that does not contain any adsorbent material. were measured under sunlight irradiation. The thermal energy (Q_{therm}) converted from solar energy as

well as the photothermal efficiency (α) are calculated using Equation (1) and Equation (2),

$$Q_{thermal} = \alpha A \int_0^t I_{solar} dt = m_{tube} C_{tube} \Delta T_{tube} \quad (1)$$

$$\alpha = \frac{m_{tube} C_{tube} \Delta T_{tube}}{A \int_0^t I_{solar} dt} \quad (2)$$

5 where A is the area (0.05 m^2) of the tube for receiving natural sunlight, I_{solar} is the solar flux, t is the solar irradiation time, m_{tube} refers to the mass of the solar-heating column (1.07 kg), C_{tube} is the heat capacity ($500 \text{ J/kg}\cdot\text{K}$) of the tube, ΔT_{tube} represents the temperature increase of the adsorption column during solar heating.

10 The optical concentration ratio (σ) of the parabolic concentrator is determined by conducting solar heating experiments under concentrated sunlight and calculated using Equation (3). Figure 4A shows the temperature increases of the adsorption column under natural and concentrated sunlight.

$$\sigma = \frac{m_{tube} C_{tube} \Delta T_{tube}}{\alpha A \int_0^t I_{solar} dt} \quad (3)$$

15 Based on the temperature profiles in Figure 4A, the overall photothermal conversion efficiency (α) of the solar heating column was 63.1%, and the optical concentration ratio (σ) of the concentrator was 1.9.

Using the above calculated values, the heating power (W) of the solar heating system under different solar intensities can be calculated using Equation (4).

$$20 \quad W = \alpha \sigma A I_{solar} \quad (4)$$

In this example, the heating power of the photothermal system was calculated to be equivalent to 30 W of electrical heating under 500 W/m^2 (0.5 sun) solar irradiation, as shown in Figure 4B.

Example 2 - performance of solar DAC system with different adsorbent ratios

The effect of varying the adsorbent ratios on the performance of the solar DAC system is demonstrated in this example. The device as set out in example 1 was
5 utilized and samples with different adsorbent ratios were evaluated at the respective conditions shown in Table 1 below:

Table 1

Sample	Lewatit VPOC 1065 (mL)	Silica Gel type A (mL)	Gas hourly Space velocity – GHSV (per hour)	Adsorbent ratio	Relative Humidity (%)
Case 1	200	200	6000	1:1	40
Case 2	320	80	3750	4:1	56
Case 3	420	80	3000	5.25:1	57

The solar DAC system is set up as described in Example 1 with the different contents of adsorbents shown in the above table.

10 The solar DAC system was subjected to cycling studies in which the system is directly exposed to natural sunlight during the desorption step following the adsorption step. The amount of carbon dioxide that is desorbed was measured in this step. Solar flux during the desorption step was measured by a pyranometer (Renke ,RS-RA). The solar flux generally ranged from 400-800 W/m² for solar
15 heating in Tianjin, China.

Various performance parameters are calculated to analyse the performance.

Carbon dioxide desorption performance

According to the cyclic results presented in Figure 5A and 5B, solar heating demonstrated remarkable performance for adsorbent regeneration, completing the

process in 52 minutes under moderate solar intensities ranging from 500-700 W/m². Nearly all the adsorbed carbon dioxide was released under sunlight for all three cases (Case 1 to Case 3), while traditional processes (temperature vacuum swing adsorption) required supplementary steam purging to achieve comparable working capacities (Elfving, J., Kauppinen, J., Jegoroff, M., Ruuskanen, V., Järvinen, L., and Sainio, T. (2021). Experimental comparison of regeneration methods for carbon dioxide concentration from air using amine-based adsorbent. *Chem. Eng. J.* *404*, 126337).

Based on the carbon dioxide loading profile, the solar DAC system produced 2.89, 5.11, and 7.24 g carbon dioxide per cycle using 200, 320, and 420 mL Lewatit resin, respectively. Moreover, the carbon dioxide loadings were entirely recoverable after desorption, indicating good stability under solar irradiation. This stability is attributed to the desorption temperatures remaining under 120 °C for all cases.

Energy consumption of solar DAC system

Based on the photothermal efficiency and optical concentration ratio (outlined in Example 1), the energy consumption (thermal energy for adsorbent regeneration - Q_{re}) was calculated based on the following Equation (5).

$$Q_{re} = \sigma \alpha A \frac{\int_0^{t_{des}} I_{solar} dt}{m_{CO_2}} - \frac{m_{tube} C_{tube} \Delta T}{m_{CO_2}} \quad (5)$$

where t_{des} is the desorption time, and m_{CO_2} is the mass of carbon dioxide collected under solar irradiation, ΔT represents the temperature increase of the adsorbents.

