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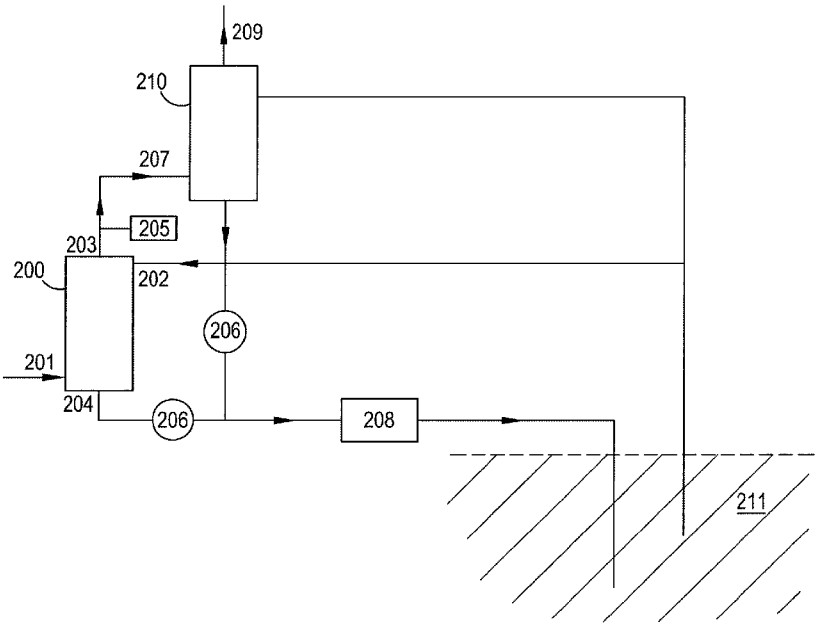

Figure 4

(57) Abstract: The present invention provides a method for capturing and storing an acidic gas (e.g. C02) from a gas comprising: (i) contacting said gas with brine to produce an acidic gas-rich brine and an acidic gas-depleted gas; and (ii) pumping said acidic gas-rich brine into a subterranean formation for storage, wherein at least some of said brine used in step (i) derives from the subterranean formation into which said acidic-gas rich brine is pumped in step (ii).

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METHOD AND SYSTEM FOR ACIDIC GAS CAPTURE AND STORAGE USING A SUBTERRANEAN FORMATION COMPRISING BRINE

INTRODUCTION

The present invention relates to a method and system for capturing and storing acidic gas, e.g. CO_2 and H_2S, from gases. As such, the method and system of the present invention provide a method of cleaning acidic gas-containing gases such as exhaust gases and fuel gases. The method and system are energy efficient and store the acidic gas in a safe form. In some preferred methods and systems a portion of captured CO_2 is purified and used, for example, in enhanced oil recovery.

BACKGROUND TO THE INVENTION

The continually increasing combustion of fossil fuel, such as coal, natural gas, and oil, has resulted in a dramatic increase in the concentration of CO_2 in the atmosphere. There is overwhelming evidence that the greenhouse effect is at least partly caused by this increased CO_2 concentration and that this has already contributed to the climate changes that have occurred over the last decades. According to simulation models, it is suspected to cause further and potentially more dramatic changes in the climate in the future.

As a result, scientists, environmentalists and politicians throughout the world are driving initiatives to reduce the amount of CO_2 discharged into the atmosphere by combustion of fossil fuel and other industrial processes. Simultaneously there is also a drive to remove acidic gases such as CO_2 and H_2S from fuel gases, e.g. natural gas recovered from subterranean formations and syngas from processes such as steam reforming and the gasification of coal. One approach being adopted is to capture CO_2 (i.e. prevent the release of CO_2) from the gas before it is released to the atmosphere in the case of exhaust gases or before it is used in energy production in the case of fuel gases.

Historically the captured CO_2 could be released into the ocean. By releasing it at significant depths, e.g. greater than 100 m, it took a significant amount of time for the CO_2 to circulate to the surface. WO99/13967, for example, discloses an apparatus that is specifically designed to utilise sea water as an absorber during a CO_2 capture process. The apparatus is provided with turbulent contactors to enable turbulent mixing of a flue gas and brine. This is described as being important to ensure efficient gas liquid contact. The brine used in the system is sea water and the CO_2 charged sea water is discharged to sea. The motivation for using sea water for the absorbent is to facilitate the disposal into the sea.

