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(54) Title: DIRECT AIR CAPTURE OF CARBON DIOXIDE

(57) Abstract: A method for removing carbon dioxide from a gas comprising carbon dioxide, the method comprising: contacting the gas comprising carbon dioxide with a fluidised solid sorbent, thereby removing carbon dioxide from the gas and forming a carbon dioxide depleted gas.

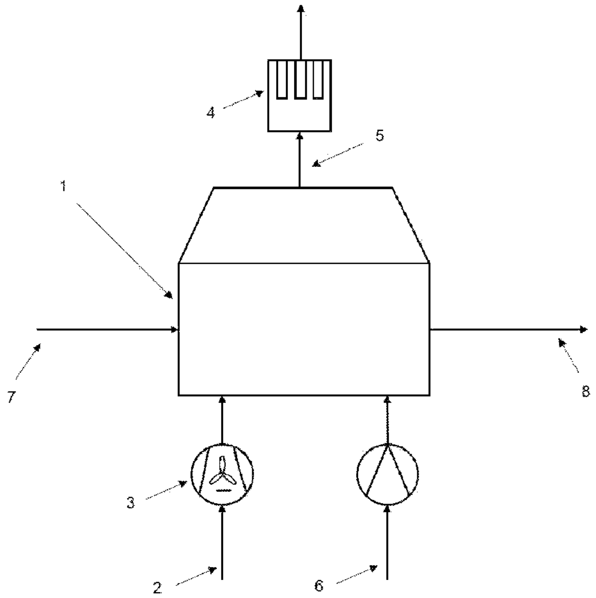

Figure 1

DIRECT AIR CAPTURE OF CARBON DIOXIDE

FIELD

The invention relates to a method for removing carbon dioxide from a gas using a solid sorbent material.

BACKGROUND

It is more important than ever to prevent global warming. The concentration in atmospheric air of carbon dioxide, one of the most significant greenhouse gases, has increased from approximately 280 ppm in the preindustrial age to around 400 ppm today. To prevent global warming, a diverse portfolio of technologies must be deployed to reduce and/or prevent new carbon dioxide emissions into the atmosphere at the source and to remove existing carbon dioxide from the atmosphere. It will be very difficult to meet ambitious climate change mitigation goals without large-scale durable removal of carbon dioxide from the atmosphere.

One way of doing this is through Direct Air Capture (DAC). DAC is a process which allows for the direct removal of carbon dioxide from the air, reducing the concentrations of carbon dioxide in the atmosphere and helping to prevent global warming.

A large number of standard DAC systems have one major challenge to overcome: they require large volumes of air to be passed through the system in order to extract the desired amount of carbon dioxide from the air because of the low concentration of carbon dioxide in atmospheric air. Ultimately, this means that, in order to be economically feasible, the air passing through a DAC system must experience a very low pressure drop between the inlet and outlet as otherwise the energy required to pump the air through the system will render the system uneconomical. The significant cost of running these standard DAC systems represents a barrier to large scale utilisation of DAC systems. Fluidised bed reactors may be used in DAC systems.

The present disclosure seeks to alleviate, at least to a certain degree, the problems and/or address at least to a certain extent, the difficulties associated with the prior art.

SUMMARY OF INVENTION

According to a first aspect of the disclosure, there is provided a method for removing carbon dioxide from a gas comprising carbon dioxide, the method comprising the steps of: contacting the gas comprising carbon dioxide with a fluidised solid sorbent, thereby removing carbon dioxide from the gas and forming a carbon dioxide depleted gas.

Removing carbon dioxide from a gas means removing some, but not necessarily all, of the carbon dioxide from a gas comprising carbon dioxide, thereby forming a carbon dioxide depleted gas. 'Contacting' the gas with a fluidised solid sorbent means bringing the gas into contact with the solid sorbent (which may be particles of the sorbent if the sorbent comprises particles). A 'fluidised' solid sorbent means that the solid sorbent is not static and has been fluidised i.e. caused to move from a static position by the force of a gas. The solid sorbent may be, but is not limited to, a solid sorbent mixture. The solid sorbent may be or may comprise, but is not limited to, a nanostructured sorbent. The solid sorbent mixture comprising a nanostructured sorbent means that, amongst other components, the solid sorbent mixture comprises a nanostructured sorbent.

"Nanostructured" as used herein to define the sorbent means that the sorbent, while not necessarily being limited to being of nanoparticle size for example in terms of nominal particle diameter (i.e. not 1 to 100 nanometre in diameter), encloses a large internal surface area that has a three-dimensional porous structural nature of nanostructure scale (~1 to 100 nanometres) which provide a surface area for reactions to occur. Advantageously, using nanostructured sorbents provides good mechanical stability when compared to non-nanostructured sorbent particles by reducing attrition rate characteristics and/or sorbent breakage and at least maintaining or improving chemical reactivity of the sorbent particles with carbon dioxide by maintaining or improving internal surface area and/or porosity. Enhancement of sorbent particles to form nanostructured sorbents as defined herein can be achieved by doping, mixing, calcining or stabilising with inert components and/or steam reactivation of the sorbent particles.

Advantageously, a fluidised solid sorbent acts like a turbulent fluid and enables a higher rate of mass and heat transfer between the solid sorbent and the gas. Advantageously, a nanostructured sorbent enables a higher rate of adsorption of carbon dioxide from the gas by increasing the internal surface area of the nanostructured sorbent.

Optionally, the gas comprising carbon dioxide is contacted with the solid sorbent in the presence of water or one or more solvents or a mixture of water and one or more solvents. Advantageously, this results in increased rates of carbonation. Carbonation is used herein to refer to the rate at which the carbon dioxide is removed from the gas stream. The water or solvents may advantageously be provided in droplet form, which may be produced using an atomiser or a diffuser.

Optionally, the water is provided by humidifying the gas comprising carbon dioxide to a humidity of substantially 100%. Alternatively, the water may be provided by bubbling the gas comprising carbon dioxide through water prior to being contacted with the solid sorbent. Alternatively, the water may be provided by injected steam.

Optionally, the gas comprising carbon dioxide is contacted with the solid sorbent in one or more reactors. Advantageously, using a reactor means that the process can be contained and the point at which the gas contacts the solid sorbent can be controlled. It is possible to use more than one reactor in the same location to increase the amount of carbon dioxide removed. Such reactors may be run in parallel or in series. Alternatively to providing more than one reactor (or in addition when more than one reactor is provided), a recycle line may be provided to recycle the carbon dioxide depleted gas back for a further pass through one or more of the reactors. Advantageously, providing more than one reactor in parallel or series and/or said recycle lines enables a degree of control over carbonation conversion to a chosen/optimal level.

Optionally, the one or more reactors may be one or more fluidised bed reactors. A fluidised bed reactor is a reactor which has a bed of material (in this case, a solid sorbent) within it which may be moved from a static bed position to a fluidised bed position through the application of a fluidising gas in order to provide the fluidised solid sorbent. Advantageously, by fluidising the solid sorbent, it is possible to increase the contact between the fluidising gas and the bed material and therefore to increase the rate of transfer between the fluidising gas and the bed material.

Optionally, the one or more fluidised bed reactors have a width to length aspect ratio in the range of 1:1 to 1:20, preferably 1:5, more preferably 1:3. Optionally, the fluidised bed reactor is a horizontal fluidised bed reactor. Advantageously, these preferred aspect ratios ensure that the fluidised bed reactors may fit in a standard shipping container making the equipment easy to transport. Advantageously, when compared to a standard vertical fluidised bed reactor with the same mass of bed material, a horizontal fluidised bed can have a much shallower bed height which results in a lower gas pressure drop across the bed. Advantageously, having a shallow bed height means the costs associated with moving the gas across the bed can be reduced.

Optionally, the gas comprising carbon dioxide is contacted (e.g. simultaneously contacted) with the solid sorbent in each of a plurality of parallelly arranged fluidised bed reactors. A respective portion of the gas comprising carbon dioxide may be contacted (e.g. simultaneously contacted) with the solid sorbent in each of the plurality of parallelly arranged fluidised bed reactors. The fluidised bed reactors may be stacked on top of each other to form a vertical stack of fluidised bed reactors.

Optionally, the one or more fluidised bed reactors include a plurality of parallelly arranged fluidised bed sub-units, wherein the gas comprising carbon dioxide is contacted (e.g. simultaneously contacted) with the solid sorbent in each of the plurality of parallelly arranged fluidised bed sub-units. A respective portion of the gas comprising carbon dioxide may be contacted (e.g. simultaneously contacted) with the solid sorbent in each of the plurality of parallelly arranged fluidised bed sub-units. The fluidised bed sub-units may be stacked on top of each other to form a vertical stack of fluidised bed sub-units. The fluidised bed sub-units may be housed within a same enclosure of the corresponding fluidised bed reactor. This is so that, in use, the fluidised bed sub-units are exposed to the same gas comprising carbon dioxide entering the corresponding fluidised bed reactor.

The vertical stacking of the gas comprising carbon dioxide through the parallelly arranged fluidised bed reactors or fluidised bed sub-units ensures that the pressure drop across each fluidised bed reactor or fluidised bed sub-unit is the same (which controls energy costs of driving the flow of the gas comprising carbon dioxide) but permits an increased volumetric throughput of the gas and thereby an increased amount of processing for a given reactor size and footprint. This in turn improves reaction efficiency and allows reductions in the overall size and material requirements of the system while maintaining a desired performance, particularly in relation to economic capture of carbon dioxide from atmospheric air, and thereby reduces the capital expenditure requirements of the system as a whole.

Furthermore, the parallel nature of the fluidised bed reactors or fluidised bed sub-units enables scaling of the system’s capacity by adding fluidised bed reactors or fluidised bed sub-units vertically and/or laterally. Such flexibility in scaling enables ready deployment and installation of the system in a variety of locations and for a variety of application requirements.

Optionally, one or more gas distributors are provided through which the gas is introduced to the one or more fluidised bed reactors. A gas distributor means any device which is capable of distributing the gas within a reactor to produce a uniform, distributed gas flow. An example of a gas distributor is a perforated distribution plate i.e. a plate which is perforated in more than one location to allow gas through and into the fluidised bed. Advantageously, by using a gas distributor, the contact between the fluidising gas and the bed material (i.e. solid sorbent) may be increased and therefore the rate of transfer between the fluidising gas and the bed material may be increased.

Optionally, one or more fans are provided to introduce the gas into the one or more fluidised bed reactors. Advantageously, using more than one fan allows a greater volume of gas to be introduced into the reactors.

Optionally, the solid sorbent is moved from a solid inlet along the length of the fluidised bed reactor to a solid outlet. Optionally, the one or more fans are configured to progressively (gradually) move the solid sorbent from the solid inlet along the length of the fluidised bed reactor to the solid outlet. Advantageously, this enables the solid sorbent to be replenished when the solid sorbent becomes fully saturated without having to stop the process and unload/reload the solid sorbent as a batch process. The rate at which the one or more fans move the solid sorbent material from the solid inlet to the solid outlet, combined with the rate by which new (and/or regenerated) solid sorbent material is added to the solid inlet, may be chosen so as to ensure that desired absorption rates are obtained. Optionally, if more than one fan is provided then they may be configured to provide a rate gradient so that the solid sorbent moves at different rates along the length of the fluidised bed reactor.

Optionally, one or more separation units are provided through which the carbon dioxide depleted gas is filtered. The carbon dioxide depleted gas is the gas which has been contacted with the solid sorbent i.e. it has passed through the bed of fluidised solid sorbent. Advantageously, by passing the carbon dioxide depleted gas stream through one or more separation units, it is possible to remove entrained particles of solid sorbent from the carbon dioxide depleted gas before the carbon dioxide depleted gas is sent for further processing/storage/utilisation etc. A separation unit is a unit capable of separating any entrained particles from the gas. There may be a separation unit within the reactor, for example, a filter, a bag filter, or there may be a separation unit outside of the reactor, for example, a cyclone. There may be multiple types of separation units.

Optionally, the one or more separation units may be or may include a filter, a bag filter, a gas cyclone or an electrostatic precipitator (ESP).

The gas comprising carbon dioxide to be contacted with the fluidised solid sorbent may be at a temperature in the range of -70°C to 500°C, preferably -70°C to 200°C, more preferably 15°C to 35°C, even more preferably 20°C to 25°C. In particular, the invention is particularly applicable to the capture of carbon dioxide from gases comprising carbon dioxide at low temperatures (e.g. atmospheric air at atmospheric temperatures), in addition to being applicable to the capture of carbon dioxide from gases comprising carbon dioxide at high temperatures (e.g. higher than atmospheric temperatures), such as flue or exhaust gas.

Optionally, the gas comprising carbon dioxide is contacted with the solid sorbent at a temperature between 450°C and ambient temperature (room temperature, e.g. substantially 20°C) and a pressure between 1 and 1.5 bar. Advantageously, this avoid high temperatures and pressures and therefore helps reduce costs which would otherwise be incurred as a result of heating and pressurising the gas.

Optionally, the method may further comprise a step of regenerating the solid sorbent, thereby releasing carbon dioxide from the solid sorbent and creating a carbon dioxide concentrated gas. Advantageously, this allows the solid sorbent to be recycled (regenerated) and reused.

Optionally, the solid sorbent is regenerated in a second reactor. Advantageously, this allows for the continual removal of carbon dioxide in a first reactor, and the regeneration of the solid sorbent in a second reactor.

Optionally, the solid sorbent is regenerated by heating to a temperature of approximately 500-900°C.

Optionally, the method further comprises the step of collecting the carbon dioxide concentrated gas. Advantageously, this allows the carbon dioxide that is removed from the gas stream to be utilised and/or stored.

Optionally, the method further comprises the step of reactivating the solid sorbent. Optionally, the reactivation step follows the regeneration step.

Optionally, the solid sorbent is reactivated in the presence of steam, at a temperature of between ambient (room temperature, e.g. substantially 20°C) and 900°C.

Optionally, the gas comprising carbon dioxide is atmospheric air. Atmospheric air is considered any air which is removed from the atmosphere.

Optionally, the gas comprising carbon dioxide comprises carbon dioxide in a concentration less than 1000 ppm, more preferably less than 800 ppm, more preferably less than 600 ppm and more preferably less than 500 ppm. Advantageously, having a higher carbon dioxide concentration will result in faster rates of carbonation. However, high carbon dioxide concentrations in the gas may mean that multiple passes need to be made through the system to completely remove all of the carbon dioxide from the gas. Advantageously, the process is optimised to remove substantially all the carbon dioxide from atmospheric gas i.e. gas comprising carbon dioxide in an amount between 500 and 400 ppm.

Optionally, the solid sorbent comprises particles of the solid sorbent and optionally particles of silica, said particles of solid sorbent and optional silica having an average particle diameter of less than 2500 microns (μm). The silica, if present, may be used to aggregate small sorbent particles into larger particles with advantageous fluidising properties by enclosing them and forming a coating like layer by electrostatic forces.

Optionally, the solid sorbent has an average particle diameter of between 20-2000 microns and an internal surface area of between 1-200m^2/g. Advantageously, reaction rates can be increased by increasing the internal surface area of the sorbents available for reactions to take place on.

Optionally, the solid sorbent is a mixed metal oxide or a mixed metal hydroxide, wherein the metal component may be selected from, or a mixture selected from, the list of Ca, Mg, Si, Al, Fe, W, Mn, Cu, Zn, Xo, Sr, Cd, Ba and Ni. Preferably, the solid sorbent is a mixed metal oxide or a mixed metal hydroxide wherein the metal component comprises Ca. Advantageously, Ca adsorbs carbon dioxide from the gas. Advantageously, the other metals may provide structural stability and resistance to attrition and sintering for the sorbent material.

Optionally, the solid sorbent may comprise one or more salts, hydroxides, nitrates, nitrites and/or carbonates of Li, Na and/or K and any combination of HBr, HCl, HNO3 and HI. Advantageously, incorporating one or more of the aforementioned components into the solid sorbent increases the rate of the carbonation reaction.

The method may include the step of cooling solid material that has left a reactor, preferably a calciner reactor, wherein the solid material is cooled using a cooling gas. The method may include the step of conveying the solid material in counterflow with the cooling gas. The method may include the step of conveying the solid material in counterflow with the cooling gas using gravity. The method may include the step of conveying the solid material in crossflow with the cooling gas.

The method may include the step of cooling the solid material in a plurality of cooling stages. The plurality of cooling stages may include a plurality of parallelly arranged cooling stages configured to, in use, cool respective portions of the solid material using the cooling gas. The plurality of cooling stages may include a plurality of sequentially arranged cooling stages configured to, in use, sequentially cool the solid material using the cooling gas.

The method may include the step of hydrating the solid material. The method may include the step of hydrating the solid material received from one of the plurality of sequentially arranged cooling stages, and/or hydrating the solid material and providing the hydrated material to another of the plurality of sequentially arranged cooling stages.

The method may include the step of using one or more fluidised bed coolers to cool the solid material using the cooling gas, wherein the cooling gas is a fluidising gas. The one or more fluidised bed coolers may be in the form of a plurality of parallelly arranged fluidised bed coolers. The or each fluidised bed cooler may include a plurality of fluidised bed cooler sub-units. The fluidised bed coolers or fluidised bed cooler sub-units may be stacked on top of each other to form a vertical stack of fluidised bed coolers or fluidised bed cooler sub-units. The fluidised bed cooler sub-units may be housed within a same enclosure of the corresponding fluidised bed cooler.

The cooling gas may be, but is not limited to, ambient air.

The method may include the step of providing the cooled solid material to a reactor, preferably a carbonator reactor.

The method may include the step of recovering heat from the cooling of the solid material.