As shown in Figure 5D, a higher adsorbent ratio was advantageous in reducing energy consumption due to increased cyclic productivity. The DAC system based on VPD required only 9.85 MJ/kg_{carbon dioxide} of thermal energy collected from sunlight for adsorbent regeneration. In comparison, TVSA and steam-assisted TVSA processes that employed VPOC 1065 as carbon dioxide adsorbents typically required 12-15 MJ/kg_{carbon dioxide} (including 1-2 MJ/kg_{carbon dioxide} electrical energy for generating vacuum conditions) energy for adsorbent regeneration, as reported in prior works (Bos, M.J., Pietersen, S., and Brilman, D.W.F. (2019). Production of

high purity carbon dioxide from air using solid amine sorbents. Chemical Engineering Science: X 2, 100020; Sabatino, F., Grimm, A., Gallucci, F., van Sint Annaland, M., Kramer, G.J., and Gazzani, M. (2021). A comparative energy and costs assessment and optimization for direct air capture technologies. Joule 5, 2047-2076.).

The solar DAC system exhibited a lower energy requirement due to the high carbon dioxide working capacity achieved through vapor promoted desorption.

Regeneration efficiency

To evaluate the efficiency of the solar DAC system, the parameter regeneration efficiency (R), is used. This parameter is defined by the Equation (6):

$$R = 1 - \frac{q_{de}}{q_{ad}} = \frac{W_c}{q_{ad}} \quad (6)$$

where W_c is the working capacity of carbon dioxide adsorbents achieved using the given desorption technology, q_{ad} and q_{de} represent carbon dioxide loadings after adsorption and desorption, respectively.

Specifically, while a steam-assisted TVSA process achieved an R value of around 76.9% at 116 °C and 50 kPa (Bos, M.J., Pietersen, S., and Brilman, D.W.F. (2019). Production of high purity carbon dioxide from air using solid amine sorbents. Chemical Engineering Science: X 2, 100020), the present process utilizing the solar DAC system was able to release 97% of the adsorbed carbon dioxide (as shown in Fig. 5B) at ambient pressures with 20% lower energy consumption.

To further limit the contact between air and adsorbents at high temperatures, the evaporation of residual co-adsorbed water was utilized as a cooling system to rapidly decrease the temperature of adsorbents after collecting carbon dioxide products (Figure 5C). During the cooling process of case 1, the outlet relative humidity approached nearly 100% due to water evaporation, leading to an impressive heat withdrawal from the column. Consequently, the temperature of the adsorbent sharply decreased by 30 °C within 40 seconds. After one minute of

cooling, the temperature could be further reduced to 70 °C, which did not cause any detectable air-induced deactivation.

Example 3 – Carbon dioxide adsorption performance of Lewatit VPOC 1065 resin – Model Studies

- 5 This example discusses the evaluation of the carbon dioxide adsorption properties of the VPOC resin used in the present invention.

The carbon dioxide adsorption performance of the Lewatit VPOC 1065 resin was simulated using a reported dual site Langmuir isotherm model (Schäppi, R., Rutz, D., Dähler, F., Muroyama, A., Haueter, P., Lilliestam, J., Patt, A., Furler, P., and
10 Steinfeld, A. (2022). Drop-in fuels from sunlight and air. *Nature* 601, 63-68). The model is provided by Equations (7), (8) and (9) below:

$$q_{CO_2} = \frac{q_1 K_1 P}{1 + K_1 P} + \frac{q_2 K_2 P}{1 + K_2 P} \tag{7}$$

$$K_1 = K_{0,1} \exp \left(\frac{-\Delta H_{ads,1}}{RT} \right) \tag{8}$$

$$K_2 = K_{0,2} \exp \left(\frac{-\Delta H_{ads,2}}{RT} \right) \tag{9}$$

15

Table 2 below shows the fitted parameters for the above model.

Table 2

Parameter	Value
q_1 (mmol/g)	1.94
q_2 (mmol/g)	1.06
$K_{0,1}$ (1/Pa)	1.11×10^{-15}
$K_{0,2}$ (1/Pa)	1.84×10^{-13}
$-\Delta H_{ads,1}$ (kJ/mol)	75.6
$-\Delta H_{ads,2}$ (kJ/mol)	51.6

From the above data, the q_{CO_2} value is determined which in turn used to determine the working capacity (W_c) of Lewatit resin from the following Equation (10).

$$W_c = q_{CO_2}(T_{ads}, P_{ads}) - q_{CO_2}(T_{des}, P_{des}) \quad (10)$$

Where, $q_{CO_2}(T_{ads}, P_{ads})$ and $q_{CO_2}(T_{des}, P_{des})$ represent calculated carbon dioxide loadings under adsorption and desorption conditions based on the proposed isotherm model. P and T are the carbon dioxide partial pressure and adsorbent temperature. In the adsorption process, T_{ads} and P_{ads} are fixed at 25 °C and 40 Pa, respectively.

The results (shown in Figure 6) indicate that the Lewatit resin exhibited impressive carbon dioxide uptake capability of 1.11 mmol/g at 20 °C and 400 ppm.

Example 4 - carbon dioxide adsorption performance of Lewatit VPOC 1065 resin under different moisture contents

The impact of moisture on carbon dioxide and H₂O adsorption behaviours of the Lewatit resin was studied by conducting breakthrough experiments at varying relative humidity levels.