US2004/0057886 discloses a similar method for removing H_2S and CO_2 from hydrocarbon streams and in particular sour natural gas. The method is based on a series of absorption towers connected in series wherein sea water is used as an absorbent for CO_2. As with WO'967, the CO_2 enriched sea water is simply discharged to sea, preferably in the deep ocean. Again the motivation for using sea water as the absorbent during capture is to facilitate its disposal at sea. US'886 recognises that the solubility of CO_2 in deep waters is higher than shallower waters and that it takes a longer time for the CO_2 to eventually rise to the surface from where it may be discharged to the atmosphere. It estimates that it may take as long as 1000 years for the CO_2 to resurface.

Neither WO'967 nor US'886 disclose a method wherein CO_2 is permanently stored. Rather the CO_2 is simply released into the sea from where it may be discharged into the atmosphere over time. The dumping of CO_2 into the sea is, however, no longer permitted due to its impact on the marine environment.

WO2011/017609 discloses a large number of different methods for capturing and storing CO_2 wherein CO_2 is contacted with an aqueous mixture and then the reaction product is sequestered in a subterranean formation. A wide range of different aqueous mixtures are disclosed for use in the method. WO2011/017609 also advocates adding various agents to the reaction product, such as proton removing agents and divalent ions. In a number of methods disclosed agents are added to the reaction product to specifically cause precipitation of solids that can be removed prior to storage of the remaining aqueous solution.More recently carbon capture and storage (CCS) processes have been developed wherein CO_2 is captured from gases and then injected into subterranean formations such as aquifers, oil wells for enhanced oil recovery or in depleted oil and gas wells. The CO_2 is injected in dense form and in relatively high purity. This is driven by the cost of pumping CO_2 into subterranean formations.

In these processes CO_2 is captured from gases such as flue gas, natural gas or syngas by means of a solvent, usually comprising an amine, carbonate or amino acid salt in an absorber column. The solvent loaded with CO_2 (called rich solvent or solution) is then sent to a regenerator where CO_2 and water is released by means of adding steam. The generation of this steam is normally the most energy intensive part of a CCS chain. The CO_2-water mixture is cooled down and water is condensed out. The almost pure CO_2 is compressed to the subcritical point where it is pumped to the required pressure (determined by the storage reservoir properties). The dense CO_2 is

transported by pipeline to a storage site where it is injected in the bottom of the reservoir.

The CO_2 injected into the reservoir will tend to migrate to the top of the reservoir. If the reservoir is a saline formation, a part of the CO_2 will begin to dissolve in the formation water. However, since this mechanism is very slow the majority of CO_2 will migrate to the top of the formation and follow the topographic structure of the reservoir. It is very difficult to predict the migration pattern of CO_2 in a reservoir and migrating CO_2 is considered the biggest risk associated with CO_2 storage.

Figure 1 illustrates the relationship between the CO_2 storage mechanism, the time necessary to achieve it and the associated safety level of such state-of-the-art CCS methods. It can be seen from this Figure that it takes approximately 1000 years for 50% of CO_2 injected into a reservoir to be trapped by dissolution in formation water. The two main mechanisms by which the majority of CO_2 injected in subterranean formations for storage today are trapped are structural and stratigraphic trapping and residual CO_2 trapping. As indicated above, the former is not ideal as it is impossible to control the migration pattern of CO_2 in the reservoir. In residual trapping, the CO_2 is at least partially adsorbed onto the surface of the formation and thus is less likely to move through the formation. It is therefore more stable than structural trapping, but if changes, e.g. in pressure, occur in the formation desorption can occur releasing CO_2. A need therefore exists for improved carbon capture and storage (CCS) methods and systems that utilise less energy and that preferably improve CO_2 storage safety. These are currently the two biggest challenges relating to CCS.