The method may include the step of heating solid material using a heating gas prior to the solid material entering a reactor, preferably a calciner reactor. The method may include the step of conveying the solid material in counterflow with the heating gas. The method may include the step of conveying the solid material in counterflow with the heating gas using gravity. The method may include the step of conveying the solid material in crossflow with the heating gas.

The method may include the step of heating the solid material in a plurality of heating stages. The plurality of heating stages may include a plurality of parallelly arranged heating stages configured to, in use, heat respective portions of the solid material using the heating gas. The plurality of heating stages may include a plurality of sequentially arranged heating stages configured to, in use, sequentially heat the solid material using the heating gas.

The method may include the step of using one or more fluidised bed heaters to cool the solid material using the heating gas, wherein the heating gas is a fluidising gas. The method may include the step of using one or more cyclone flash heaters to heat the solid material using the heating gas. The one or more fluidised bed heaters may be in the form of a plurality of parallelly arranged fluidised bed heaters. The or each fluidised bed heater may include a plurality of fluidised bed heater sub-units. The fluidised bed heaters or fluidised bed heater sub-units may be stacked on top of each other to form a vertical stack of fluidised bed heaters or fluidised bed heater sub-units. The fluidised bed heater sub-units may be housed within a same enclosure of the corresponding fluidised bed heater.

The method may include the step of receiving the to-be-heated solid material from a reactor, preferably a carbonator reactor.

The method may include the step of maintaining a solid material heating temperature of below 550°C, preferably below 500°C.

The method may include the step of heating the heating gas using recovered heat from the cooling of the solid material.

The solid material in the foregoing methods of the invention preferably refers to the solid sorbent.

The heat recovery mechanism according to the invention, particularly the use of counterflow cooling/heating and the heat recovery between the carbonator and the calciner, improves the efficiency of the heat recovery by increasing the temperature difference across the heat exchanger and thereby decreasing the energy requirement for the DAC process. Furthermore, the heat recovery mechanism according to the invention is beneficial in terms of saving sensible heat and thus a large portion of the energy associated with the regeneration of the solid sorbent. This enhances the economic feasibility of the invention, thus allowing the system of the invention to be a viable DAC option.

According to another aspect of the invention, there is provided a system for removing carbon dioxide from a gas comprising carbon dioxide, the system comprising a solid sorbent, wherein the system is configured to, in use, contact the gas comprising carbon dioxide with the fluidised solid sorbent, thereby removing carbon dioxide from the gas and forming a carbon dioxide depleted gas.

The system may be configured to, in use, contact the gas comprising carbon dioxide with the solid sorbent in the presence of water or one or more solvents or a mixture of water and one or more solvents. The system is configured to, in use, humidify the gas comprising carbon dioxide to a humidity of approximately 100% so as to provide the water. For example, the system may include a humidifying device to perform such humidification. The system may be configured to, in use, bubble the gas comprising carbon dioxide through water prior to being contacted with the solid sorbent. For example, the system may include a bubbling device to perform such bubbling.

The system may include one or more reactors configured to, in use, contact the gas comprising carbon dioxide with the solid sorbent. The one or more reactors may be one or more fluidised bed reactors. The one or more fluidised bed reactors may have a width to length aspect ratio in the range of 1:1 to 1:20, preferably 1:5, more preferably 1:3. The system may include a plurality of parallelly arranged fluidised bed reactors or fluidised bed sub-units configured to, in use, contact the gas comprising carbon dioxide with the solid sorbent, wherein the gas comprising carbon dioxide is contacted (e.g. simultaneously contacted) with the solid sorbent in each of the plurality of parallelly arranged fluidised bed reactors or fluidised bed sub-units. The plurality of fluidised bed sub-units may be included in a same fluidised bed reactor. A respective portion of the gas comprising carbon dioxide may be contacted (e.g. simultaneously contacted) with the solid sorbent in each of the plurality of parallelly arranged fluidised bed reactors or fluidised bed sub-units. The fluidised bed reactors or fluidised bed sub-units may be stacked on top of each other to form a vertical stack of fluidised bed reactors or fluidised bed sub-units. The fluidised bed sub-units may be housed within a same enclosure of the corresponding fluidised bed reactor.

The system may include one or more gas distributors through which, in use, the gas is introduced to the one or more fluidised bed reactors. The system may include one or more fans configured to, in use, introduce the gas into the one or more fluidised bed reactors.

The system may include a solid inlet and a solid outlet. The system may be configured to move the solid sorbent from the solid inlet along the length of the one or more fluidised bed reactors to the solid outlet. The one or more fans may be configured to, in use, move the solid sorbent from the solid inlet along the length of the one or more fluidised bed reactors to the solid outlet. Optionally, the one or more fans are configured to progressively move the solid sorbent from the solid inlet along the length of the one or more fluidised bed reactors to the solid outlet.

The system may include one or more separation units through which, in use, the carbon dioxide depleted gas is filtered. The one or more separation units may be or may include a filter, a bag filter, a gas cyclone or an electrostatic precipitator (ESP).

The system may be configured to, in use, contact the gas comprising carbon dioxide with the solid sorbent at a temperature of between 450°C and ambient and a pressure of between 1 and 1.5 bar.

The system may be configured to, in use, regenerate the solid sorbent, thereby releasing carbon dioxide from the solid sorbent and creating a carbon dioxide concentrated gas. The system may include a regeneration device to perform such regeneration. The system may include a second reactor configured to, in use, regenerate the solid sorbent.

The system may be configured to, in use, heat the solid sorbent to a temperature of approximately 500-900°C so as to regenerate the solid solvent. For example, the system may include a heat source to perform such heating.

The system may be configured to, in use, collect the carbon dioxide concentrated gas. For example, the system may include a gas collector to perform such gas collection.

The system may be configured to, in use, reactivate the solid sorbent. The system may be configured to, in use, reactivate the solid sorbent in the presence of steam, at a temperature of between ambient and 900°C. For example, the system may include a reactivation device for performing such reactivation.

The system may include a cooling apparatus configured to, in use, cool solid material that has left a reactor, preferably a calciner reactor, wherein the cooling apparatus is configured to, in use, cool the solid material using a cooling gas. The cooling apparatus may be configured to convey the solid material in counterflow with the cooling gas. The cooling apparatus may be configured to convey the solid material in counterflow with the cooling gas using gravity. The cooling apparatus may be configured to convey the solid material in crossflow with the cooling gas.

The cooling apparatus may include a plurality of cooling stages. The plurality of cooling stages may include a plurality of parallelly arranged cooling stages configured to, in use, cool respective portions of the solid material using the cooling gas. The plurality of cooling stages may include a plurality of sequentially arranged cooling stages configured to, in use, sequentially cool the solid material using the cooling gas.

The cooling apparatus may include a hydration stage configured to, in use, hydrate the solid material. The hydration stage may be configured to receive the solid material from one of the plurality of sequentially arranged cooling stages, and/or wherein another of the plurality of sequentially arranged cooling stages is configured to, in use, receive the solid material from the hydration stage.

The cooling apparatus may includes one or more fluidised bed coolers configured to, in use, cool the solid material using the cooling gas, wherein the cooling gas is a fluidising gas. The one or more fluidised bed coolers may be in the form of a plurality of parallelly arranged fluidised bed coolers. The or each fluidised bed cooler may include a plurality of fluidised bed cooler sub-units. The fluidised bed coolers or fluidised bed cooler sub-units may be stacked on top of each other to form a vertical stack of fluidised bed coolers or fluidised bed cooler sub-units. The fluidised bed cooler sub-units may be housed within a same enclosure of the corresponding fluidised bed cooler.

The cooling gas may be, but is not limited to, ambient air.

The cooling apparatus may be configured to, in use, provide the cooled solid material to a reactor, preferably a carbonator reactor.

The system may include a heat exchanger configured to, in use, recover heat from the cooling of the solid material by the cooling apparatus.

The system may include a heating apparatus configured to, in use, heat solid material using a heating gas prior to the solid material entering a reactor, preferably a calciner reactor. The heating apparatus may be configured to convey the solid material in counterflow with the heating gas. The heating apparatus may be configured to convey the solid material in counterflow with the heating gas using gravity. The heating apparatus may be configured to convey the solid material in crossflow with the heating gas.

The heating apparatus may include a plurality of heating stages. The plurality of heating stages may include a plurality of parallelly arranged heating stages configured to, in use, heat respective portions of the solid material using the heating gas. The plurality of heating stages may include a plurality of sequentially arranged heating stages configured to, in use, sequentially heat the solid material using the heating gas.

The heating apparatus may include one or more fluidised bed heaters configured to, in use, cool the solid material using the heating gas, wherein the heating gas is a fluidising gas. The heating apparatus may include one or more cyclone flash heaters configured to, in use, heat the solid material using the heating gas. The one or more fluidised bed heaters may be in the form of a plurality of parallelly arranged fluidised bed heaters. The or each fluidised bed heater may include a plurality of fluidised bed heater sub-units. The fluidised bed heaters or fluidised bed heater sub-units may be stacked on top of each other to form a vertical stack of fluidised bed heaters or fluidised bed heater sub-units. The fluidised bed heater sub-units may be housed within a same enclosure of the corresponding fluidised bed heater.

The heating apparatus may be configured to, in use, receive the to-be-heated solid material from a reactor, preferably a carbonator reactor.

The heating apparatus may be configured to, in use, maintain a solid material heating temperature of below 550°C, preferably below 500°C.

The heating apparatus may be configured to, in use, heat the heating gas using recovered heat from the cooling of the solid material by the cooling apparatus.

It will be appreciated that the use of the terms "first" and "second", and the like, in this patent specification is merely intended to help distinguish between similar features, and is not intended to indicate the relative importance of one feature over another feature, unless otherwise specified.

Within the scope of this application it is expressly intended that the various aspects, embodiments, examples and alternatives set out in the preceding paragraphs, and the claims and/or the following description and drawings, and in particular the individual features thereof, may be taken independently or in any combination. That is, all embodiments and all features of any embodiment can be combined in any way and/or combination, unless such features are incompatible. The applicant reserves the right to change any originally filed claim or file any new claim accordingly, including the right to amend any originally filed claim to depend from and/or incorporate any feature of any other claim although not originally claimed in that manner.

It is within the scope of this disclosure that the optional and preferred features presented above may be combined together in any combination.

BRIEF DESCRIPTION OF THE DRAWINGS

The present disclosure may be carried out in various ways and examples of the disclosure will now be described by way of example with reference to the accompanying drawings, in which:

Figure 1	shows a schematic example of a fluidised bed reactor configured to perform a method according to the present invention;
Figure 2	shows a schematic example of a fluidised bed reactor and a calciner reactor configured to perform a method according to the present invention;
Figure 3a	shows a photograph of a lab-scale fluidised bed set-up configured to perform a method according to the present invention;
Figure 3b	shows a diagram of the fluidised bed set-up of Figure 3a;
Figure 4	shows how the concentration of carbon dioxide in the outlet gas stream changes over time as a result of changes to the temperature

	of the fluidised bed reactor, obtained using the set-up of Figures 3a and 3b;
Figure 5	shows a thermogravimetric analysis of a metal oxide sorbent and a mixed metal oxide sorbent;
Figure 6	shows a thermogravimetric analysis of a metal oxide after 5 cycles of carbon dioxide sorption at 50°C and subsequent regeneration at 800°C;
Figure 7	shows an exemplary fluidised bed reactor configured according to the present invention;
Figure 8	shows an exemplary electric fluidised bed calciner system configured according to the present invention;
Figure 9	shows an example of parallelly arranged fluidised bed reactors;
Figure 10	shows another example of parallelly arranged fluidised bed reactors;
Figure 11	shows a view of an exemplary system comprising an integrated carbonator and calciner assembly;
Figure 12	shows another view of an exemplary system comprising an integrated carbonator and calciner assembly;
Figure 13	shows an exemplary layout of a system according to an embodiment of the invention; and
Figures 14, 15, 16	show other exemplary layouts of a system according to an embodiment of the invention.

DETAILED DESCRIPTION

A detailed description of an example method and system in accordance with the present disclosure for removing carbon dioxide from a gas will now be given with reference to the accompanying Figures. The example method and system are described with reference to a solid sorbent mixture and a nanostructured sorbent but are applicable mutatis mutandis to a solid sorbent and/or a non-nanostructured sorbent.

Figure 1 illustrates a reactor 1 of a system for removing carbon dioxide from a gas stream 2 by carrying out a method in accordance with the present disclosure. A gas stream is passed into the reactor. The gas stream may be any gas stream comprising carbon dioxide. For example, the gas may be atmospheric air, an exhaust gas stream from a power plant, or an exhaust gas stream for an industrial process. In particular, the gas stream may contain carbon dioxide at a concentration of between 400 and 500 ppm i.e. the current concentration of carbon dioxide in atmospheric air. The gas stream may be at ambient temperature and ambient pressure. In particular, the gas stream may be at a temperature of between 450°C and ambient temperature and may have a pressure of between 1 and 1.5 bar. The temperature and pressure may be increased above these values. It is likely that increases in temperature and pressure would result in increases to the carbon dioxide capture rate, but they would also result in increases to the cost of the process as a result of heating and pressuring the gas stream. The process may be used to remove carbon dioxide from gas streams having carbon dioxide concentrations higher than 400 – 500 ppm. For example, the process could be used to remove carbon dioxide from a gas stream having a carbon dioxide concentration of 1000 ppm, or 800 ppm, or 600 ppm, or less than 500 ppm. With increasing carbon dioxide concentrations, it may become necessary to adjust the flow rate of the gas stream to ensure that the desired amount of carbon dioxide can be removed from the gas stream. The process is optimised for removal of carbon dioxide from a gas stream being atmospheric air and hence having a carbon dioxide concentration of between 400 and 500 ppm.

The reactor may be a fluidised bed reactor. Other reactor types may be used, for example, a circulating fluidised bed reactor, or entrainment flow reactors, or drop tube reactors, or packed bed reactors or reactor cyclones.

The fluidised bed reactor may be a horizontal rectangular fluidised bed reactor. The fluidised bed has a length, a width and a height. For example, the width to length ratio of the fluidised bed reactor may be approximately 1:1 to 1:20. By utilising a horizontal fluidised bed reactor, it is possible to process a large volume of air without increasing the pressure drop of the gas introduced to the fluidised bed reactor. A horizontal type fluidised bed reactor is preferred.

The gas stream 2 is introduced into the reactor 1 using one or more external fans 3. Alternatively, one or more blowers, compressors or the like may be used to introduce the gas stream into the reactor. The external fans, blowers, compressors, or the like may be arranged horizontally such that the gas is introduced at multiple locations along the length of the reactor. Alternatively, a single fan, compressor, blower or the like may be used to introduce a single gas stream which may then be split and introduced into the reactor 1, such that only one means for introducing the gas stream is required. For example, if a fluidised bed reactor is used as reactor 1 then the fluidised bed may have 1-10, or more specifically 4-6 entrances for the gas stream 2 (not shown on Figure 1). The different gas streams (or different parts of the same gas stream) may be configured such that there is a gradient in gas stream velocity across the length of the fluidised bed reactor 1. The electricity consumption for the fans to blow gas through the reactor is given by Equation 1.

Equation 1
$$P_f = \frac{2.72\times10^{-5} Q\Delta P}{\mu_f \mu_m}$$

Where P_f is the fan power (kW), Q is the volumetric flow rate through the fan, P is the reactor bed pressure drop, μ_f is the fan efficiency and μ_m is the motor efficiency. Maintaining a low fan electricity consumption is important for ensuring the process is economically feasible. It is clear that in order to reduce fan electricity consumption, the pressure drop over the fluidised bed must be minimised. The pressure drop for a fluidised bed can be calculated according to Equation 2, assuming that the gas flow rate is sufficiently high that the minimum fluidisation velocity has been reached. The minimum fluidisation velocity is the gas velocity at which the drag force on the upward moving gas becomes equal to the weight of the particles in the fluidised bed, causing the particles in the bed to move from a static bed position to a fluidised bed position.

Equation 2
$$\Delta P = \left(\rho_s\left(1 - \epsilon_{mf}\right) - \rho_{Air}\right) g H_{Bed}$$

Where ρ_s is the sorbent density, ρ_{Air} is the air density, ϵ_{mf} is the bed voidage fraction, g is gravitational acceleration and H_{Bed} is the bed height. In order to reduce the pressure drop over the fluidised bed and therefore the electricity consumption associated with the fans, the bed height must be reduced. Having a horizontal fluidised bed allows for the same volume of sorbent to be used as would be used in a narrower fluidised bed, but allows for the sorbent bed height to be reduced and spread out over the length of the fluidised bed reactor. This means that a horizontal fluidised bed reactor can process large volumes of air with a relatively low pressure drop.

On entering the fluidised bed reactor 1, the gas streams may (optionally) be passed through a gas distributor, for example, a perforated distribution plate (not shown in Figure 1) to ensure uniform distribution of the gas stream and uniform gas velocities. The perforated distribution plate may cover the entire length of fluidised bed reactor 1, alternatively, a number of discrete distribution plates may be used that correspond to the number of gas stream inlets. Any other method for ensuring a uniform distribution of the gas stream through the reactor and uniform gas velocities, may be used. The gas stream enters the fluidised bed reactor 1 at or near the base of the fluidised bed reactor and passes upwards through the fluidised bed reactor.

After passing through the perforated distribution plate, the uniformly distributed gas stream passes through a mesh/filter (not shown) within the fluidised bed reactor 1 which suspends a static bed of solid sorbent mixture. The mesh/filter may be sized such that the solid sorbent mixture cannot fall through the mesh/filter, but such that the gas stream can pass through the mesh/filter. The mesh/filter may be made from any suitable material. The gas distributor ensures that the gas stream fluidises and contacts the bed of solid sorbent evenly.