The breakthrough experiments were performed using a set up as shown in Figure 7A. A stainless-steel tube of 8 cm in length and 1 cm in diameter was employed as the adsorption column. The adsorbent temperature was controlled by a thermostat oven 300 set to 28 °C. Compressed air with 410 ppm carbon dioxide was introduced to the adsorption column at a gas-hourly space velocity (GHSV) of 12000 /h. The outlet carbon dioxide concentrations were monitored by an infrared carbon dioxide sensor (Dynament, 0-1000 ppm), while the feed and outlet relative humidity were continuously recorded by two humidity sensors (Ningbo Keshun KS-SHT and Vaisala HMT338). Breakthrough experiments were performed under different humidities, using a humidified 200 to adjust humidity, to investigate the impact of varying humidity levels on carbon dioxide adsorption behaviour. A humidifier placed in a water bath at 28 °C was used to precisely control the required relative humidity.

The results (shown in Figure 7B) indicate that moisture substantially promoted carbon dioxide adsorption, leading to increased carbon dioxide uptakes. When compared to adsorption using dry air, the carbon dioxide uptakes at 35%, 60%, and 85% RH were observed to increase by 6.9%, 29.2%, and 62.5%, respectively.

5 However, higher carbon dioxide uptakes and inferior adsorption kinetics under high humidity conditions necessitated more adsorption time to achieve adsorption equilibrium. The reduced adsorption rate might be attributed to the mass transfer restrictions in Lewatit resin with higher water loadings.

Mechanism of carbon dioxide adsorption

10 Fourier Transform Infrared spectroscopy (FTIR) was performed to determine the mechanism of adsorption of the carbon dioxide. The data was collected using a Nicolet iS50 FTIR Spectrometer. In-situ FTIR was used to investigate the changes in surface species during the desorption process of VPOC 1065 with a Bruker Tensor 27 spectrometer. Before measurement, the sample was treated with 25 °C

15 and 30% RH air overnight to adsorb carbon dioxide and H₂O. The results (shown in Figure 7C) revealed the formation of carbamate species.

Then, the sample was treated with 100 °C N₂ flow while spectra were collected on the spectrometer every 5 min. In this regard, the carbon dioxide desorption process was reflected in decreases of the absorbance at 1380, 1510 and 1584 cm⁻¹ (see

20 Figure 7D), corresponding to the symmetric stretching vibration of -COO⁻, C-N stretching vibration (amide II) and antisymmetric deformation of NH₃⁺ in ammonium carbamate structures, respectively (see Afonso, R., Sardo, M., Mafrá, L., and Gomes, J.R.B. (2019). Unravelling the structure of chemisorbed CO₂ species in mesoporous aminosilicas: A critical survey. *Environ. Sci. Technol.* 53, 2758-2767; Bacsik, Z., Ahlsten, N., Ziadi, A., Zhao, G., Garcia-Bennett, A.E.,

25 Martín-Matute, B., and Hedin, N. (2011). Mechanisms and kinetics for sorption of CO₂ on bicontinuous mesoporous silica modified with n-propylamine. *Langmuir* 27, 11118-11128; Danon, A., Stair, P.C., and Weitz, E. (2011). FTIR study of CO₂ adsorption on amine-grafted SBA-15: Elucidation of adsorbed species. *The Journal of Physical Chemistry C* 115, 11540-11549; and Bacsik, Z., Atluri, R., Garcia-

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Bennett, A.E., and Hedin, N. (2010). Temperature-induced uptake of CO₂ and formation of carbamates in mesocaged silica modified with n-propylamines. *Langmuir* 26, 10013-10024.) Therefore, the dominant mechanism for atmospheric carbon dioxide adsorption is considered to be the formation of ammonium carbamate.

Mechanism of degradation

Experiments were also conducted to ascertain the mechanism by which the adsorbent degrades. Specifically, it was observed (see Figure 7E) that the working capacity of the carbon dioxide adsorbent decreased when the adsorption was performed at 150 °C as opposed to 120 °C. This carbon dioxide-induced deactivation mechanism was investigated using in-situ FTIR under a carbon dioxide atmosphere at 150 °C. The sample was treated with pure carbon dioxide at 80 °C for 3 hours and 150 °C for 15 min before measurement, and spectra were collected every 60 min at 150 °C. The results (shown in Figures 7F) indicate that the degradation is primarily caused by the formation of open-chain and cyclic ureas.

Example 5 – water adsorption performance of VPOC 1065 and silica gel type A

This example describes the water adsorption properties of both the Lewatit VPOC 1065 resin and the silica gel. These measurements were conducted using the BEL Japan Belsorp-max-II at 25 °C, 35 °C and 45 °C. The samples were degassed for 12 h at 120 °C before measurement.

The results are shown in Figures 8A and 8B. The Lewatit resin has a relatively limited water uptake at low relative humidity levels. This is presumably due to its hydrophobic styrene-divinylbenzene structure. On the other hand, silica gel was able to adsorb more than 10 wt% water even under 30% RH conditions.