SUMMARY OF INVENTION

Thus viewed from a first aspect the present invention provides a method for capturing and storing an acidic gas (e.g. CO_2) from a gas comprising:

(i) contacting said gas with brine to produce an acidic gas-rich brine and an acidic gas-depleted gas; and

(ii) pumping said acidic gas-rich brine into a subterranean formation for storage, wherein at least some of said brine used in step (i) derives from the subterranean formation into which said acidic-gas rich brine is pumped in step (ii).

In one preferred embodiment the gas from which the acidic gas is captured is an exhaust gas, e.g. from a power station, from steam generation, from an industrial process such as the manufacture of cement or from hydrocarbon recovery operations.

In another preferred embodiment the gas from which the acidic gas is captured is a fuel gas, e.g. natural gas or syngas.

Viewed from a further aspect, the present invention provides a system for capturing and storing an acidic gas (e.g. CO_2) from a gas comprising:

(a) a means for supplying said gas to a contact vessel;

(b) a means for supplying brine to said contact vessel;

(c) a contact vessel for contacting said gas with said brine to produce an acidic gas-rich brine and an acidic gas-depleted gas;

(d) an outlet for said acidic gas-depleted gas;

(e) an outlet for said acidic-gas rich brine; and

(f) a pump for transporting said acidic gas-rich brine into a subterranean formation.

In preferred embodiments the contact vessel is selected from an absorption tower, a horizontal tunnel comprising treatment sections or a transport channel for transporting gas to an acidic gas capture plant.

DESCRIPTION OF THE INVENTION

By the term “acidic gas” is meant a gas which when dissolved in water produces a pH of less than 7. The acidic gas may be, for example, CO_2, H_2S, SO_2, CS_2, HCN, COS, NO_2 or mercaptans. Most often, however, the acidic gas will be H_2S or CO_2, especially CO_2. The acidic gas may, for example, be present in an exhaust gas and/or in a fuel gas.

By the term “exhaust gas” is meant a flue gas from an industrial process. The process may be, for example, the combustion of coal, organic waste or oil, steam generation or the manufacture of cement. The gas may also be acidic gas, e.g. CO_2, produced during hydrocarbon recovery, especially when in situ combustion or enhanced recovering techniques using CO_2 are employed.

By the term “fuel gas” is meant a gas that is combusted to generate energy. Representative examples of fuel gas include natural gas and syngas.

By the term “brine” is meant water comprising dissolved salts such as sodium chloride and potassium chloride. A typical example of brine is sea water.

By the term “acidic gas-rich brine” is meant brine containing a higher concentration of acidic gas than the original brine used in the method. Similarly by the term “acidic gas-depleted gas” is meant a gas containing a lower concentration of acidic gas than the gas treated in the method. The production of an acidic gas-rich brine and an acidic gas-depleted gas indicates the process has been successful since it means the acidic gas has been stripped or sequestered from the gas into the brine.

The method and system of the present invention are advantageous because they utilise brine, e.g. sea water, which is available in abundance to capture an acidic gas from gases to be treated. The method and system are also highly advantageous as they also utilise the brine to safely store the CO_2 in a subterranean formation. As far as the Applicant is aware, an acidic gas such as CO_2 or H_2S has not been pumped to subterranean storage whilst dissolved in brine in practice. Rather in the prior art methods, the focus has been on providing pure CO_2 in gaseous form that can be compressed and pumped.

In the methods and systems of the present invention the acidic gas/brine mixture is pumped into a subterranean formation wherein the acidic gas, e.g. CO_2, is safely stored. The acidic gas-rich brine is typically more dense than the brine naturally present in the formation therefore it sinks towards the bottom of the reservoir. This prevents the acidic gas, e.g. CO_2 from migrating, i.e. it is effectively stored in place by solubility trapping (see Figure 1). The CO_2 is physically dissolved in the brine and can only escape therefrom by a decrease in the pressure in the formation or by an increase in its temperature. Such changes are, however, unlikely to occur and/or can be prevented from happening.

In preferred methods of the invention the brine used in step (i) has a salinity of 3 to 20 % by weight, more preferably 3.2 to 15.0 % by weight. Preferably the brine used in step (i) has a composition as described in the table below.