The solid sorbent mixture is comprised of a solid sorbent, and may optionally comprise an amount of silica. The solid sorbent mixture (the mixture comprising the solid sorbent) may have an average particle diameter of less than 2500 microns. If present, the silica is beneficial in that it has been found to help with the fluidisation of the solid sorbent. The solid sorbent is a mix of particles. The solid sorbent may be a mixed metal oxide or mixed metal hydroxide, which chemically reacts with carbon dioxide to form a carbonated material. The solid sorbent is in the form of a solid powder and may have an average particle diameter of 20-2000 microns. More preferably, the average particle diameter of the solid sorbent within the solid sorbent mixture may be 1000-2000 microns, and more preferably may be approximately 1500 microns. The solid sorbent particles are nanostructured (as defined herein), that is while not necessarily being limited to being of nanoparticle size in terms of nominal particle diameter (i.e. not 1 to 100 nanometre in diameter), the particles enclose a large internal surface area that has a three-dimensional porous structural nature of the nanostructure scale (~1 to 100 nanometres) which provide a surface area for reactions to occur. The nanostructured solid sorbent particles have a high internal surface area. For example, the nanostructured solid sorbent may have an internal surface area of approximately 1-200 m^2/g. The high internal surface area of the solid sorbent is achieved by the porosity of the sorbent particles. Advantageously, the properties of the pores (such as the presence and number of mesopores and micropores, and total internal surface area) may be controlled to achieve fast gas diffusion into the pores while also achieving fast reaction rates.

The metal in the mixed metal oxide or mixed metal hydroxide may be chosen from one or more of calcium (Ca), magnesium (Mg), silicon (Si), aluminium (Al), iron (Fe), tungsten (W), manganese (Mn), copper (Cu), zinc (Zn), xanthine (Xo), strontium (Sr), cadmium (Cd), barium (Ba) and nickel (Ni). The Ca adsorbs the carbon dioxide (CO_2), and the other metals may be inert or reactive to CO_2 but may also provide structural stability, and resistance to attrition and sintering for the sorbent material. For example, the metal in the mixed metal oxide or mixed metal hydroxide may comprise Calcium and one or more of magnesium (Mg), silicon (Si), aluminium (Al), iron (Fe), tungsten (W), manganese (Mn), copper (Cu), zinc (Zn), xanthine (Xo), strontium (Sr), cadmium (Cd), barium (Ba) and nickel (Ni). The nanostructured sorbent may comprise one or more salts, hydroxides, nitrates, nitrites or carbonates of Lithium (Li), Sodium (Na) and/or Potassium (K). The nanostructured sorbent may comprise one or more of Hydrogen Bromide (HBr), Hydrogen Chloride (HCl), Nitric acid (HNO3) and Hydrogen Iodide (HI).

Prior to the introduction of the gas into the fluidised bed reactor 1, the bed of solid sorbent mixture is unfluidized i.e. it is static on the mesh/filter. The static bed height will be 0.5-20cm, preferably 1-10cm, more preferably 1-5cm, even more preferably 1-3cm or 4cm. Operating a shallow bed height allows the pressure drop across the bed to be minimised, which prevents high energy requirements, whilst proving an effective amount of the sorbent mixture for carbon dioxide removal from the gas stream comprising carbon dioxide.

The introduction of the gas stream 2 fluidises the solid sorbent mixture, causing the solid sorbent mixture to behave like a turbulent fluid. The fluidisation of the solid sorbent mixture improves the contact between the solid sorbent mixture and the gas stream, increasing the rate at which the carbon dioxide is adsorbed by the solid sorbent mixture by improving the rates of mass and heat transfer.

As the gas stream 2 contacts the solid sorbent mixture inside the reactor 1, carbon dioxide is adsorbed from the gas stream 2 onto the solid sorbent mixture and the solid sorbent in the solid sorbent mixture is carbonated. Because of the high rates of mass and heat transfer, the majority of the carbon dioxide is able to be stripped from the gas by the solid sorbent in the order of seconds. The reaction (carbonation reaction) of the nanostructured metal hydroxide sorbent with the carbon dioxide gives a metal carbonate and water, according to Equation 3.

Equation 3 $Me(OH)_2 + CO_2 \text{-->} MeCO_3 + H_2O$

Where $Me(OH)_2$ is a metal hydroxide, CO_2 is carbon dioxide, $MeCO_3$ is a metal carbonate and H_2O is water.

After the gas stream 2 contacts the solid sorbent mixture, a carbon dioxide depleted gas stream 5 results and passes out of the fluidised bed reactor 1. If atmospheric air is used as the gas stream, the carbon dioxide depleted gas stream may be passed back to atmosphere. Alternatively, the carbon dioxide depleted gas stream may be used elsewhere for heating, cooling, ventilation, oxidation, or otherwise, or may be sent for further treatment.

Before being released to atmosphere or further treatment processes, the carbon dioxide depleted gas stream 5 is passed through one or more gas-solid separation units 4 to remove entrained particles of the solid sorbent mixture that may be elutriated in the carbon dioxide depleted gas stream 5. The separation unit 4 may for example be bag filters, a cyclone, an electrostatic precipitator (ESP), or any combination thereof. This prevents solid sorbent mixture particles being entrained and leaving the fluidised bed reactor with the carbon dioxide depleted gas stream. The one or more separation units 4 may be contained within the fluidised bed reactor, for example, in the case of a bag filter, or alternatively there may be one or more separation units outside the fluidised bed reactor, for example, in the case of a cyclone or ESP. Any other type of suitable separation units may be used.

The carbonation reaction inside the reactor 1 may be conducted in the presence of water or mixtures of water and solvents with low vapour pressures. The water or mixtures of water and solvents will form a thin layer on the surface of the solid sorbent mixture thereby increasing the rate of carbonation, which the inventors understand is a result of the liquid layer facilitating the absorption and the adsorption of carbon dioxide into the sorbent. Water or mixtures of water and solvents may be introduced in a number of ways, for example, an amount of water or mixture of water and organic solvents 6 may be directly introduced into the reactor. The solvents may, for example, be glycerol, liquid amines and/or ionic liquids. Introducing the water into the reactor may be achieved using an atomiser, internal spray nozzle or nebulizer, for example, or other suitable equipment. Smaller droplets may be desirable as they increase the surface area for carbon dioxide absorption. Alternatively, the gas stream may be humidified by, for example, passing the gas stream through a water tank, or other body of fluid. The gas stream may be humidified to approximately 100% H_2O. Alternatively, the solid sorbent mixture may be kept under humid conditions for several minutes to hours until the solid sorbent mixture is approximately fully hydrated before being exposed to the gas stream. The exact conditions will vary depending on, for example, the mass of sorbent to be hydrated.

Regeneration

Once the gas stream has contacted the solid sorbent mixture and the solid sorbent mixture is saturated with carbon dioxide, the solid sorbent mixture needs to be replaced as it has limited further carbon dioxide adsorption abilities and possibly can no longer adsorb carbon dioxide from the gas stream. Providing a gradient in gas stream velocity across the length of the fluidised bed reactor causes the solid sorbent mixture to move progressively from one side of the fluidised bed reactor (an entrance side 7) to a second side of the fluidised bed reactor (an exit side 8), and fresh solid sorbent mixture may be added in at the entrance side (i.e. a continuous process). Alternatively, the solid sorbent mixture may be moved from an entrance side to an exit side using any suitable method. For example, a vibrating fluidised bed could be used to vibrate the mixture from an entrance side to an exit side. After leaving the fluidised bed reactor, the solid sorbent mixture is regenerated i.e. the solid sorbent is regenerated. Alternatively, the solid sorbent mixture may be regenerated in the fluidised bed reactor (i.e. a batch process). Regeneration involves thermal processing to destroy adsorbed components contained on the surface of the sorbent.

Figure 2 shows a set-up configured so that the solid sorbent mixture is passed to a second reactor (a calciner reactor 9) and heated (by heat source 10) in order to release the carbon dioxide from the solid sorbent and to regenerate the solid sorbent. Alternatively, the solid sorbent mixture may be regenerated within the fluidised bed reactor. The solid sorbent mixture may be heated using, for example, heaters, microwave heating, electric heating, gas fired heating, radiative heating, heating via waste heat gas streams or any other suitable method as the heat source 10. The solid sorbent mixture is heated to approximately 500-900°C for approximately 1-60 minutes at ambient pressure.

Upon heating, the carbon dioxide adsorbed to the solid sorbent is released, according to Equation 4.

Equation 4 $MeCO_3 + Heat \rightarrow MeO + CO_2$

Where $MeCO_3$ is a metal carbonate, MeO is a metal oxide and CO_2 is carbon dioxide.

The released carbon dioxide is removed from the calciner reactor 9 using a gas stream 11 which is introduced into the calciner reactor 9 using one or more fans 12. There may be more than one gas stream 11. The gas stream may be a stream of carbon dioxide, steam or a mixture of carbon dioxide and steam. The steam may be superheated using a superheater and/or electric heat sources (such as electric heating coils) and/or a pre-heater.

The gas stream used to remove the carbon dioxide from the calciner reactor 9 is passed through one or more gas-solid separation units 13 to remove entrained particles of the solid sorbent mixture. The gas-solid separation units may for example be bag filters or cyclone filters. The gas-solid separation units may be contained within the calciner, for example, in the case of a bag filter, or alternatively there may be one or more filters outside the calciner, for example, in the case of a cyclone filter.

If the gas stream contains steam, the gas stream is cooled and condensed in condenser 14 after regeneration, producing a water stream 15 and a stream of pure carbon dioxide 16. If the gas stream 11 used to remove the carbon dioxide is pure carbon dioxide, no cooling or condensing is necessary. A heat exchanger may be used to recover excess heat as a result of condensation. The recovered excess heat may be used in a heater (e.g. a superheater or a pre-heater) to heat the gas stream 11 and/or a gas stream for another reactor or apparatus and/or steam.

The stream of pure carbon dioxide 16 may be compressed using compressor 17 to produce a compressed stream of pure carbon dioxide 18. The stream of carbon dioxide 16 may, for example, be compressed to between 100 and 150 bar. A four-stage centrifugal compressor may, for example, be used to compress the carbon dioxide. The compressed carbon dioxide may be sequestered for storage or utilisation.

Reactivation

Once the carbon dioxide has been desorbed from the solid sorbent mixture, the nanostructured sorbent is reactivated according to Equation 5.

Equation 5 $MeO + H_2O \dashrightarrow Me(OH)_2 + \text{Heat}$

Where MeO is a metal oxide, H_2O is water, and $Me(OH)_2$ is a metal hydroxide.

Steam 19 is used to reactivate the sorbent and to cool the sorbent after the regeneration step. The steam has been found to create a nano-structured reaction surface area on the metal hydroxide solid sorbent, and produces a hydrated material for enhanced carbonation rates in the adsorption step. The reaction according to Equation 5 also produces heat which may be captured using a heat exchanger. The captured heat may be used in a heater (e.g. a superheater or a pre-heater) to heat the gas stream 11 and/or the steam 19 and/or a gas stream for another reactor or apparatus and/or steam for another reactor or apparatus. Although reactivation occurs in the same reactor as the regeneration of the solid sorbent in this example, it will be readily understood that a separate reactor could be used for reactivation of the sorbent. The reactivation reaction between the steam 19 and solid sorbent may be carried out at a temperature of between ambient and 900°C. The temperature is chosen to ensure mechanical stability and reactivity of the solid sorbent particles.

The rate of desorption in the regeneration step is fast compared to the rate of adsorption, and therefore the solid sorbent mixture from multiple fluidised bed reactors may be fed into a single calciner 9.

Once the solid sorbent mixture has been regenerated and reactivated, it can be recycled and added back into the fluidised bed reactor to remove more carbon dioxide from the gas stream.

Other methods for reactivating the sorbent may be used. For example, the carbonation reaction may occasionally be run for longer than would otherwise be needed and this has been found to result in the solid sorbent being carbonated beyond the usual amount in the cycle. It has been found that on an extended carbonation cycle of this type the material becomes denser than on usual shorter cycles and it is believed that as a result of this, when the material is subsequently calcined in the regeneration step, the CO_2 molecules that are released leave behind new and/or renewed internal pore space and reactive surface area. Accordingly, when the solid sorbent is regenerated in accordance with this method, there can advantageously be more effective pore space and reactive surface area available compared to the non-regenerated sorbent but also compared to the original fresh sorbent material.

Alternatively, during the calcination step, it is possible to rapidly heat the solid sorbent in the presence of gas flow. This results in the formation of interior reactive areas from the fast exit/explosion of CO_2 and H_2O molecules from calcium carbonate and calcium hydroxide solid particles.

A series of sensors are used to monitor the temperature, pressure, humidity, gas velocity, gas concentrations, gas flow rate and other parameters within the reactors, and both before entering the one or more reactors and after exiting the one or more reactors.

The system of the invention may comprise an integrated humidity control system for supply air, whereby the system may include one or more of:

- A relative humidity sensor (e.g. a hygrometer) in a supply duct;
- A humidifier (e.g. an air atomiser) for humidification of ambient air;
- A dust collector (e.g. a dust collection cyclone).

The fluidised bed reactor and the calciner may be housed within either a 20ft long shipping container or a 40ft shipping container.

Experimental

Figure 3a shows a photograph of a lab-scale fluidised bed reactor used to remove carbon dioxide from ambient atmospheric air using sorbents by way of a method according to the present disclosure. Figure 3b shows a piping and instrumentation diagram (P&ID) of the set-up of Figure 3a.

The fluidised bed reactor shown in Figure 3a was made of quartz and had an internal diameter of 15 mm. The fluidised bed reactor was fitted with a thermocouple to enable in-situ temperature measurements during the experiments. The fluidised bed reactor had an inlet which can be used to pass steam at 170°C, ambient air and/or nitrogen into the reactor with the use of external mass flow controllers (Bronkhurst MFCs) and through the sorbent bed. The sorbent bed inventory used (that is, the amount of sorbent used) for each experiment was ~2.5–3 ml to result in an un-fluidised sorbent bed height of ~11–13 mm. Steam was generated using a water pump. The fluidised bed reactor is used for both the carbonation and calcination reactions. A quartz filter is fitted on the outlet of the fluidised bed reactor and is designed to remove any elutriated sorbent material from the outlet gas. After passing through the filter, the outlet gas is cooled using an ice bath and is then pumped to a gas analyser.

Figure 4 shows experimental data obtained using the set-up shown in Figures 3a and 3b. Figure 4 shows how the concentration of carbon dioxide in the outlet gas changes over time, in response to changes in the reactor operating temperature. The fluidised bed was initially filled with a Havelock limestone as the sorbent material in metal carbonate form comprising a nanostructure (a nanostructured sorbent) as defined herein obtainable by, for example, calcining in fluidised conditions. The particle sizing of the sorbent material was between 250 and 425 μm.

At time 0 minutes, the temperature within the reactor is ambient and the concentration of carbon dioxide is close to that expected in ambient air i.e. 400 ppm. This stage is shown on Figure 4 as stage (1). During stage (2), the ambient air flow is replaced with nitrogen, and the carbon dioxide concentration is reduced to approximately 0 ppm. At the same time, the reactor system is heated to 800°C which results in a large spike in carbon dioxide concentration in the outlet gas as carbon dioxide is released from the sorbent material. The carbon dioxide concentration eventually returns to close to 0 ppm as all the carbon dioxide is released from the sorbent material and the temperature of the reactor system tends back towards ambient. In stage (3), the nitrogen flow through the fluidised bed reactor is replaced with ambient air. As the air contacts the sorbent material, the temperature in the reactor increases slightly as a result of the exothermic carbonation reaction. The carbon dioxide concentration in the outlet gas stays at approximately 0 ppm as the carbon dioxide is being adsorbed by the sorbent material, showing nearly complete removal of carbon dioxide from the inlet ambient air. In stage (4), the gas sampling line ultimately attached to the CO_2 analyser (via the filters, ice bath, and pump), was removed from the reactor to measure the concentration of carbon dioxide in ambient conditions, to confirm the initial reading from stage (1). In stage (5), the temperature in the reactor is increased to approximately 800°C and the carbon dioxide adsorbed by the sorbent during stage (3) is released and the sorbent is regenerated. The flow rate of ambient air and/or nitrogen during the process shown in Figure 4 was maintained at 700 ml/min. It has been found that a higher flow rate of 1000 ml/min of air and/or nitrogen should be used if particle sizing in the range of 500 – 710 μm is used for the sorbent material.

Figure 5 shows the results of a thermogravimetric analysis carried out on the two sorbent materials using the reactor set up shown in Figures 3a and 3b, one sorbent being a metal oxide sorbent (Havelock limestone) and a second a mixed metal oxide sorbent (a synthesised mixed metal oxide sorbent comprising 85% Ca and 15% Mg). The mixed metal oxide sorbent used was synthesised by the hydrothermal treatment of an aqueous solution of xylose, urea, and glycine together with calcium and magnesium precursors at 180°C for 24 hours and simultaneous hydrolysis of urea, precipitating a mixture of $CaCO_3$ and MgCO, followed by calcination in air at 800°C, removing the carbonaceous template and creating internal nanostructured pores. Both sorbents were in fine powder form (<50μm).

Figure 5 shows the change in temperature and normalised weight of the mixed metal oxide sorbent and the metal oxide sorbent. A thermogravimetric analyser was used to determine the changes in normalised weights of the sorbents (occurring as a result of calcination, hydration and carbonation of the sorbents). At the beginning of the experiments, the fluidised bed was initially filled with carbonate forms of the sorbents.