Example 6 – Cycling performance in vapor promoted desorption

This example illustrates the cycling performance of the adsorbents when subjected to adsorption-desorption cycles under the effect of electrical heating.

Experimental setup employed

- 5 The schematic of the system utilized is shown in Figure 9A. An adsorption column 100, 60 cm in length and 4 cm in diameter, constructed of stainless steel was employed.

- Fresh air with 410-450 ppm carbon dioxide, provided by an air compressor, was utilized as the feed gas for carbon dioxide and H₂O adsorption. The system included
10 a humidifier 200 for adjusting the humidity of the input air.

- GHSV was regulated by flow meters and ranged from 3000 to 10000 /h based on the volume of carbon dioxide adsorbent. The outlet carbon dioxide concentrations were monitored by an infrared carbon dioxide sensor (Dynamet, 0-1000 ppm), while the feed and outlet relative humidity were continuously recorded by two
15 humidity sensors (Ningbo Keshun KS-SHT and Vaisala HMT338). For the cycling experiments conducted under specific relative humidity conditions, one of the air streams was passed through a 26 °C water bath to control the feed gas humidity. Various volumes of carbon dioxide and water adsorbents were tested for production of carbon dioxide and water from the air. This study focused on investigating the
20 performance of adsorbent ratios of 1 and 4, where the adsorbent ratio is defined as the volume ratio of VPOC 1065 resin to silica gel.

- A thermocouple was positioned at the centre of VPOC 1065 to measure the temperature profile during adsorption-desorption cycles. The carbon dioxide uptake ($q_{CO_2}^{ads}$, mmol/g) during an adsorption process is calculated based on the following
25 Equation (11).

$$q_{CO_2}^{ads} = \int_0^{t_{ads}} \frac{n_{air}(C_{CO_2,in} - C_{CO_2,out})}{m} dt \quad (11)$$

where t_{ads} is the adsorption time, n_{air} is the flow rate of the inlet air, $C_{CO_2,in}$ is the atmospheric carbon dioxide concentration, $C_{CO_2,out}$ is the carbon dioxide concentration in the outlet gas and m is the mass of VPOC 1065. The water adsorption capacity is determined by the same calculation method.

- 5 Thermal energy, supplied by electrical heating was utilized to regenerate the adsorbents and generate high purity carbon dioxide and water products. The adsorption column used for electrical heating is illustrated in Figure 9B and includes an adsorption column 1 an electrical heating coils 120 surrounding the column 1. An adsorption column 1, 60 cm in length and 4 cm in diameter,
10 constructed of stainless steel was employed..

The electrical heating power used was 90 W.

- The desorption process was initiated by turning on the electrical heating. During the desorption process, the outlet valve of the column was closed while the inlet 3-way valve was switched and directly connected to a condenser and syringe for
15 product collection.

- As the adsorbent temperature increased, the carbon dioxide product was collected by the syringe for recording the product volume profile. The final collected product was stored in gas sampling bags and analyzed using gas chromatography. with a thermal conductivity detector. For real-time carbon dioxide purity investigation, a
20 carbon dioxide sensor (Dynament, 0-100%) was directly connected to the condenser and syringe. The volume profile of desorbed carbon dioxide can be expressed as

$$V_{CO_2,t_{des}} = \int_0^{t_{des}} C_{CO_2,t_{des}} \frac{\partial V_{p,t_{des}}}{\partial t} dt \quad (11)$$

- where $V_{CO_2,t_{des}}$ is the carbon dioxide volume in products at a certain desorption time
25 (t_{des}), $V_{p,t_{des}}$ is the product volume at t_{des} , $C_{CO_2,t_{des}}$ is the real time carbon dioxide purity of the product at t_{des} . After obtaining the volume profile of desorbed carbon dioxide, the carbon dioxide loading of VPOC 1065 during the desorption step could be easily determined. The water product was collected from the condenser and

analyzed by ^1H NMR spectra (Varian VNMRs 600 MHz). For analyzing the water vapor pressure inside the column during desorption, a humidity sensor (Vaisala HMT338) was directly connected to the column to measure the humidity and temperature around VPOC 1065. Water vapor pressure was further calculated by the Antoine equation for vapor-pressure data. Upon completion of the desorption, the column was purged with fresh air to rapidly reduce the adsorbent temperature and start the next adsorption cycle.