Element	Preferred % wt	More preferred % wt
Chlorine	1.5-12.0	1.6-10.0
Sodium	1.0-7.0	1.08-6.80
Magnesium	0.040-0.150	0.045-0.130
Calcium	0.030-0.700	0.035-0.650
Potassium	0.035-0.800	0.039-0.700

Preferably the brine used in step (i) has a density of 1.020 to 1.150 kg/m^3, still more preferably 1.020 to 1.120 kg/m^3, yet more preferably 1.020 to 1.100 kg/m^3.

In the methods and systems of the present invention at least some (e.g. all) of the brine used in step (i) derives from the subterranean formation into which said acidic-gas rich brine is pumped. Still more preferably substantially all of the brine (e.g. all of the brine) used in step (i) derives from the subterranean formation into which said acidic-gas rich brine is pumped. Preferred methods of the invention therefore comprise the steps:

(ia) obtaining brine from a subterranean formation;

(ib) contacting said gas with said brine to produce an acidic gas-rich brine and an acidic gas-depleted gas; and

(ii) pumping said acidic gas-rich brine into said subterranean formation for storage.

This is highly beneficial for at least three reasons. First by extracting brine from the formation, the volume and space available for storage of acidic gas-rich brine is increased, thus increasing storage capacity. Second by pumping the acidic gas-rich brine back into the formation from which it derives the overall pressure in the formation is kept constant (i.e. pressure build-up due to storage significantly reduced) and the acidic-gas therefore remains dissolved in the brine. Third using brine from the formation to be used for storage, ensures that the acidic gas-rich brine pumped into the formation has a higher density than the formation water and will therefore migrate to the bottom of the reservoir. This means that the acidic gas, e.g. CO_2, will be significantly more safe compared to state-of-the-art methods wherein significant amounts of CO_2 migrate to the top of the formation.

The brine may be removed from the formation by pumping using conventional equipment. The brine may be stored in tanks prior to use in the methods and systems of the invention or it may be used directly. More preferably it is stored. Depending on the gas to be treated or cleaned in the method of the invention, the brine may be cooled and/or pressurised prior to use. Cooling and pressurisation may be carried out using conventional equipment. In some cases it may be preferable to add corrosion inhibitors and/or scale inhibitors to the brine to protect the equipment used in the methods of the present invention. More preferably, however, the brine is untreated prior to contact with the gas. As used herein the term “untreated” means that no chemicals are added to the brine and no constituents of the brine are removed. Particularly preferably proton removing agents are not added to the brine. Particularly preferably cations (e.g. divalent cations) are not added to the brine. Particularly preferably no constituent of the brine is removed prior to contact with the gas.

The gas treated in the methods and systems of the present invention may be any gas comprising an acidic gas. Typically the gas treated in the methods of the present invention is an exhaust gas or a fuel gas. Representative examples of exhaust gases are flue gases (e.g. produced during the generation of electricity in gas or coal power plants and steam generation) and gases from industrial manufacturing processes (e.g. cement production). Another type of exhaust gas comprising acidic gas, e.g. CO_2, is the gas produced during hydrocarbon recovery operations, especially when in situ combustion or enhanced recovering techniques using CO_2 are employed.

Representative examples of fuel gases include natural gas (e.g. sour gas or acidic gas) and syngas (e.g. from reforming processes or from goal gassification (e.g. underground coal gasification)). When the gas treated is an exhaust gas, the acidic gas-depleted gas is typically released to the atmosphere following treatment. When the gas treated is a fuel gas, the acidic gas-depleted gas is typically routed to a plant for further treatment or sent for storage prior to use.

The total concentration of acidic gas in the gas to be treated varies but is typically in the range 1-80 mol%, e.g. 5-50 mol %. The concentration of CO_2 in the gas to be treated is typically in the range 1-80 mol %, e.g. 5-50 mol%. The concentration of acidic gas in the gas to be treated depends on, e.g. whether it is an exhaust gas or a fuel gas. Some preferred values for different types of gases are set out in the table below.