From 0-50 minutes, the temperature inside the reactor is increased from ambient to 800°C and the carbonated metal sorbents are calcined, releasing carbon dioxide and reducing their normalised weight to approximately 0. The temperature in the reactor was then reduced and reaches 50°C around 100 minutes. From 100 minutes to 400 minutes, moist air at ambient temperature is passed through the fluidised bed and the metal oxides increase in weight due to a combination of carbonation and hydration. At 400 minutes, the air is replaced with nitrogen and the temperature in the reactor is increased from ambient to 800°C. There are three clear step changes in the normalised weight of the metal oxides during this temperature increase: the first occurs as a result of excess water in the sorbents being evaporated, the second is a result of water chemically bonded to the sorbent material being dehydrated, and the third is a result of the carbon dioxide being desorbed from the sorbent. These three step changes are shown as stages (1), (2) and (3) on Figure 5. It is clear from Figure 5 that the mixed metal oxide sorbent shows a much-improved carbonation capacity (>10%) compared to the metal oxide sorbent.

Figure 6 shows the change in temperature and normalised weight of a metal oxide sorbent (Havelock limestone, with particle size <50μm) over repeated cycles of calcination and carbonation of the sorbent material. At time 0 mins, the temperature in the reactor is increased to approximately 800°C and nitrogen is fed to the reactor. The normalised weight of the metal oxide sorbent is reduced to 0. The temperature in the reactor is then reduced and the nitrogen is replaced with ambient air. The normalised weight of the metal oxide increases to approximately 0.4 as the sorbent adsorbs carbon dioxide. This cycle of calcination and carbonation was repeated four further times. In the last cycle, the normalised weight of the metal oxide increased to approximately 0.35. This shows that the sorbent material is relatively chemically stable and has large CO_2 adsorption capacities.

Non-limiting examples of embodiments of the invention and features thereof are described as follows, and may be implemented in or as part of, or combined with, any embodiment of the invention described in this specification.

Figure 7 shows an exemplary horizontal, static fluidised bed reactor 20 for capturing carbon dioxide from air. The fluidised bed reactor 20 is suitable for use with a range of nanostructured sorbents, particularly calcium oxide and calcium carbonate. In a preferred embodiment, the fluidised bed reactor 20 has a total of 29 m^2 fluidised area, by way of a gas distributor plate, and a filtration area of 1600 m^2, which allows an air velocity of 1.5 m/s through the fluidised bed surface. A dividing plate is provided between drying areas of a drying section. An overflow weir (e.g. a pneumatically actuated overflow weir) is provided at the end of the drying section. Product layer thickness is adjustable by manually changing the weir height when the fluidised bed reactor 20 is offline. An airlock valve (e.g. a rotary airlock valve) may be mounted at an inlet of the fluidised bed reactor.

Optionally the fluidised bed reactor 20 includes a separation unit in the form of an exhaust gas filter 22 integrated into a suction hood, which can be operated to keep fine product particles inside the fluidised bed reactor 20. Preferably the exhaust gas filter 22 is a pulse-jet filter. As stated above, the filtration area of the filter 22 is exemplarily 1600 m^2. Bag filters of the filter 22 may be made of fabric, such as polyester needle felt. The fluidised bed reactor 20 may include one or more exhaust fans 24 (e.g. a centrifugal fan) that is connected to the exhaust gas filter 22 by ductwork. The one or more exhaust fans 24 are configured to direct the exhaust gas from the exhaust gas filter 22 to one or more exhaust ports 26 (e.g. a chimney).

Figure 8 shows an exemplary electric fluidised bed calciner system.

The calciner system includes an electric heating jacket 28 wrapped around a calciner reactor 30. Optionally, the electric heating jacket 28 may be configured to provide separate heating at different temperatures to different zones of the calciner reactor 30, which can be used to provide a temperature gradient inside the calciner reactor 30. The electric heating jacket 28 may be replaced by a different type of heater.

The calciner system further includes an inlet gas distributor (e.g. an inlet gas distribution nozzle), a filter 32 (e.g. a high temperature metallic filter) and a steam heater 34 (e.g. a steam superheater). The filter 32 is configured as a separation unit to remove solid particles from the exhaust gas leaving the calciner reactor 30. Hot CO_2 exits the base of the filter 32. The steam heater 34 is in the form of a once-through boiler that recovers heat from the calciner exhaust gas, thereby cooling the calciner exhaust gas. The recovered heat is used to boil water, which enters the steam heater 34 at ambient temperature, in order to raise steam that can be used as a fluidising gas inside the calciner reactor 30 or be used in a different reactor or apparatus.

The calciner system further includes an internal gas-solid heat exchanger 36 (e.g. a coil/solid pneumatic transport tube) inside and at/near the base of the calciner reactor. The solid sorbent material (e.g. a mixture of calcium carbonate and calcium hydroxide) enters the calciner reactor 30 via a feed port 38 which is preferably located in or near the ceiling of the calciner reactor 30, while metal oxide from the regeneration process exits the calciner reactor 30 via a discharge port 40 which is preferably located in/near the base of the calciner reactor. Preferably the calciner reactor 30, the filter 32 and the steam heater 34 are partially or completely enclosed in insulation material to minimise heat loss and limit surface temperature.

The calciner in embodiments of the invention may be a rotary calciner (e.g. a rotary kiln). That is to say, the rotary calciner may replace the fluidised bed calciner. The rotary calciner may, for example, comprise one or more of a rotary calciner shell, a furnace (e.g. an electrically heated furnace, optionally with 330 kW or 550kW nominal capacity), internal insulation (e.g. ceramic fibre insulation), high temperature heating elements, multi-zone temperature control, and end seals for heat conservation (e.g. ceramic fiber tadpole end seals). A drive system for the rotary calciner may include a chain-drive system, an auxiliary drive and a mechanical gear reducer.

Preferably the calciner in embodiments of the invention may interact, or may be combined or integrated, with an additional heat exchanger system for pre-heating cold solids entering the calciner and cooling (and recovering heat from) hot solids leaving the calciner.

Figures 9 and 10 show examples of parallelly arranged fluidised bed sub-units 41 of a fluidised bed reactor, preferably for use as a carbonator in the system of the invention. In embodiments of the invention, the gas comprising carbon dioxide 42 is distributed to flow in parallel through the parallelly arranged fluidised bed sub-units 41 so as to be contacted with the solid sorbent mixture 44 in a plurality of parallelly arranged fluidised bed sub-units 41. A respective portion of the gas comprising carbon dioxide 42 is contacted (preferably simultaneously contacted) with the solid sorbent mixture 44 in each of the plurality of parallelly arranged fluidised bed sub-units 41. In the embodiment shown, the fluidised bed sub-units 41 are housed within a same enclosure of the fluidised bed reactor. Each fluidised bed sub-unit 41 is associated with a respective gas distributor (e.g. a gas distributor plate) through which the gas is introduced to the fluidised bed sub-unit 41.

Preferably the fluidised bed sub-units 41 are stacked on top of each other to form a vertical stack of fluidised bed sub-units 41, but in other embodiments the stack of fluidised bed sub-units 41 may be substantially or nearly vertical. In other embodiments, the fluidised bed sub-units 41 may be arranged at different heights but in different vertical planes so that the fluidised bed sub-units 41 are not stacked on top of each other. In further other embodiments, the fluidised bed sub-units 41 may be arranged in the same horizontal plane.

It will be appreciated that the parallelly arranged fluidised bed sub-units 41 may form an integrated arrangement, array or stack of fluidised bed sub-units 41, or may be in the form of modules that can be freely assembled and disassembled to form arrangements, arrays or stacks of modules in different layouts and/or of different numbers, which depend on the performance and footprint requirements of the system.

The parallelly arranged fluidised bed sub-units 41 may share the same gas inlet 46 (Figure 9) or may have respective individual gas inlets in other embodiments. The fluidised bed sub-units 41 may share the same gas outlet 48 (Figure 9) or may have respective individual gas outlets in other embodiments.

The parallelly arranged fluidised bed sub-units 41 may share the same solid inlet for feeding of solid material or may have respective individual solid inlets 47 (Figure 10). The parallelly arranged fluidised bed sub-units 41 may share the same solid outlet 49 for discharge of solid material (Figure 10) or may have respective individual solid outlets.

The vertical stacking of the gas comprising carbon dioxide 42 through the parallelly arranged fluidised bed sub-units 41 ensures that the pressure drop across each fluidised bed sub-unit 41 is the same (which controls fan electricity costs) but permits an increased volumetric throughput of the gas and thereby an increased amount of captured CO_2 for a given reactor size and footprint. This in turn improves carbonation efficiency and allows reductions in the overall size and material requirements of the carbonator while maintaining a desired performance, and thereby reduces the capital expenditure requirements of the system as a whole.

Furthermore, the parallel nature of the fluidised bed sub-units 41 enables scaling of the carbonator’s capacity by adding fluidised bed sub-units vertically and/or laterally. Such flexibility in scaling enables ready deployment and installation of the system in a variety of locations and for a variety of application requirements.

In alternative embodiments, the parallelly arranged fluidised bed sub-units 41 may be replaced by a plurality of parallelly arranged fluidised bed reactors, which are distinct units from each other.

In embodiments of the invention, the system may include a heat recovery mechanism, particularly for heat recovery from hot solids leaving a reactor (e.g. a calciner) and for using the recovered heat to heat cold solids before entering a reactor (e.g. a calciner).

The system may comprise an air flow circuit including a driving fan to circulate air as a heat transfer medium between heat exchanger fluidised beds;

The system may comprise a cooling apparatus, for example in the form of a hydration chamber, preferably with a fluidised bed rector design, more preferably with a counterflow (and/or crossflow) arrangement of solids and gases to maximise heat recovery efficiency. The hydration chamber is connected, preferably integrally, to the inlet to the carbonator. The hydration chamber may include water sprays for hydration and cooling of the incoming material. The hydration chamber is configured to discharge cooled solid material to the carbonator. An airlock (e.g. a mechanical rotary airlock) may be employed to control the discharging of material to the carbonator while maintaining a positive gas seal between the hydration chamber and carbonator to prevent steam egress from the hydration chamber. The solid material may exit the hydration chamber via an overflow weir, with a manual underflow gate for discharge of material during clean-out. The hydration chamber is preferably made of a material capable of withstanding high temperatures, such as stainless steel, and may be enclosed in insulation material.

The system may comprise a heating apparatus, for example in the form of a pre-heater chamber, preferably with a fluidised bed rector design, more preferably with a counterflow (and/or crossflow) arrangement of solids and gases to maximise heat recovery efficiency. Hot gas is used to pre-heat solids, whereby the hot gas may be taken from the exhaust of the hydration chamber. The cooled exhaust gas from the pre-heater chamber may optionally be used as a fluidising gas in the hydration chamber. The pre-heater chamber is preferably made of a material capable of withstanding high temperatures, such as stainless steel, and may be enclosed in insulation material.

The system may comprise both the cooling and heating apparatus.

Figures 11 and 12 show an exemplary system comprising an integrated carbonator and calciner assembly. The assembly includes a carbonator 50, a calciner 52, a pre-heater 54 and a hydration chamber 56. The carbonator 50 is a single plate, fluidised bed reactor, while the calciner 52 is an electric fluidised bed reactor. A fluidising gas used in the calciner 52 may be in the form of steam that may be heated by a superheater, which may use heat recovered from the exhaust 58 of the hydration chamber 56. The pre-heater 54 is configured to heat solid material before it is fed to the calciner 52. The hydration chamber 56 is configured to hydrate and cool solid material received from the calciner 52 by way of a gravity feed. The hydration chamber 56 is configured to discharge cooled solid material to the carbonator 50 by way of a gravity feed. In the embodiment shown, the hydration chamber 56 is integrally connected between the calciner 52 and the carbonator 50.

The cooling apparatus may be configured to include a plurality of parallelly or sequentially arranged cooling stages for cooling the solid material. Each cooling stage may have a fluidised bed reactor design. For example, the cooling apparatus may include a plurality of vertically and sequentially arranged cooling stages, whereby the solid material (e.g. from the calciner) is conveyed downwards (e.g. by gravity) from a chamber of the top cooling stage, through the chamber(s) of the intermediate cooling stage(s) and to the chamber of the bottom cooling stage, while a cooling gas flows upwards from the chamber of the bottom cooling stage, through the chamber(s) of the intermediate cooling stage(s) and to the chamber of the top cooling stage. In an exemplary embodiment, the top cooling stage(s) may reduce the temperature of the solid material exiting a calciner reactor to 100°C from 850°C. The next cooling stage(s) introduces water (e.g. using an atomiser or spray) to hydrate the solid material exothermically and raise its temperature to approximately 300°C. The remaining cooling stage(s) will then cool the solid material to close to ambient temperatures before entering the carbonator reactor. The fluidising gas entering the bottom cooling stage and travelling upwards the chain of cooling stages will be ambient air, and will increase in temperature to close to 750-800°C towards the end of the chain of cooling stages. It will be appreciated that the stated temperatures are exemplary only to illustrate the working principle of this embodiment.

The heating apparatus may be configured to include a plurality of parallelly or sequentially arranged heating stages for heating the solid material. Each heating stage may have a fluidised bed reactor design or flash cyclone design. For example, the heating apparatus may include a plurality of vertically and sequentially arranged heating stages, whereby the solid material (e.g. from the carbonator) is conveyed downwards (e.g. by gravity) from a chamber of the top heating stage, through the chamber(s) of the intermediate heating stage(s) and to the chamber of the bottom heating stage, while a heating gas flows upwards from the chamber of the bottom heating stage, through the chamber(s) of the intermediate heating stage(s) and to the chamber of the top heating stage. In an exemplary embodiment, cool solids from the carbonator will enter the top heating stage and are heated in counterflow with the heating gas flowing through the heating stages, whereby the heating gas may originate from the cooling stages. The solid materials leave the bottom heating stage at a temperature around 500-550°C before entering the carbonator reactor. The hydroxide material will dehydrate and release steam which can be recycled to a cooling or hydrator equipment (such as the examples described throughout the specification). The temperature in the heating apparatus is kept below 550°C, preferably below 500°C, so as to ensure calcination does not occur and thus release and waste the desired product CO_2 into the air stream.

The number of cooling and/or heating stages may be configured to provide a high cooling/heating throughout to achieve a high percentage of heat recovery. The system may include one or more passive flow controllers, such as mechanical deflectors or guide channels, or one or more active flow controllers, such as fans, to guide the gas to flow in parallel through the parallelly arranged cooling stages.

The counterflow and staged arrangement improves the heat recovery compared to single stage equilibrium fluid bed reactors, thus achieving high heat recovery efficiency while recovering hydration reaction heat and reduce the electric load on the calciner.

Figure 13 shows an exemplary system based on a calciner having a fluidised bed reactor design. The system comprises a carbonator 60, a calciner 62 and a hydration chamber 64.

Solid sorbet mixture is fed from a sorbent supply 61 to a sorbent hopper 66 for storage. Once the sorbent hopper 66 is filled with the required amount of solid sorbent mixture, the supply of solid sorbent mixture may be stopped. The sorbent hopper 66 may be topped up with additional solid sorbent mixture as necessary.

Air (i.e. the gas comprising carbon dioxide) is supplied, using a carbonator inlet fan 68, to provide a fluidising gas to the carbonator 60. Water in droplet form may be added to the air using, for example, an atomiser or sprayer 70. The water may be sourced from a mains water source 63 and optionally a condensate return 65.

The sorbent hopper 66 dispenses a controlled amount of solid sorbent mixture into a screw conveyor 72. The solid sorbent mixture is transferred by the screw conveyor 72 to a sorbent heating apparatus 74, through the calciner 62 and then to a sorbent cooling apparatus 76 (or alternatively may be directly transferred by the screw conveyor 72 to the sorbent cooling apparatus 76). The solid sorbent mixture is hydrated using the hydration chamber 64 before being transferred into the carbonator 60, inside which the fluidising gas is contacted with the solid sorbent mixture. Thereafter, the carbonator 60 outputs the solid sorbent mixture onto a conveyor belt 78 that transfers the solid sorbent mixture back to the sorbent hopper 66.

Water is supplied to the hydration chamber 64 from the mains water source 63 and optionally the condensate return 65. Air is supplied, using a hydrator fan 80, to provide a fluidising gas to the hydration chamber 64. Water in droplet form may be added to the air using, for example, an atomiser or sprayer 70. The water may be sourced from the mains water source 63 and optionally the condensate return 65.

After being contacted with the gas comprising carbon dioxide, the solid sorbent mixture entering the sorbent hopper 66 is then conveyed to the sorbent heating apparatus 74 for pre-heating before entering the calciner 62. A heating gas for the sorbent heating apparatus 74 may be taken from the exhaust of the hydration chamber 64 and/or the cooling apparatus 76. Steam heated by a steam superheater 82 is provided as the fluidising gas to the calciner 62. The water for the steam may be provided by the mains water source 63 and optionally the condensate return 65. The water may pass through a boiler 84 that recovers heat from exhaust gas leaving the calciner 66. A separation unit 86 separates the exhaust of the calciner and the boiler.

The regenerated solid sorbent mixture is then conveyed from the calciner 62 to the sorbent cooling apparatus 76 and hydration chamber 64 for hydration and cooling before being conveyed to the carbonator 60.

Figures 14, 15 and 16 show alternative layouts for the system of the invention, particularly based on a calciner 88 having an electric rotary kiln calciner design. The components of the systems of Figures 14, 15 and 16 are similar in structure and operation to the corresponding components of the system of Figure 13, and like features share the same reference numerals. Additional components may include one or more of a carbon dioxide cooler 90, a condensate knock-out drum 92, a circulation fan 94 and a carbonator outlet fan 96. In Figure 14, the cooled exhaust gas from the sorbent heating apparatus 76 may optionally be used as a fluidising gas in the hydration chamber, whereby the cooled exhaust gas may be circulated using the circulation fan 94 and may have water added to it. In Figure 16, the carbonator 98 is based on an arrangement of parallelly arranged fluidised bed reactors, examples of which are described throughout the specification.