Results

Working capacity, temperature and time of desorption

Using 180 mL resin and 180 mL silica gel, the cyclic performance of DAC based on VPD (Figure 9A-9B) was investigated and the carbon dioxide loading profiles were calculated to determine the working capacity in different cycles (Figure 9C). At a feed GHSV of 10000 /h, the desorption processes only accounted for a quarter of the total cyclic time and required approximately 40-60 minutes. Remarkably, VPD achieved a stable cyclic capacity between 0.95-1.05 mmol/g (Figure 9D) over nine cycles, resulting in a carbon dioxide productivity of ~ 2.86 g per cycle. Desorption temperature profiles (Figure 9E) revealed that VPD led to a decrease in desorption temperature and required regeneration time, which was attributed to the co-adsorbed water introduced by silica gel. Given that moisture has been shown to be beneficial for enhancing the stability of amine adsorbents, VPD thus possesses the ability to prevent the deactivation of carbon dioxide adsorbents and improve cyclic stabilities because of the relatively low desorption temperature and increased water vapor amount. Without water adsorbents, the low water uptake led to a temperature increase from 110 °C to around 150 °C, causing a sharp decline in cyclic working capacity (Figure 9D). The shaded areas in Figure 9F representing temperature fluctuations under different cycles revealed that regeneration temperatures were humidity-sensitive without silica gel, with increased RH reducing desorption temperatures. These findings highlighted the crucial importance of water adsorbents and co-adsorbed water.

Product volume and purity

Product volumes and real-time carbon dioxide purity were measured during carbon dioxide collection via vapor promoted desorption (Figure 9F). Within the first 15 min, air (N_2 and O_2) remaining in the column was collected by the purging effect of desorbed carbon dioxide and H_2O . With increasing desorption time and temperature, carbon dioxide purity sharply increased from 1 to 99%, indicating the ability of the present DAC system to produce high-purity carbon dioxide from atmosphere. The gas chromatography (GC) analysis of the products collected after 20 minutes of desorption showed a carbon dioxide concentration of 97.7% and an O_2 concentration of 0.5%. With the production of carbon dioxide, O_2 -induced degradation of the amine groups was expected to be avoided because of the low O_2 concentrations inside the column.

Example 7 – Cycling performance in vapor promoted desorption – Increasing productivity

- 15 This example demonstrates increased productivity while maintaining stability during cycling experiments. The experiments were performed in accordance with Example 6 with the exception of the amount of adsorbents used. In this example, to further increase carbon dioxide productivity, the cyclic DAC process was conducted utilizing 320 mL of resin and 80 mL of silica gel (Figure 10).
- 20 The DAC system operated with remarkable stability even with a reduced volume of silica gel, exhibiting working capacities ranging from 0.85-1.00 mmol/g and productivities of approximately 4.71 g carbon dioxide per cycle (Figure 10A and Figure S10A). The water productivity ranged from 5.0 to 6.5 g per cycle and was influenced by the atmospheric humidity.
- 25 Moreover, the produced water exhibited high purity, as confirmed by the 1H NMR results (Figure 10C). The regeneration temperature profile displayed no significant differences compared to the case employing 180 mL of desiccants (Figure 10B), indicating that the co-adsorbed water was still sufficient for adsorbent regeneration.

To assess the necessary amount of co-adsorbed water for VPD, the relationship between the molar ratio of adsorbed H₂O to carbon dioxide and the regeneration temperature was established. As shown in Figure 10D, vapor promoted desorption could be achieved at temperatures as low as 110 °C when the molar ratio was higher than approximately 11. Moreover, an increased H₂O/carbon dioxide ratio could lower the required desorption temperature, thus stabilizing the Lewatit resin.

Example 8 – desorption performance under vacuum assisted condition

In this example, the effect of applying a vacuum on the desorption performance was investigated. Theoretically, reducing the desorption pressure can lower the water desorption temperature, thereby facilitating water vapor generation at lower temperatures. As vapor promoted desorption utilizes water vapor to decrease the equilibrium carbon dioxide loading of the adsorbent, we anticipate that the carbon dioxide desorption temperature will decrease proportionally with the reduction of the water desorption temperature. When a sufficient amount of water is adsorbed, the desorption temperature is expected to be close to or slightly higher than the boiling point of water at the desorption pressure.

Experimental

A similar set up as employed in Examples 6 and 7 was employed with the exception of a vacuum generation system that is installed between the condenser and the gas collector.

Another change was that the carbon dioxide adsorbent employed was Polyethyleneimine (PEI) grafted HP 20 macroporous resin, which was prepared through physical impregnation with polyethyleneimine (Mw=800) loading at 33%.

For direct air capture, a mixture of 200 mL of PEI-grafted resin and 200 mL of silica gel was used as the adsorbents.

The feedstock for the adsorption process consisted of air with a carbon dioxide concentration of 350 ppm and a relative humidity of 50%. After saturation with air at room temperature (25 °C) for adsorbing atmospheric carbon dioxide and H₂O, the pressure inside the adsorption column was reduced to the desired levels (30 kPa,

20 kPa, and 10 kPa) using a vacuum pump. Subsequently, the adsorption column and the adsorbents were heated by electrical heating with a power of 60 W. The gas products were then collected while maintaining the desorption pressure using the vacuum pump, and the desorption process lasted for 50 minutes. After desorption, 5 air was introduced into the column to lower the adsorbent temperature and initiate a new adsorption cycle. Desorption experiments were also conducted under a pressure of 100 kPa (without using the vacuum pump) as a control to investigate the effect of vacuum on vapor promoted desorption.