Type of gas	Source	[CO_2] (mol%)	[H_2S] mol%	Total [acidic gas] mol%
Exhaust gas	Flue gas from gas power plant	3-5	<1	3-5
Exhaust gas	Flue gas from coal power plant	10-15	<1	10-15
Exhaust gas	Gas from cement production	18-25	<1	18-25
Exhaust gas	Gas from steam generator	6-10	<1	6-10
Fuel gas	Sour gas	5-40	1-40	5-80
Fuel gas	Acid gas	3-80	<1	3-80
Fuel gas	Syngas from coal gasification	20-50	<1	20-50
Fuel gas	Syngas from natural gas reforming	20-30	<1	20-30

The gas may be treated or untreated prior to carrying out the methods of the present invention. For instance the gas may be compressed prior to carrying out the method of the invention. Alternatively or additionally the gas may be cooled prior to carrying out the method of the invention. In preferred processes, an exhaust gas is compressed and/or cooled. Fuel gases are typically at higher pressures than exhaust gases so are less likely to require compression. Nevertheless in some cases a fuel

gas may be compressed and/or cooled prior to carrying out the method of the invention.

In the methods of the present invention the gas comprising an acidic gas is contacted with brine to produce an acidic gas-rich brine and an acidic-gas depleted gas stream. In preferred methods of the invention, the acidic gas-rich brine produced in step (i) is a solution. In further preferred methods of the invention, the acidic gas-rich brine produced in step (i) does not comprise solids.

The contacting may be carried out in any mass transfer device known in the art. When the gas enters the contacting device, the gas is preferably at a temperature of 5-40 °C and more preferably 5-15 °C. The pressure of the gas on entry to the contact device is preferably 50-200 barg, more preferably 80-150 barg. The brine will typically be supplied to the contact device at a temperature of 5-40 °C and more preferably 5-15 °C. The pressure of the brine on entry to the contact device is preferably 50-200 barg, more preferably 80-150 barg. In preferred methods of the invention no chemicals are added during the contacting step.

Preferably the contacting is carried out in an absorption tower, a horizontal tunnel comprising treatment sections or in a channel used to transport the gas to the acidic gas capture plant.

Preferably the contacting is in at least one absorption column. By an absorption column is meant any elongated structure having a body, at least one inlet and at least one outlet. The column may be any shape, e.g. cylindrical or oblong. Absorption columns are well known in the art and any conventional absorption column may be used. Absorption columns are generally used in a vertical orientation.

In some preferred methods of the invention the contacting is in one absorption column. In this case the acidic gas-rich brine produced in the method is preferably pumped straight to a subterranean formation for storage and the acidic gas-depleted gas is preferably sent to storage for future use as a fuel in the case of fuel gas or released to the atmosphere in the case of exhaust gas. Alternatively the acidic gas-rich brine may be pumped to a subterranean formation for storage and the acidic gas-depleted gas stream recycled to the inlet of the column wherein it is contacted with further brine. The latter may be done, for example, if the acidic gas-depleted gas still contains too high a concentration of acidic gas for sending to storage or release to the atmosphere.

In other preferred methods, however, the contacting is in a plurality of absorption columns connected in series. In this case the acidic gas-rich brine is preferably pumped straight to a subterranean formation for storage but the acidic-gas

depleted gas is supplied to the inlet of a second absorption column wherein it is contacted with further brine. The acidic gas-rich brine is again preferably pumped to a subterranean formation for storage. The acidic gas-depleted gas may be sent to storage for future use as a fuel, released to the atmosphere or supplied to the inlet of a third absorption column. There is no limit on the number of absorption columns. This may be, for example, 2, 3, 4 or 5. The columns may have the same or different structures. The columns may be operated under the same or different conditions. The skilled man will readily be able to ascertain the optimal working arrangement.

In the methods and systems of the present invention, the gas and the brine may be in cocurrent or countercurrent flow in said column. Preferably, however, the gas and the brine are in countercurrent flow in said column.

The structure and operation of the absorption column used in the methods and systems of the present invention are conventional and as described in the prior art. Thus the average temperature and pressure of the absorption column will be typical in the art. Usually the column will comprise collection trays and packing as is conventional in the art.