It will be appreciated that the numerical values used in the description and drawings are merely intended to help illustrate the working of the invention and may vary depending on the requirements of the invention and associated applications.

The listing or discussion of an apparently prior-published document or apparently prior-published information in this specification should not necessarily be taken as an acknowledgement that the document or information is part of the state of the art or is common general knowledge.

Preferences and options for a given aspect, feature or parameter of the invention should, unless the context indicates otherwise, be regarded as having been disclosed in combination with any and all preferences and options for all other aspects, features and parameters of the invention.

CLAIMS

1. A method for removing carbon dioxide from a gas comprising carbon dioxide, the method comprising:

contacting the gas comprising carbon dioxide with a fluidised solid sorbent, thereby removing carbon dioxide from the gas and forming a carbon dioxide depleted gas.

2. A method according to claim 1, wherein the gas comprising carbon dioxide is contacted with the solid sorbent in the presence of water or one or more solvents or a mixture of water and one or more solvents.

3. A method according to claim 2, wherein the water is provided by humidifying the gas comprising carbon dioxide to a humidity of approximately 100%, or by bubbling the gas comprising carbon dioxide through water prior to being contacted with the solid sorbent.

4. A method according to any preceding claim, whereby the gas comprising carbon dioxide is contacted with the solid sorbent in one or more reactors.

5. A method according to claim 4, whereby the one or more reactors is one or more fluidised bed reactors.

6. A method according to claim 5, wherein the one or more fluidised bed reactors have a width to length aspect ratio in the range of 1:1 to 1:20, preferably 1:5, more preferably 1:3.

7. A method according to any one of claims 5-6, wherein the gas comprising carbon dioxide is contacted with the solid sorbent in each of a plurality of parallelly arranged fluidised bed reactors.

8. A method according to claim 7, wherein the fluidised bed reactors are stacked on top of each other to form a vertical stack of fluidised bed reactors.

9. A method according to any one of claims 5-8, wherein the one or more fluidised bed reactors include a plurality of parallelly arranged fluidised bed sub-units, wherein the gas comprising carbon dioxide is contacted with the solid sorbent in each of the plurality of parallelly arranged fluidised bed sub-units.

10. A method according to claim 9, wherein the fluidised bed sub-units are stacked on top of each other to form a vertical stack of fluidised bed sub-units.

11. A method according to any one of claims 5-10, wherein one or more gas distributors are provided through which the gas is introduced to the one or more fluidised bed reactors.

12. A method according to any one of claims 5-11, wherein one or more fans are provided to introduce the gas into the one or more fluidised bed reactors.

13. A method according to any one of claims 5-12, wherein the solid sorbent is moved from a solid inlet along the length of the one or more fluidised bed reactors to a solid outlet.

14. A method according to claim 13 when dependent on claim 12, wherein the one or more fans are configured to move the solid sorbent from the solid inlet along the length of the one or more fluidised bed reactors to the solid outlet, optionally wherein the one or more fans are configured to progressively move the solid sorbent from the solid inlet along the length of the one or more fluidised bed reactors to the solid outlet.

15. A method according to any one of claims 5-14, wherein one or more separation units are provided through which the carbon dioxide depleted gas is filtered.

16. A method according to claim 15, wherein the one or more separation units are or include a filter, a bag filter, a gas cyclone or an electrostatic precipitator (ESP).

17. A method according to any preceding claim, wherein the gas comprising carbon dioxide is contacted with the solid sorbent at a temperature of between 450°C and ambient and a pressure of between 1 and 1.5 bar.

18. A method according to any preceding claim, further comprising a step of regenerating the solid sorbent, thereby releasing carbon dioxide from the solid sorbent and creating a carbon dioxide concentrated gas.

19. A method according to claim 18, whereby the solid sorbent is regenerated in a second reactor or a kiln.

20. A method according to any one of claims 18-19, whereby the solid sorbent is regenerated by heating the solid sorbent to a temperature of approximately 500-900°C.

21. A method according to any one of claims 18-20, further comprising the step of collecting the carbon dioxide concentrated gas.

22. A method according to any one of claims 18-21, further comprising the step of reactivating the solid sorbent.

23. A method according to claim 22, whereby the solid sorbent is reactivated in the presence of steam, at a temperature of between ambient and 900°C.

24. A method according to any preceding claim, whereby the gas comprising carbon dioxide is atmospheric air.

25. A method according to any preceding claim, whereby the gas comprising carbon dioxide comprises carbon dioxide in a concentration less than 1000 ppm, more preferably less than 800 ppm, more preferably less than 600 ppm and more preferably less than 500 ppm.

26. A method according to any preceding claim, whereby the solid sorbent comprises particles of the solid sorbent and optionally comprises silica particles, said particles of solid sorbent and silica having an average particle diameter of less than 2500 microns.

27. A method according to any preceding claim, wherein the solid sorbent has an average particle diameter of between 20-2000 microns and an internal surface area of between 1-200m^2/g.

28. A method according to any preceding claim, wherein the solid sorbent is a mixed metal oxide or a mixed metal hydroxide, and wherein the metal oxide or metal hydroxide comprises one or more of Ca, Mg, Si, Al, Fe, W, Mn, Cu, Zn, Xo, Sr, Cd, Ba and Ni.

29. A method according to claim 28, wherein the solid sorbent comprises a mixed metal oxide or a mixed metal hydroxide comprising Ca, and optionally further comprising one or more of Mg, Si, Al, Fe, W, Mn, Cu, Zn, Xo, Sr, Cd, Ba and Ni.

30. A method according to any preceding claim, wherein the solid sorbent comprises one or more salts, hydroxides, nitrates, nitrites and/or carbonates of Li, Na and/or K and any combination of HBr, HCl, HNO_3 and HI.

31. A method according to any preceding claims, wherein the solid sorbent is Havelock limestone or a mixed metal oxide comprising 85 wt% Ca and 15 wt% Mg.

32. A method according to any preceding claim including the step of cooling solid material that has left a reactor, preferably a calciner reactor, wherein the solid material is cooled using a cooling gas.

33. A method according to claim 32 including the step of conveying the solid material in counterflow with the cooling gas.

34. A method according to claim 33 including the step of conveying the solid material in counterflow with the cooling gas using gravity.

35. A method according to claim 32 including the step of conveying the solid material in crossflow with the cooling gas.

36. A method according to any one of claims 32-35 including the step of cooling the solid material in a plurality of cooling stages.

37. A method according to claim 36, wherein the plurality of cooling stages includes a plurality of parallelly arranged cooling stages configured to, in use, cool respective portions of the solid material using the cooling gas.

38. A method according to claim 36 or claim 37, wherein the plurality of cooling stages includes a plurality of sequentially arranged cooling stages configured to, in use, sequentially cool the solid material using the cooling gas.

39. A method according to any one of claims 32-38 including the step of hydrating the solid material.

40. A method according to claims 38 and 39 including the step of hydrating the solid material received from one of the plurality of sequentially arranged cooling stages,

and/or hydrating the solid material and providing the hydrated material to another of the plurality of sequentially arranged cooling stages.

41. A method according to any one of claims 32-40 including the step of using one or more fluidised bed coolers to cool the solid material using the cooling gas, wherein the cooling gas is a fluidising gas.

42. A method according to any one of claims 32-41 wherein the cooling gas is ambient air.

43. A method according to any one of claims 32-42 including the step of providing the cooled solid material to a reactor, preferably a carbonator reactor.

44. A method according to any one of claims 32-43 including the step of recovering heat from the cooling of the solid material.

45. A method according to any preceding claim including the step of heating solid material using a heating gas prior to the solid material entering a reactor, preferably a calciner reactor.

46. A method according to claim 45 including the step of conveying the solid material in counterflow with the heating gas.

47. A method according to claim 46 including the step of conveying the solid material in counterflow with the heating gas using gravity.

48. A method according to claim 45 including the step of conveying the solid material in crossflow with the heating gas.

49. A method according to any one of claims 45-48 including the step of heating the solid material in a plurality of heating stages.

50. A method according to claim 49, wherein the plurality of heating stages includes a plurality of parallelly arranged heating stages configured to, in use, heat respective portions of the solid material using the heating gas.

51. A method according to claim 49 or claim 50, wherein the plurality of heating stages includes a plurality of sequentially arranged heating stages configured to, in use, sequentially heat the solid material using the heating gas.

52. A method according to any one of claims 45-51 including the step of using one or more fluidised bed heaters to cool the solid material using the heating gas, wherein the heating gas is a fluidising gas.

53. A method according to any one of claims 45-52 including the step of using one or more cyclone flash heaters to heat the solid material using the heating gas.

54. A method according to any one of claims 45-53 including the step of receiving the to-be-heated solid material from a reactor, preferably a carbonator reactor.

55. A method according to any one of claims 45-54 including the step of maintaining a solid material heating temperature of below 550°C, preferably below 500°C.

56. A method according to claim 44 in combination with any one of claims 45-55, the method including the step of heating the heating gas using recovered heat from the cooling of the solid material.

57. A method according to any preceding claim wherein the solid sorbent is a solid sorbent mixture.

58. A method according to any preceding claim wherein the solid sorbent is or comprises a nanostructured sorbent.

59. A system for removing carbon dioxide from a gas comprising carbon dioxide, the system comprising a solid sorbent, wherein the system is configured to, in use, contact the gas comprising carbon dioxide with the fluidised solid sorbent, thereby removing carbon dioxide from the gas and forming a carbon dioxide depleted gas.

60. A system according to claim 59, wherein the system is configured to, in use, contact the gas comprising carbon dioxide with the solid sorbent in the presence of water or one or more solvents or a mixture of water and one or more solvents.

61. A system according to claim 60, wherein the system is configured to, in use, humidify the gas comprising carbon dioxide to a humidity of approximately 100% so

as to provide the water, or wherein the system is configured to, in use, bubble the gas comprising carbon dioxide through water prior to being contacted with the solid sorbent.

62. A system according to any one of claims 59-61, wherein the system includes one or more reactors configured to, in use, contact the gas comprising carbon dioxide with the solid sorbent.

63. A system according to claim 62, whereby the one or more reactors is one or more fluidised bed reactors.

64. A system according to claim 63, wherein the one or more fluidised bed reactors have a width to length aspect ratio in the range of 1:1 to 1:20, preferably 1:5, more preferably 1:3.

65. A system according to any one of claims 63-64 including a plurality of parallelly arranged fluidised bed reactors configured to, in use, contact the gas comprising carbon dioxide with the solid sorbent, wherein the gas comprising carbon dioxide is contacted with the solid sorbent in each of the plurality of parallelly arranged fluidised bed reactors.

66. A system according to claim 65, wherein the fluidised bed reactors are stacked on top of each other to form a vertical stack of fluidised bed reactors.

67. A system according to any one of claims 63-66, wherein the one or more fluidised bed reactors include a plurality of parallelly arranged fluidised bed sub-units configured to, in use, contact the gas comprising carbon dioxide with the solid sorbent, wherein the gas comprising carbon dioxide is contacted with the solid sorbent in each of the plurality of parallelly arranged fluidised bed sub-units.

68. A system according to claim 67, wherein the fluidised bed sub-units are stacked on top of each other to form a vertical stack of fluidised bed sub-units.

69. A system according to any one of claims 63-68, wherein the system includes one or more gas distributors through which, in use, the gas is introduced to the one or more fluidised bed reactors.

70. A system according to any one of claims 63-69, wherein the system includes one or more fans configured to, in use, introduce the gas into the one or more fluidised bed reactors.

71. A system according to any one of claims 63-70, wherein the system includes a solid inlet and a solid outlet, wherein the system is configured to move the solid sorbent from the solid inlet along the length of the one or more fluidised bed reactors to the solid outlet.

72. A system according to claim 71 when dependent on claim 70, wherein the one or more fans are configured to, in use, move the solid sorbent from the solid inlet along the length of the one or more fluidised bed reactors to the solid outlet, optionally wherein the one or more fans are configured to progressively move the solid sorbent from the solid inlet along the length of the one or more fluidised bed reactors to the solid outlet.

73. A system according to any one of claims 63-72, wherein the system includes one or more separation units through which, in use, the carbon dioxide depleted gas is filtered.

74. A system according to claim 73, wherein the one or more separation units are or include a filter, a bag filter, a gas cyclone or an electrostatic precipitator (ESP).

75. A system according to any one of claims 59-74, wherein the system is configured to, in use, contact the gas comprising carbon dioxide with the solid sorbent at a temperature of between 450°C and ambient and a pressure of between 1 and 1.5 bar.

76. A system according to any one of claims 59-75, wherein the system is configured to, in use, regenerate the solid sorbent, thereby releasing carbon dioxide from the solid sorbent and creating a carbon dioxide concentrated gas.

77. A system according to claim 76 including a second reactor or a kiln configured to, in use, regenerate the solid sorbent.

78. A system according to any one of claims 76-77, wherein the system is configured to, in use, heat the solid sorbent to a temperature of approximately 500-900°C so as to regenerate the solid solvent.

79. A system according to any one of claims 76-78, wherein the system is configured to, in use, collect the carbon dioxide concentrated gas.

80. A system according to any one of claims 76-79, wherein the system is configured to, in use, reactivate the solid sorbent.

81. A system according to claim 80, wherein the system is configured to, in use, reactivate the solid sorbent in the presence of steam, at a temperature of between ambient and 900°C.

82. A system according to any one of claims 59-81, whereby the gas comprising carbon dioxide is atmospheric air.

83. A system according to any one of claims 59-82, whereby the gas comprising carbon dioxide comprises carbon dioxide in a concentration less than 1000 ppm, more preferably less than 800 ppm, more preferably less than 600 ppm and more preferably less than 500 ppm.

84. A system according to any one of claims 59-83, whereby the solid sorbent comprises particles of the solid sorbent and optionally comprises silica particles, said particles of solid sorbent and silica having an average particle diameter of less than 2500 microns.

85. A system according to any one of claims 59-84, wherein the solid sorbent has an average particle diameter of between 20-2000 microns and an internal surface area of between 1-200m^2/g.

86. A system according to any one of claims 59-85, wherein the solid sorbent is a mixed metal oxide or a mixed metal hydroxide, and wherein the metal oxide or metal hydroxide comprises one or more of Ca, Mg, Si, Al, Fe, W, Mn, Cu, Zn, Xo, Sr, Cd, Ba and Ni.

87. A system according to claim 86, wherein the solid sorbent comprises a mixed metal oxide or a mixed metal hydroxide comprising Ca, and optionally further comprising one or more of Mg, Si, Al, Fe, W, Mn, Cu, Zn, Xo, Sr, Cd, Ba and Ni.

88. A system according to any one of claims 59-87, wherein the solid sorbent comprises one or more salts, hydroxides, nitrates, nitrites and/or carbonates of Li, Na and/or K and any combination of HBr, HCl, HNO_3 and HI.

89. A system according to any one of claims 59-88, wherein the solid sorbent is Havelock limestone or a mixed metal oxide comprising 85 wt% Ca and 15 wt% Mg.

90. A system according to any one of claims 59-89, the system including a cooling apparatus configured to, in use, cool solid material that has left a reactor, preferably a calciner reactor, wherein the cooling apparatus is configured to, in use, cool the solid material using a cooling gas.

91. A system according to claim 90, wherein the cooling apparatus is configured to convey the solid material in counterflow with the cooling gas.

92. A system according to claim 91, wherein the cooling apparatus is configured to convey the solid material in counterflow with the cooling gas using gravity.

93. A system according to claim 90, wherein the cooling apparatus is configured to convey the solid material in crossflow with the cooling gas.

94. A system according to any one of claims 90-93, wherein the cooling apparatus includes a plurality of cooling stages.

95. A system according to claim 94, wherein the plurality of cooling stages includes a plurality of parallelly arranged cooling stages configured to, in use, cool respective portions of the solid material using the cooling gas.

96. A system according to claim 94 or claim 95, wherein the plurality of cooling stages includes a plurality of sequentially arranged cooling stages configured to, in use, sequentially cool the solid material using the cooling gas.

97. A system according to any one of claims 90-96, wherein the cooling apparatus includes a hydration stage configured to, in use, hydrate the solid material.

98. A system according to claims 96 and 97, wherein the hydration stage is configured to receive the solid material from one of the plurality of sequentially arranged cooling stages, and/or wherein another of the plurality of sequentially

arranged cooling stages is configured to, in use, receive the solid material from the hydration stage.

99. A system according to any one of claims 90-98, wherein the cooling apparatus includes one or more fluidised bed coolers configured to, in use, cool the solid material using the cooling gas, wherein the cooling gas is a fluidising gas.

100. A system according to any one of claims 90-99 wherein the cooling gas is ambient air.

101. A system according to any one of claims 90-100 wherein the cooling apparatus is configured to, in use, provide the cooled solid material to a reactor, preferably a carbonator reactor.

102. A system according to any one of claims 90-101 including a heat exchanger configured to, in use, recover heat from the cooling of the solid material by the cooling apparatus.

103. A system according to any one of claims 90-102, the system including a heating apparatus configured to, in use, heat solid material using a heating gas prior to the solid material entering a reactor, preferably a calciner reactor.

104. A system according to claim 103, wherein the heating apparatus is configured to convey the solid material in counterflow with the heating gas.

105. A system according to claim 104, wherein the heating apparatus is configured to convey the solid material in counterflow with the heating gas using gravity.