Results

10 Based on the temperature profiles presented in Figure 11A, it is evident that at desorption pressures of 30 kPa, 20 kPa, and 10 kPa, the desorption temperatures were maintained at 71 °C, 62 °C, and 53 °C, respectively. Remarkably, these temperatures are in proximity to the boiling point of water at the corresponding pressures, indicating that the desorption temperature of vapor promoted desorption 15 is controllable through the desorption pressure. Vapor promoted desorption under vacuum at low temperatures is applicable to amine-grafted adsorbents with low stability at high temperatures, thus enabling stable operation of these adsorbents.

According to the product volume profile (Figure 11B), even at such low desorption temperatures, the adsorbents can still desorb and release a large amount of carbon dioxide, achieving a working capacity of 1.14-1.27 mmol/g under 10-30 kPa 20 desorption pressures within 50 min. And a low desorption pressure can promote the desorption rate of carbon dioxide. In addition, we analyzed the concentration of carbon dioxide products. After drying with 3A molecular sieve, the concentration of carbon dioxide products collected at 10 kPa can reach 99%, and those collected 25 at 20 kPa and 30 kPa can reach 98%, slightly higher than the concentration of carbon dioxide products (around 97%) desorbed at atmospheric pressure. Therefore, conducting carbon dioxide desorption under vacuum conditions is beneficial to increase the concentration of products, as the air inside the adsorption column is removed by the vacuum pump prior to heating and carbon dioxide 30 collection.

As used herein, the singular forms "a," "an," and "the" designate both the singular and the plural, unless expressly stated to designate the singular only.

5 The term "about" and the use of ranges in general, whether or not qualified by the term about, means that the number comprehended is not limited to the exact number set forth herein, and is intended to refer to ranges substantially within the quoted range while not departing from the scope of the invention. As used herein, "about" will be understood by persons of ordinary skill in the art and will vary to some extent on the context in which it is used. If there are uses of the term which are not
10 clear to persons of ordinary skill in the art given the context in which it is used, "about" will mean up to plus or minus 10% of the particular term.

Percentages (%) referred to herein are based on weight percent (w/w or w/v) unless otherwise indicated.

15 Throughout this specification and the claims which follow, unless the context requires otherwise, the word "comprise", and variations such as "comprises" and "comprising", will be understood to imply the inclusion of a stated integer or step or group of integers or steps but not the exclusion of any other integer or step or group of integers or steps.

20 The reference in this specification to any prior publication (or information derived from it), or to any matter which is known, is not, and should not be taken as an acknowledgment or admission or any form of suggestion that that prior publication (or information derived from it) or known matter forms part of the common general knowledge in the field of endeavour to which this specification relates.

25 Variations and modifications may be made to the parts previously described without departing from the spirit or ambit of the disclosure.

CLAIMS

1. A method of extracting carbon dioxide from a gas stream, the method
5 comprising:
- contacting a CO₂ adsorbent with a moist gas stream containing CO₂ to
capture CO₂ from the moist gas stream in the presence of moisture;
- capturing a portion of the water from the moist gas stream using a moisture
sorbent material;
- 10 regenerating the CO₂ adsorbent to produce an output stream comprising
steam and CO₂, the regenerating comprising:
- heating the moisture sorbent material to release water captured by
the moisture sorbent material as steam;
- exposing the CO₂ adsorbent to the steam to liberate captured CO₂
15 from the CO₂ adsorbent and generate the output stream.
2. A method according to claim 1, wherein the CO₂ adsorbent is contacted by the
moist gas stream upstream of exposing the moisture sorbent material to the
moist gas stream.
- 20
3. A method according to claims 1 or 2, wherein regenerating the CO₂ adsorbent
is conducted at a temperature in the range of 40 °C – 150 °C.
4. A method according to any one of claims 1 to 3, wherein regenerating the CO₂
25 adsorbent comprises applying a vacuum during the heating of the moisture
sorbent material to promote formation of steam.

5. A method according to any one of claims 1 to 4, comprising, after contacting the CO₂ adsorbent with the moist gas stream, purging the atmosphere around the CO₂ adsorbent to remove oxygen from said atmosphere.
- 5 6. A method according to claim 5, wherein the purging comprises displacing oxygen from the atmosphere around the CO₂ adsorbent using the steam.
7. A method according to any one of claims 1 to 6, wherein a molar ratio of water captured by the moisture sorbent material to CO₂ captured by the CO₂ adsorbent
10 is at least 8.
8. A method according to any one of claims 1 to 7, wherein a volume ratio of the carbon dioxide adsorbent to the moisture sorbent material is less than 7.
- 15 9. A method according to any one of claims 1 to 8, wherein the moisture sorbent material is chosen from a group comprising silica gel; aluminosilicate gel; sorbead; Sepiolite; Bentonite; Kaolin; metal organic frameworks comprising MIL-101, MIL-100, MOF-801, CAU-10, CAU-23, UIO-66, UIO-67, MOF-841, DUT-67, DUT-51, MOF-808, MOF-5, and MOF-74; zeolite comprising
20 small-pore zeolites comprising 3A, 4A, 5A, 13X, and 10X, zeolite frameworks comprising ZSM-5, Y, Beta, FAU, MOR, and AIPO, and molecular sieves comprising SAPO, ITQ-29, SSZ-13, MCM-41, KIT-6, TNU-9, B-ZSM-5, and UTD-1; carbon materials comprising activated carbon, biomass carbon, activated carbon fibres, carbon molecular sieves, and mesoporous carbon; salt-
25 impregnated desiccants comprising one or more of LiCl, CaCl₂, CuCl₂, CuSO₄, MgSO₄, an ionic liquid or a mixture thereof impregnated into a porous material comprising activated carbon, silica, or clay; alumina; polymers comprising hydrophilic functional groups in their polymer chain units.