106. A system according to claim 103, wherein the heating apparatus is configured to convey the solid material in crossflow with the heating gas.

107. A system according to any one of claims 103-106, wherein the heating apparatus includes a plurality of heating stages.

108. A system according to claim 107, wherein the plurality of heating stages includes a plurality of parallelly arranged heating stages configured to, in use, heat respective portions of the solid material using the heating gas.

109. A system according to claim 107 or claim 108, wherein the plurality of heating stages includes a plurality of sequentially arranged heating stages configured to, in use, sequentially heat the solid material using the heating gas.

110. A system according to any one of claims 103-109, wherein the heating apparatus includes one or more fluidised bed heaters configured to, in use, cool the solid material using the heating gas, wherein the heating gas is a fluidising gas.

111. A system according to any one of claims 103-110, wherein the heating apparatus includes one or more cyclone flash heaters configured to, in use, heat the solid material using the heating gas.

112. A system according to any one of claims 103-111 wherein the heating apparatus is configured to, in use, receive the to-be-heated solid material from a reactor, preferably a carbonator reactor.

113. A system according to any one of claims 103-112, wherein the heating apparatus is configured to, in use, maintain a solid material heating temperature of below 550°C, preferably below 500°C.

114. A system according to claim 96 in combination with any one of claims 103-113, wherein the heating apparatus is configured to, in use, heat the heating gas using recovered heat from the cooling of the solid material by the cooling apparatus.

115. A system according to any one of claims 59-114 wherein the solid sorbent is a solid sorbent mixture.

116. A system according to any one of claims 59-115 wherein the solid sorbent is or comprises a nanostructured sorbent.

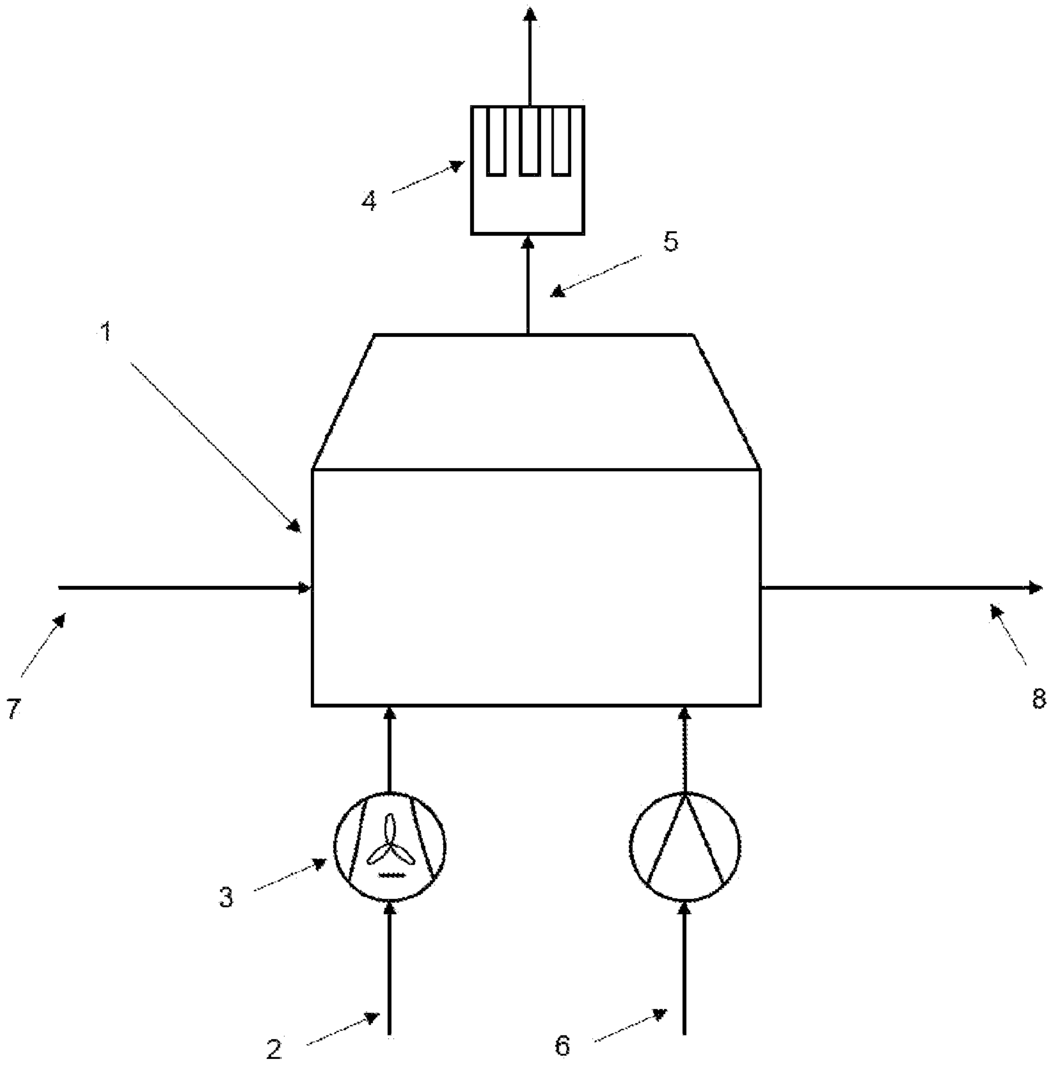

Figure 1

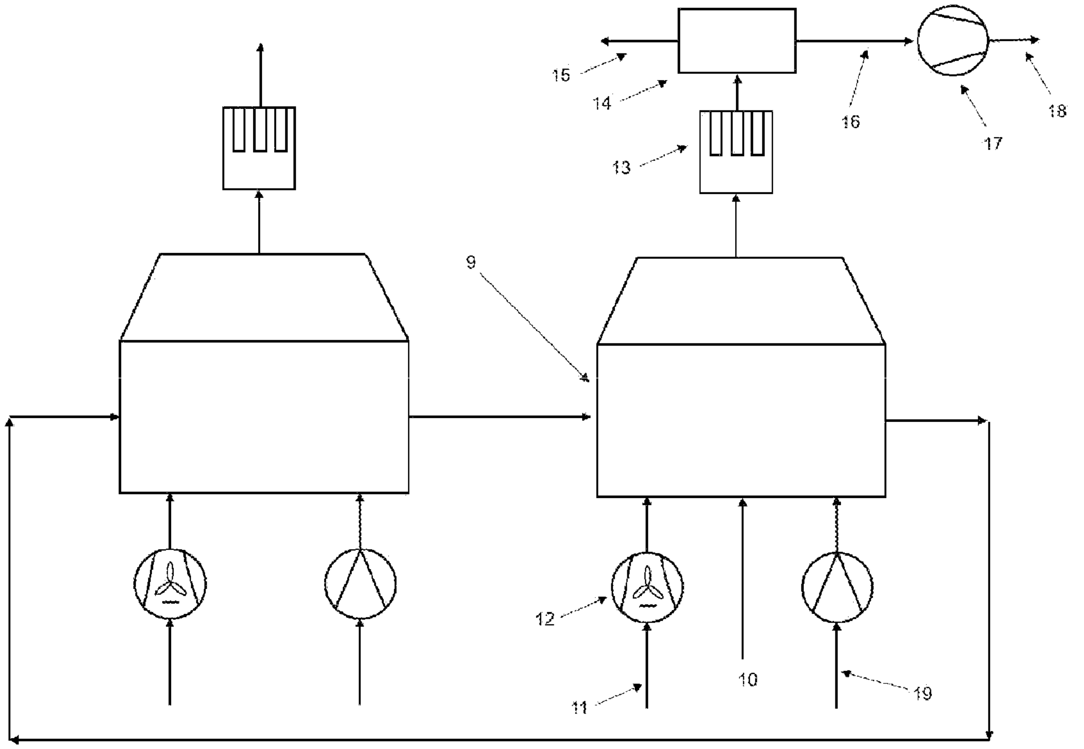

Figure 2

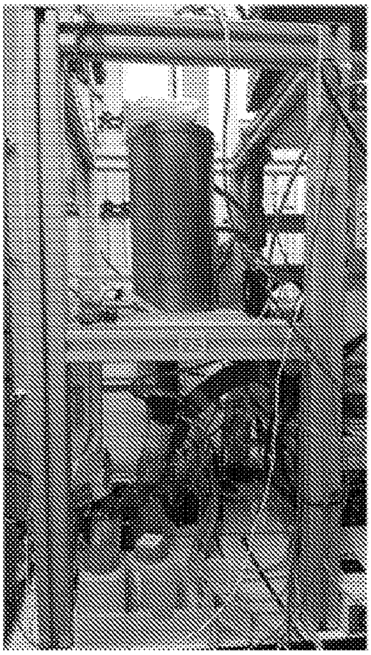

Figure 3a

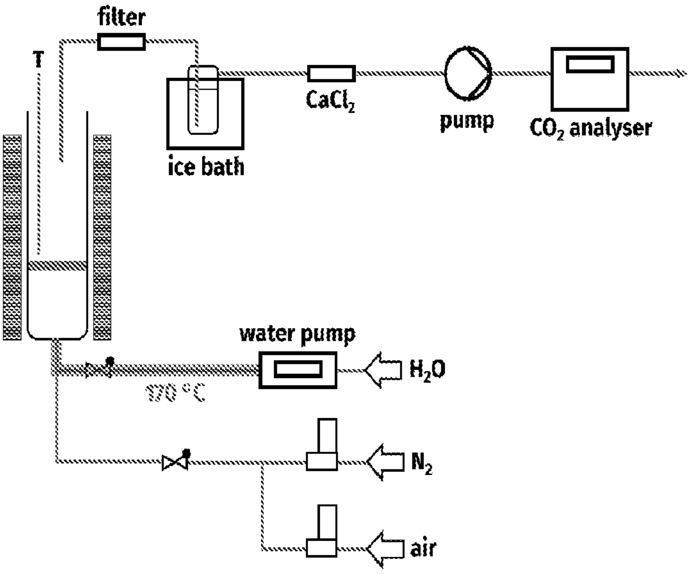

Figure 3b

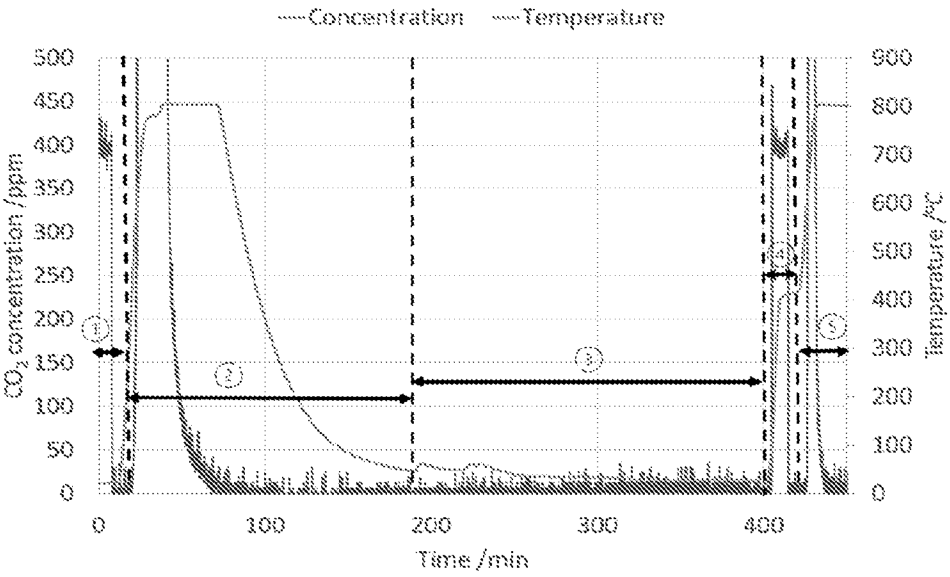

Figure 4

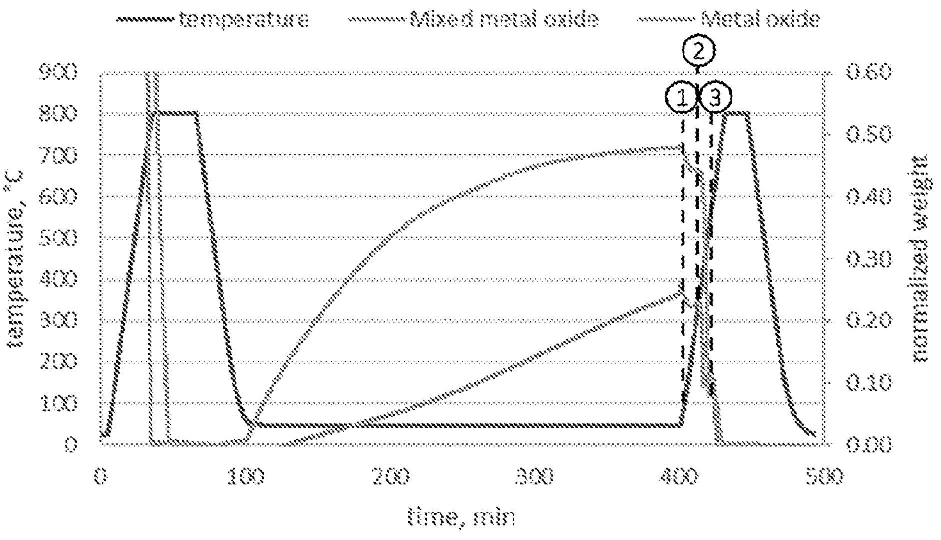

Figure 5

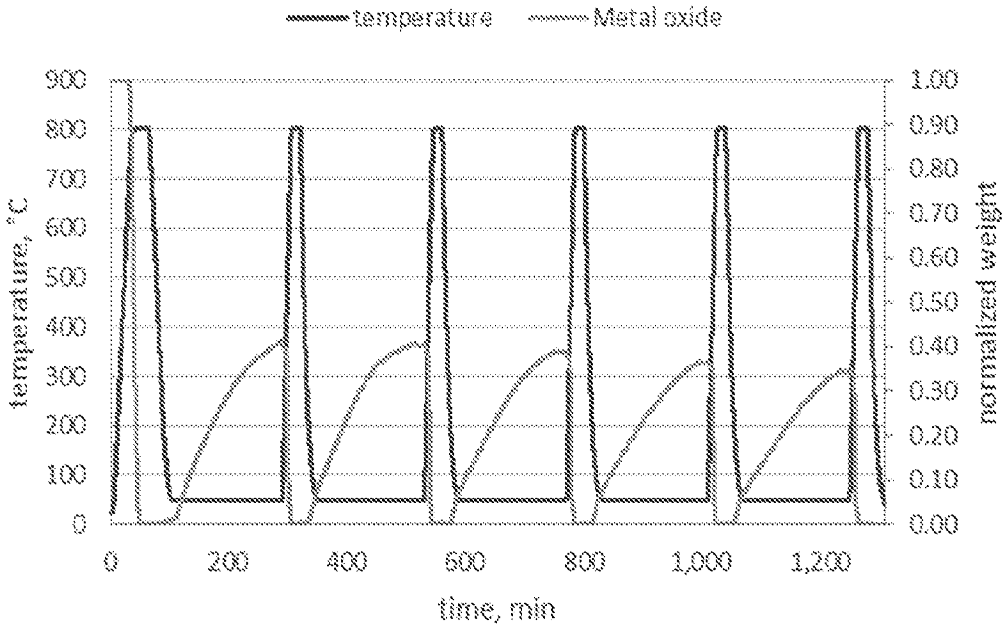
temperature
Metal oxide
900
800
700
600
500
400
300
200
100
0
temperature, °C
1.00
0.90
0.80
0.70
0.60
0.50
0.40
0.30
0.20
0.10
0.00
normalized weight
0
200
400
600
800
1,000
1,200
time, min

Figure 6

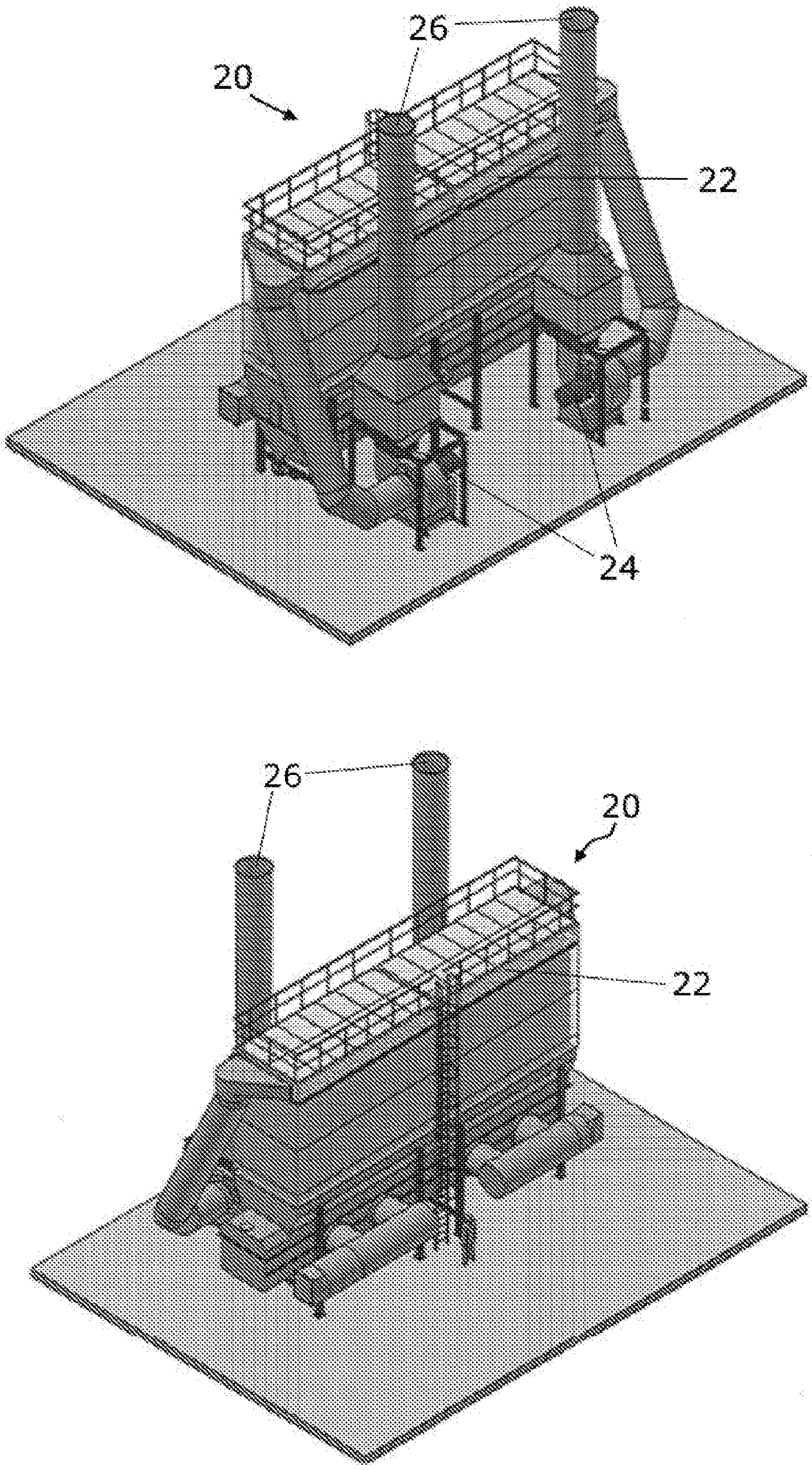

Figure 7

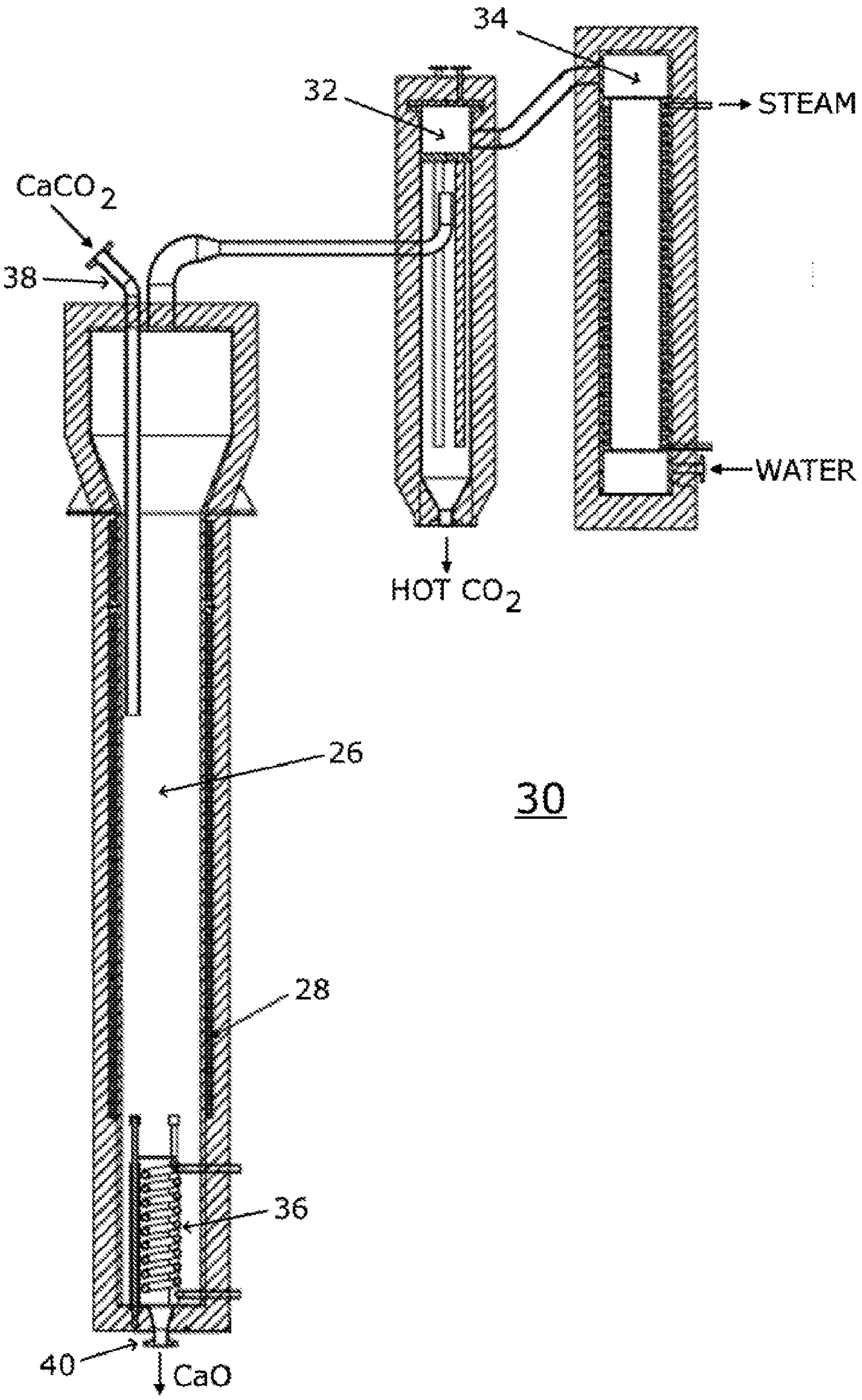

Figure 8

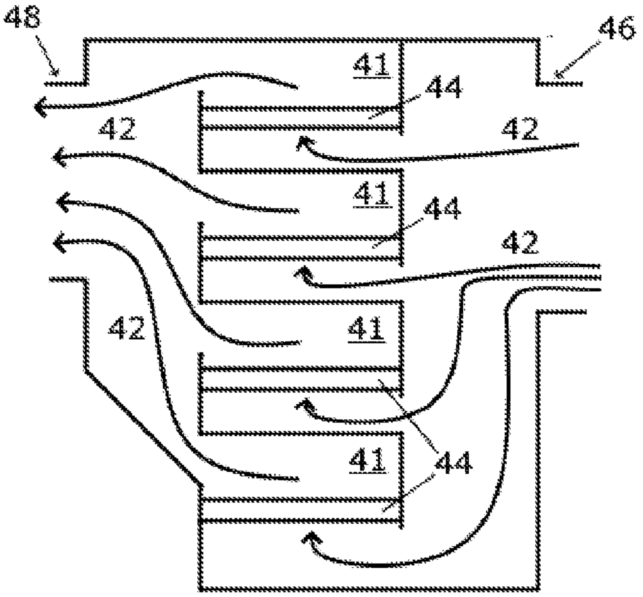

Figure 9

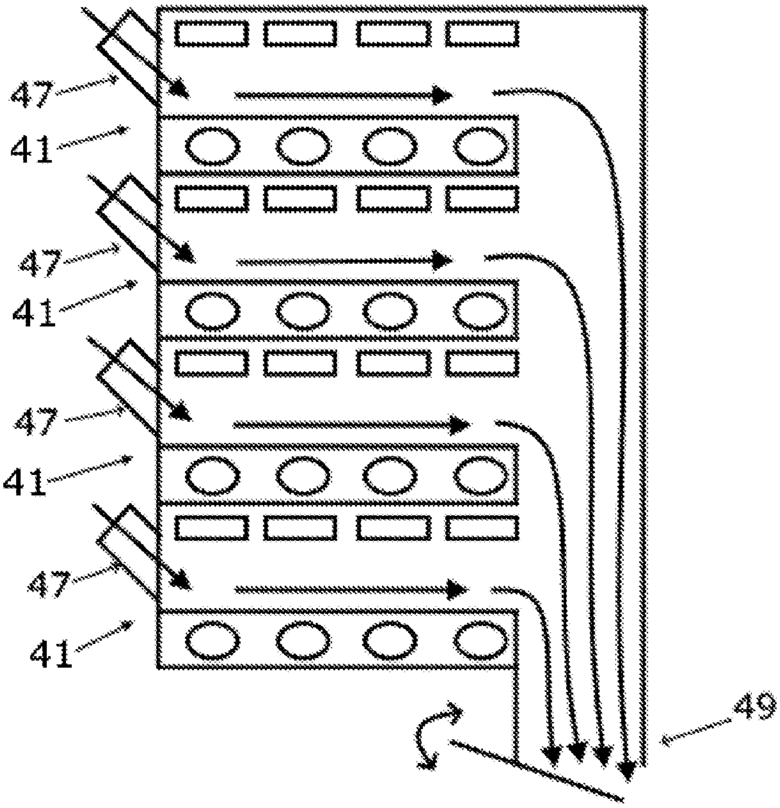

Figure 10

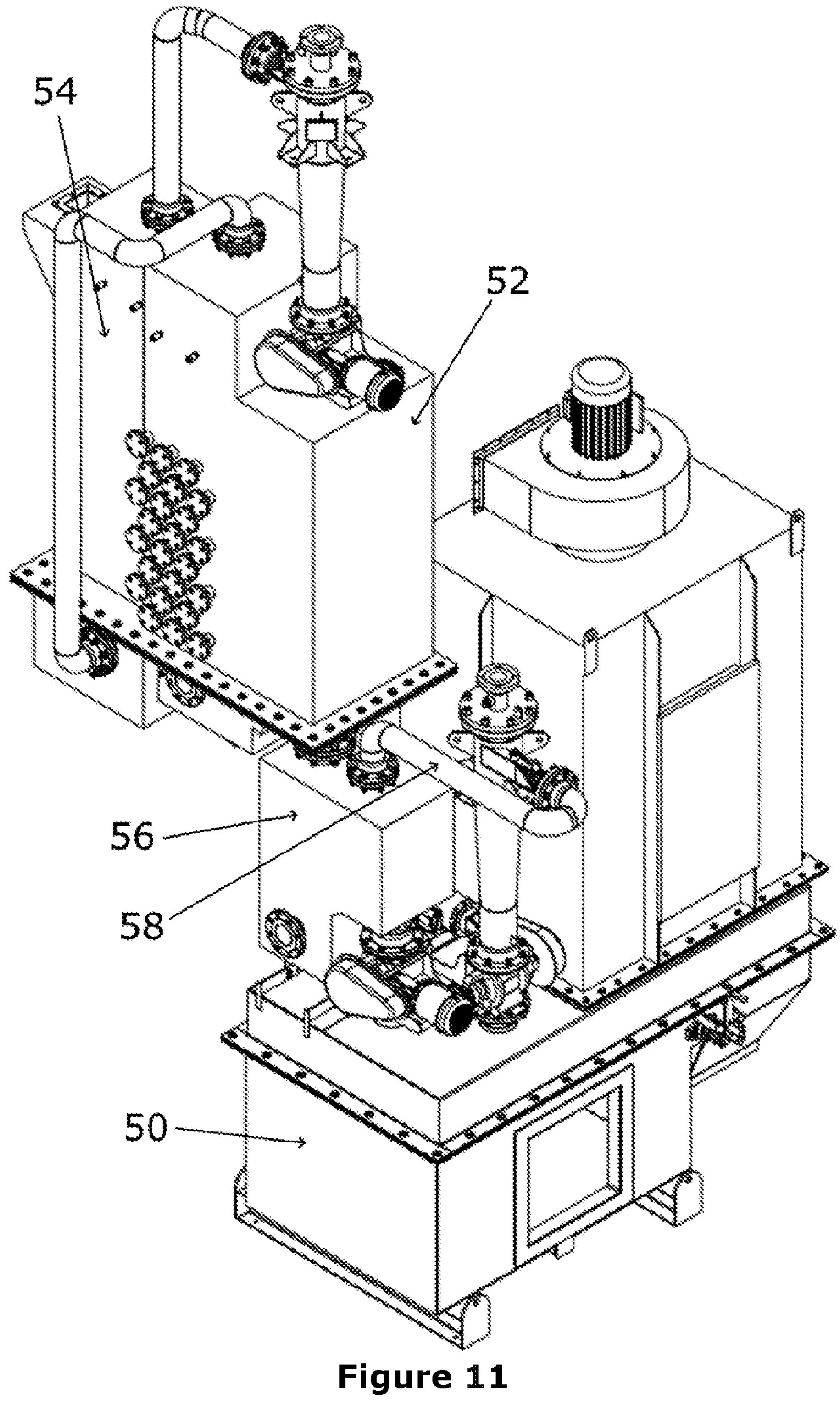

Figure 11

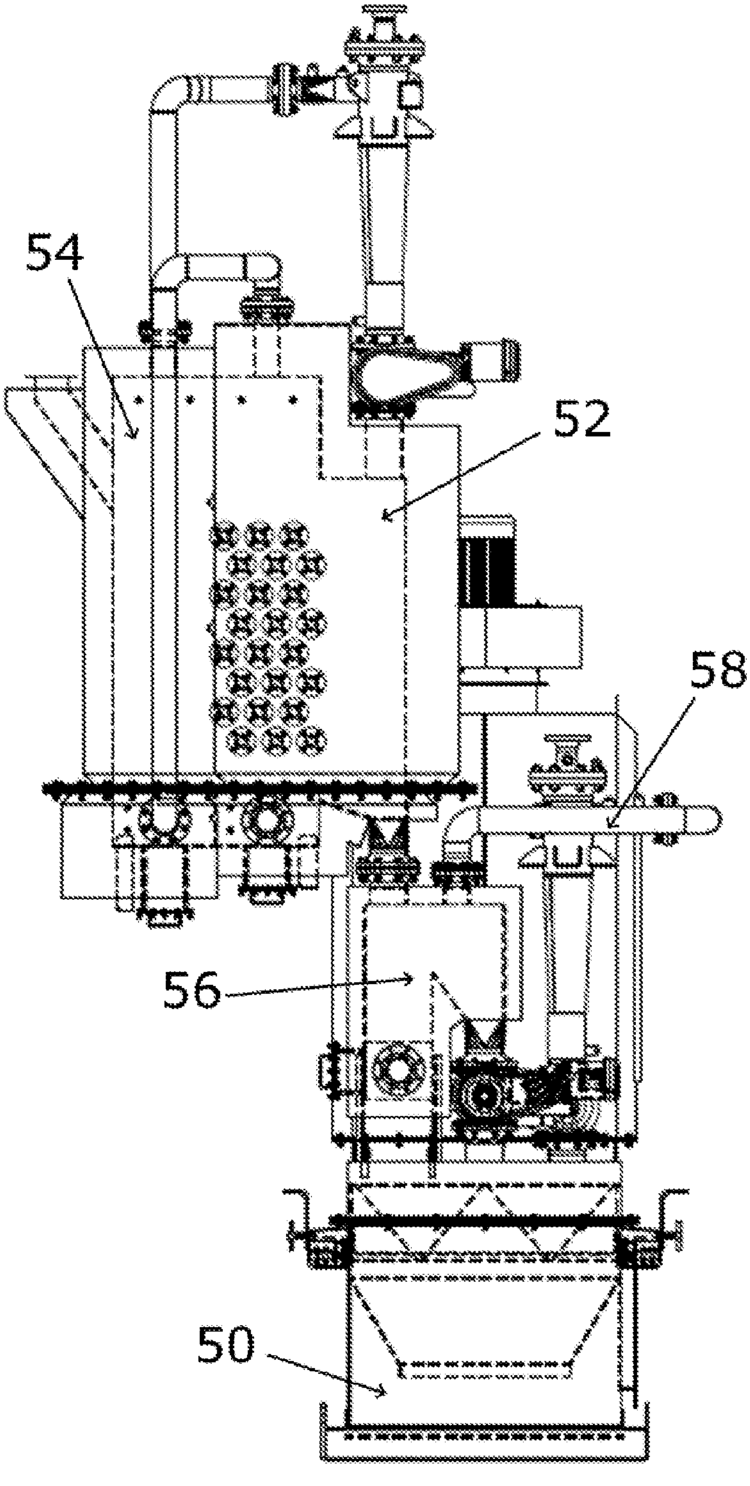

Figure 12

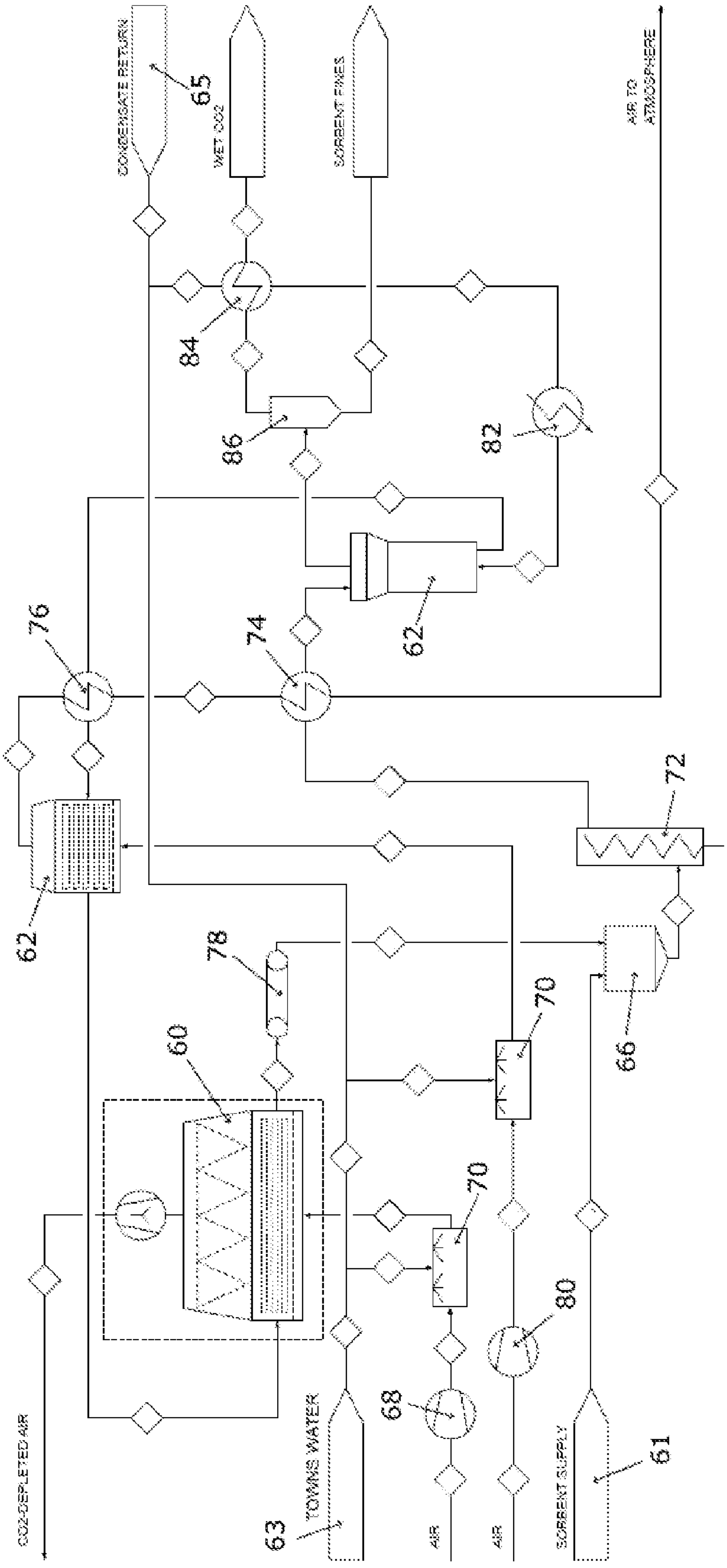
CONDENSATE RETURN
65
WET CO2
SORBENT FINES
AIR TO ATMOSPHERE
84
86
82
76
74
62
62
78
60
70
70
72
66
68
80
61
63
CO2-DEPLETED AIR
TOWNS WATER
AIR
AIR
SORBENT SUPPLY