10. A method according to any one of claims 1 to 9, wherein the CO₂ adsorbent is an amine-based CO₂ adsorbent or a salt-impregnated CO₂ adsorbent.
11. A method according to claim 10, wherein the CO₂ adsorbent is a salt-impregnated CO₂ adsorbent formed by impregnating alkali carbonates, ionic liquids, or a mixture thereof into a porous material selected from the group consisting of: activated carbon, silica, clay, or combinations thereof.
12. A method according to claim 10, wherein the CO₂ adsorbent is an amine-based CO₂ adsorbent selected from the group consisting of: an impregnated amine-based adsorbent formed by the deposition of tetraethylenepentamine (TEPA), pentaethylenhexamine (PEHA), polyethylenimine (PEI), polyallylamine (PAA), monoethanolamine (MEA) impregnated into the pores or on a surface of a solid support, said solid support comprising carbon, silica, clay, zeolite, metal-organic framework, metal oxide, cellulose, polymer, or combinations thereof; a covalently bonded amine-based adsorbent formed using 3-aminopropyltriethoxysilane (APS), aminopropyl (APS) silanes or diethylenetriamine (DT) silanes to covalently bond amine groups to a surface of a porous material; polymers comprising amine groups incorporated from styrene-divinyl benzene co-polymer.
13. A method according to any one of claims 1 to 12, wherein the relative humidity level of the moist gas stream is between 15 – 95%.
14. A method according to any one of claims 1 to 13, comprising separating CO₂ from the output stream to produce a CO₂-rich stream.
15. A method according to claim 14, wherein separating comprises condensing steam from output stream to form a CO₂-rich stream.

16. A method according to claims 14 or 15, wherein the CO₂-rich stream is 97 to 99% CO₂.
- 5 17. A method of extracting carbon dioxide from a gas stream, the method comprising:
- contacting a CO₂ adsorbent with a first gas stream containing carbon dioxide to capture carbon dioxide from the first stream;
- capturing water from a second stream containing water using a moisture sorbent material;
- 10
- regenerating the CO₂ adsorbent to produce an output stream comprising steam and carbon dioxide, the regenerating comprising:
- heating the moisture sorbent material to release water captured by the moisture sorbent material as steam;
- 15
- exposing the CO₂ adsorbent to the steam to liberate captured carbon dioxide from the CO₂ adsorbent and generate the output stream.
18. A method according to claim 17, wherein the first gas stream is a moist gas stream and the second stream is a vapor stream.
- 20
19. A method according to claims 17 or 18, wherein regenerating the CO₂ adsorbent is conducted at a temperature in the range of 40 °C – 150 °C.
20. A method according to any one of claims 17 to 19, wherein regenerating the
- 25 CO₂ adsorbent comprises applying a vacuum during the heating of the moisture sorbent material to promote formation of steam.

21. A method according to any one of claims 17 to 20, comprising, after contacting the CO₂ adsorbent with the first gas stream, purging the atmosphere around the CO₂ adsorbent to remove oxygen from said atmosphere.
- 5 22. A method according to claim 21, wherein the purging comprises displacing oxygen from the atmosphere around the CO₂ adsorbent using the steam.
23. A method according to any one of claims 17 to 22, wherein a molar ratio of water captured by the moisture sorbent material to carbon dioxide captured by the CO₂ adsorbent is at least 8.
- 10 24. A method according to any one of claims 17 to 23, wherein a volume ratio of the CO₂ adsorbent to the moisture sorbent material is less than 7.
- 15 25. A method according to any one of claims 17 to 24, wherein the moisture sorbent material is chosen from a group comprising silica gel; aluminosilicate gel; sorbead; Sepiolite; Bentonite; Kaolin; metal organic frameworks comprising MIL-101, MIL-100, MOF-801, CAU-10, CAU-23, UIO-66, UIO-67, MOF-841, DUT-67, DUT-51, MOF-808, MOF-5, and MOF-74; zeolite comprising small-pore zeolites comprising 3A, 4A, 5A, 13X, and 10X, zeolite frameworks comprising ZSM-5, Y, Beta, FAU, MOR, and AIPO, and molecular sieves comprising SAPO, ITQ-29, SSZ-13, MCM-41, KIT-6, TNU-9, B-ZSM-5, and UTD-1; carbon materials comprising activated carbon, biomass carbon, activated carbon fibres, carbon molecular sieves, and mesoporous carbon; salt-impregnated desiccants comprising one or more of LiCl, CaCl₂, CuCl₂, CuSO₄, MgSO₄, an ionic liquid or a mixture thereof impregnated into a porous material comprising activated carbon, silica, or clay; alumina; polymers comprising hydrophilic functional groups in their polymer chain units.
- 20
- 25