Figure 13

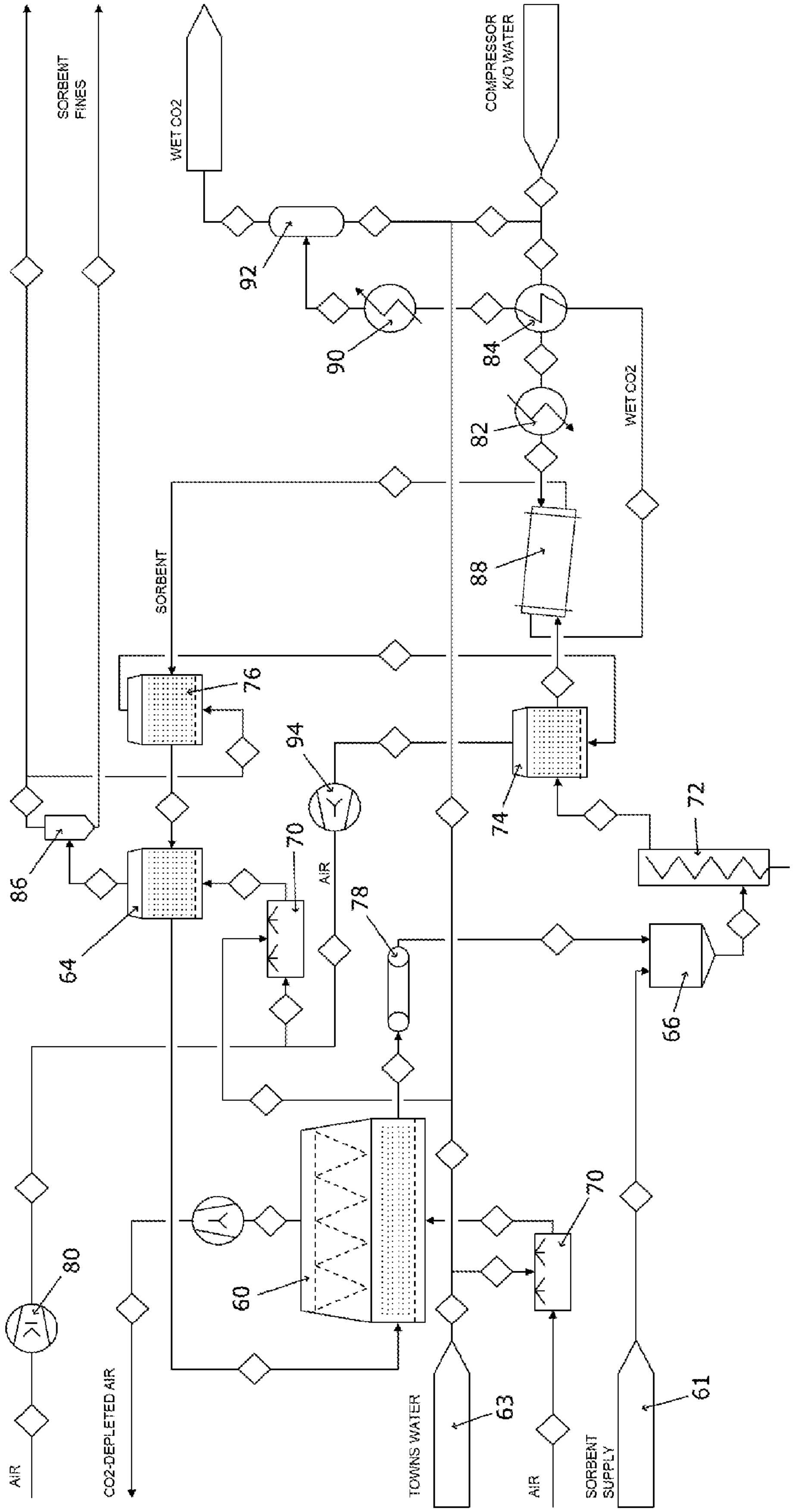
AIR
CO2-DEPLETED AIR
TOWNS WATER
AIR
SORBENT SUPPLY
80
60
63
70
61
64
86
70
AIR
78
66
94
74
72
76
SORBENT
SORBENT FINES
88
82
WET CO2
90
84
92
WET CO2
COMPRESSOR K/O WATER

Figure 14

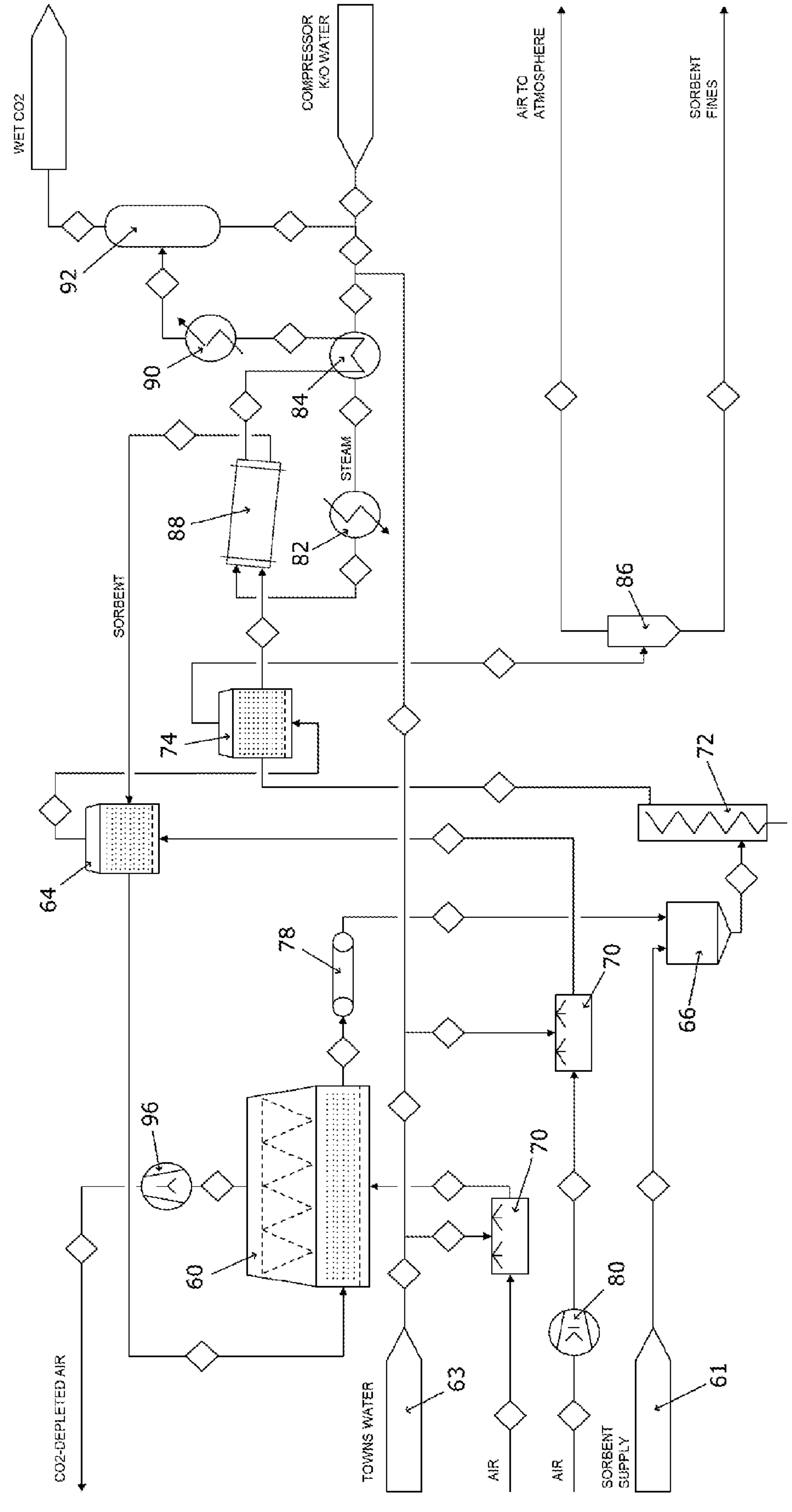
CO2-DEPLETED AIR
TOWNS WATER
63
AIR
AIR
SORBENT SUPPLY
61
60
96
80
70
70
78
66
64
72
74
SORBENT
88
82
STEAM
84
90
92
WET CO2
COMPRESSOR K/O WATER
AIR TO ATMOSPHERE
SORBENT FINES
86

Figure 15

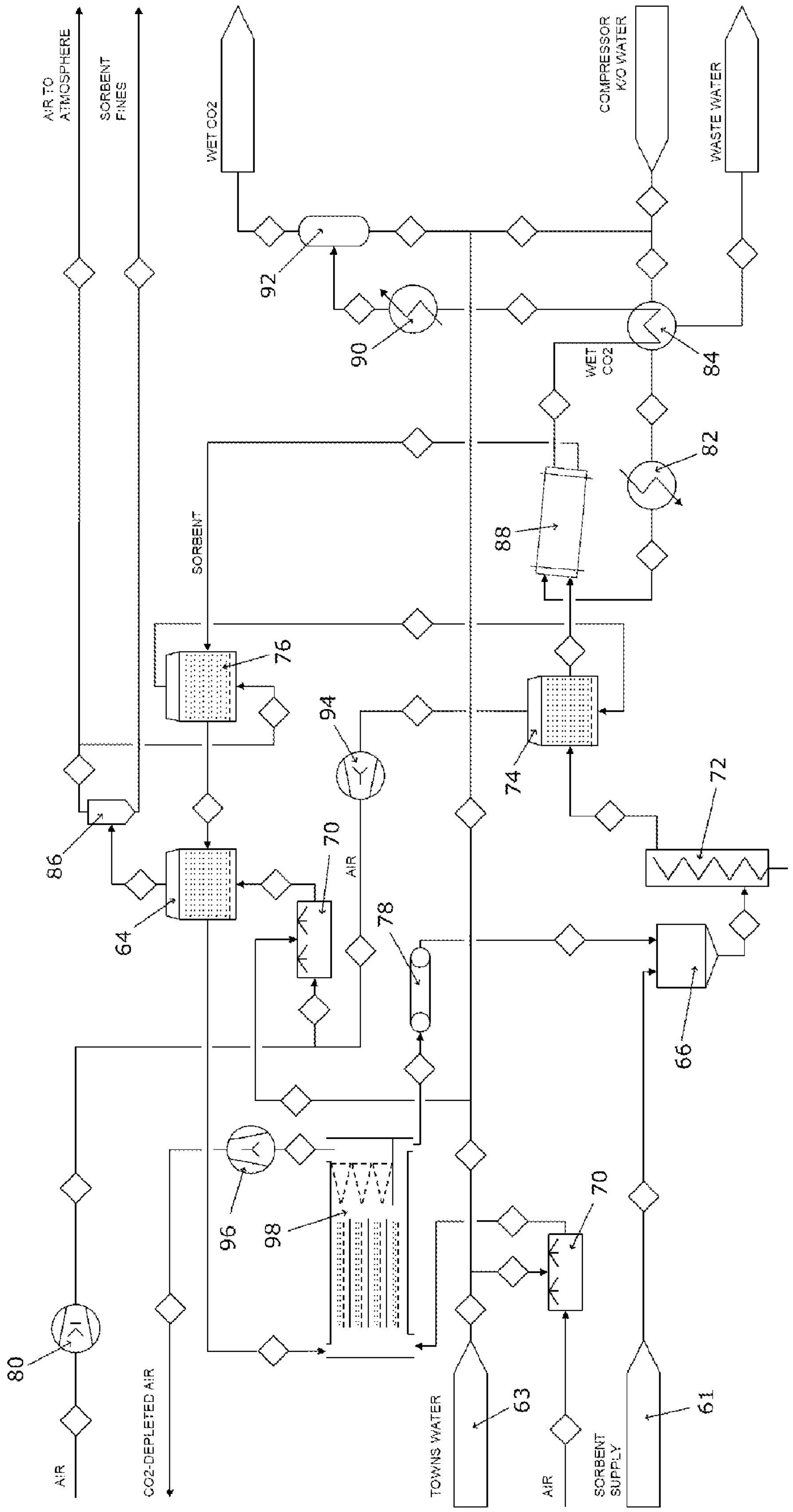
AIR TO ATMOSPHERE
SORBENT FINES
WET CO2
COMPRESSOR K/O WATER
WASTE WATER
92
90
84
WET CO2
82
88
SORBENT
76
94
74
72
86
64
70
AIR
78
66
80
96
98
70
AIR
CO2-DEPLETED AIR
TOWNS WATER
63
AIR
SORBENT SUPPLY
61

Figure 16

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2024/051437

A. CLASSIFICATION OF SUBJECT MATTER
INV. B01D53/08 B01D53/12
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
B01D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data, COMPENDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2016/185387 A1 (RELIANCE IND LTD [IN]) 24 November 2016 (2016-11-24) figure 1A page 6, lines 9-14 page 7, lines 5-11 ----- -/--	1,4-6, 11-14, 22,23, 30,59, 62-64, 69-72, 80,81,88

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance;; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance;; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search 13 August 2024	Date of mailing of the international search report 17/09/2024
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Harf, Julien

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C(Continuation). **DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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X	US 2012/258029 A1 (KRUTKA HOLLY [US] ET AL) 11 October 2012 (2012-10-11) figure 6 -----	1,4-6, 11,13, 15,16, 59, 62-64, 69,71, 73,74
X	US 6 387 337 B1 (PENNLINE HENRY W [US] ET AL) 14 May 2002 (2002-05-14) figure 1 column 3, lines 38-48,55-56,63-65 -----	1,4-6, 11,13, 28,29, 59, 62-64, 69,71, 86,87
X	EP 4 169 603 A1 (CONSEJO SUPERIOR INVESTIGACION [ES]) 26 April 2023 (2023-04-26) claims 1,12; figure 12 paragraph [0045] -----	1-6,11, 13, 17-21, 24,25, 28,29, 39,40, 57, 59-64, 69,71, 75-79, 82,83, 86,87, 97,98, 115

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INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2024/051437

C(Continuation). **DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2004/037369 A2 (ENVIROSCRUB TECHNOLOGIES CORP [US]; PAHLMAN KATHLEEN S HF [US] ET AL.) 6 May 2004 (2004-05-06) claims 1,4,5,8,11; figures 1,2 page 9, lines 12-16 page 11, lines 20-26 page 13, lines 11-14 page 48, line 31 - page 49, line 2 page 55, lines 19-22 -----	1-5, 7-14, 17-19, 26-29, 31-38, 41-56, 58-63, 65-72, 75-77, 84-87, 89-96, 99-114, 116
A	DATABASE COMPENDEX [Online] ENGINEERING INFORMATION, INC., NEW YORK, NY, US; 22 October 2021 (2021-10-22), RAJAMATHI R ET AL: "Porous CaO-MgO Nanostructures for CO2Capture", XP002812018, Database accession no. E20214311043531 abstract & ACS APPLIED NANO MATERIALS 20211022 AMERICAN CHEMICAL SOCIETY USA, vol. 4, no. 10, 22 October 2021 (2021-10-22), pages 10969-10975, DOI: 10.1021/ACSANM.1C02428 -----	58,116

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/GB2024/051437

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		EP 4419239 A1	28-08-2024
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