26. A method according to any one of claims 17 to 25, wherein the CO₂ adsorbent is an amine-based CO₂ adsorbent or a salt-impregnated carbon dioxide adsorbent.
- 5 27. A method according to claim 26, wherein the CO₂ adsorbent is a salt-impregnated CO₂ adsorbent formed by impregnating alkali carbonates, ionic liquids, or a mixture thereof into a porous material selected from the group consisting of: activated carbon, silica, clay, or combinations thereof.
- 10 28. A method according to claim 26, wherein the CO₂ adsorbent is an amine-based CO₂ adsorbent selected from the group consisting of: an impregnated amine-based adsorbent formed by the deposition of tetraethylenepentamine (TEPA), pentaethylenhexamine (PEHA), polyethylenimine (PEI), polyallylamine (PAA), monoethanolamine (MEA) impregnated into the pores or on a surface
15 of a solid support, said solid support comprising carbon, silica, clay, zeolite, metal-organic framework, metal oxide, cellulose, polymer, or combinations thereof; a covalently bonded amine-based adsorbent formed using 3-aminopropyltriethoxysilane (APS), aminopropyl (APS) silanes or diethylenetriamine (DT) silanes to covalently bond amine groups to a surface
20 of a porous material; polymers comprising amine groups incorporated from styrene-divinyl benzene co-polymer.
29. A method according to claim 18 or any one of claims 19 to 28 when dependent from claim 18, wherein the relative humidity level of the first gas stream is
25 between 15 – 95%.
30. A method according to any one of claims 17 to 29, comprising separating carbon dioxide from the output stream to produce a carbon dioxide-rich stream.

31. A method according to claim 30, wherein separating comprises condensing steam from output stream to form a carbon dioxide-rich stream.
32. A method according to claims 30 or 31, wherein the carbon dioxide-rich stream
5 is 97 to 99% CO₂.
33. A system for extracting carbon dioxide from a gas stream, the system comprising:
10 a moisture capture zone and a CO₂ capture zone in fluid connection with the moisture capture zone, wherein the moisture capture zone has a moisture sorbent material configured to capture moisture from a moist gas stream and the CO₂ capture zone has a CO₂ adsorbent configured to capture CO₂ from the moist gas stream;
15 a regeneration means configured to produce an output stream comprising steam and CO₂, the regeneration means comprising a heating arrangement configured to heat the moisture sorbent material so that water captured by the moisture sorbent material is released as steam; wherein the moisture capture zone and a CO₂ capture zone are configured for exposing the CO₂ adsorbent to the steam to liberate captured CO₂ from the CO₂ adsorbent and generate the
20 output stream.
34. A system according to claim 33, wherein the moisture capture zone and CO₂ capture zone are located adjacent each other in a single column reactor.
- 25 35. A system according to claim 33, wherein the moisture capture zone and CO₂ capture zone are located in separate reactors fluidly connected with one another.
36. A system for extracting carbon dioxide from a gas stream, the system comprising:

a moisture capture zone and a CO₂ capture zone, wherein the CO₂ capture zone has a CO₂ adsorbent configured to capture CO₂ from a first stream containing carbon dioxide and the moisture capture zone has a moisture sorbent material configured to capture moisture from a second stream containing water;

5 a regeneration means configured to produce an output stream comprising steam and CO₂, the regeneration means comprising a heating arrangement configured to heat the moisture sorbent material so that water captured by the moisture sorbent material is released as steam; wherein the moisture capture zone and a CO₂ capture zone are configured for exposing the CO₂ adsorbent to the steam to liberate captured CO₂ from the CO₂ adsorbent and generate the output stream.

37. A system according to one of claims 33 to 36, wherein the heating arrangement is powered by a heating coil, solar concentrator or a heat exchange arrangement
15 configured to recover heat from an industrial process and provide the recovered heat to the moisture sorbent material.

38. A system according to claim 37, wherein the solar concentrator is a parabolic solar concentrator.
20

39. A system according to claims 37 or 38, wherein the heating arrangement further comprises a vacuum insulation layer that surrounds at least the moisture capture zone so as to prevent heat loss from the moisture capture zone.

25 40. A system according to claim 39 when dependent from claim 38, wherein the vacuum insulation layer is transparent to solar radiation directed towards the moisture capture zone from the parabolic solar concentrator.

41. A carbon dioxide capture plant for extracting CO₂ from a moist gas stream, the plant comprising a plurality of systems according to any one of claims 33 to 40.
42. A carbon dioxide capture plant according to claim 41, wherein the plant is a
5 direct-air capture plant configured to capture carbon dioxide from ambient atmosphere.