The method of the invention typically involves introducing a gas to be treated into the bottom of an absorption column wherein the gas flows upwards and countercurrent to a flow of brine in one or more contact sections of the column. The contact sections may optionally comprise a structural or random packing to increase the contact area between the brine and the gas. After leaving the contact sections the acidic gas-depleted gas is preferably washed and is then withdrawn through a line at the top of the column. Alternatively, after leaving the contact sections, the acidic gas-depleted gas may be recycled to the bottom of the absorption column or to another absorption column wherein it is contacted with further brine.

The brine, rich in acidic gas, is typically collected (e.g. on collection trays) and withdrawn by a line at the bottom of the column. It is then fed to a storage tank for subsequent pumping to a subterranean formation or is pumped directed to a subterranean formation.

In other preferred methods of the present invention the contacting is in a horizontal tunnel comprising treatment sections. A suitable horizontal tunnel for use in the methods of the invention is described in WO2008/156374, the entire contents of which are hereby incorporated by reference. The horizontal tunnel preferably comprises an absorption section and a cleaning section. The absorption section optionally comprises filler. The tunnel also preferably comprises an inlet for gas to be treated into the tunnel structure and downstream of the absorption and cleaning

sections, an outlet for acidic gas-depleted gas. Preferably the outlet for acidic gas-depleted gas is connected to a heat exchanger. Preferably the horizontal tunnel further comprises a cooling section downstream and/or upstream of the absorption section. Preferably the tunnel comprises one or more outlets for acidic gas-rich brine.

The geometry of the horizontal tunnel is not restricted and its cross section may be any shape, e.g. circular, square, rectangular or oval. The tunnel may be linear or may comprise curves or bends. The cross-section may be any size but advantageously is large enough to provide relatively low gas velocities through the tunnel. Preferably the velocity of gas to be treated through the tunnel is in the range 1 to 10 m/s, more preferably 2 to 7 m/s and still more preferably 2 to 5 m/s.

In the method of the invention utilising a horizontal tunnel the gas to be treated is preferably fed into the essentially horizontal tunnel in a horizontal flow. The gas is optionally cooled and then contacted with brine. The brine absorbs acidic gas, e.g. CO_2, from the flow to produce an acidic gas-depleted gas and an acidic gas-rich brine. The acidic gas-depleted gas is cleansed in the cleansing section. Optionally the acidic-gas-depleted gas is cooled. The acidic gas-rich brine is preferably collected at the bottom of the tunnel. The acidic gas-rich brine is preferably fed to a storage tank for subsequent pumping to a subterranean formation or is pumped directed to a subterranean formation.

In the cooling section, water with a temperature below the desired gas temperature is preferably sprayed as droplets onto the gas stream flowing horizontally therethrough. The water droplets absorb heat from the gas as they fall through the stream. The cooled gas flows horizontally from the cooling section into the absorbing section. Preferably means are provided for collecting the water at the bottom of the tunnel. The water used in the cooling section may be fresh water or may be brine. When brine is used, preferably brine from the subterranean formation into which the acidic gas-rich brine is to be stored is used. This cooling water is likely to contain some acidic gas. Preferably therefore brine used for cooling is pumped to the subterranean formation.

In the absorbing section, the brine is preferably brought into contact with the gas flow. Preferably the brine is sprayed onto the gas flow using nozzles. The brine may be allowed to partly follow the horizontal gas stream as its droplets fall to the bottom of the tunnel. Alternatively the absorption section may include filler whereon the absorbent forms a liquid film. This increases the contact surface between the brine and the gas phases. Preferably means are provided for collecting the acidic gas-rich brine at the bottom of the tunnel. The brine is then fed to a storage tank for

subsequent pumping to a subterranean formation or is pumped directed to a subterranean formation.

To remove brine droplets and prevent them from being transported with the gas into the next section, the gas preferably passes through a demister before leaving the absorption section. The demister collects the droplets of brine and directs them to the reservoir from where it is pumped to the subterranean reservoir.

The acidic gas-depleted gas flows horizontally into the next section of the tunnel structure where the gas is preferably washed or cleansed. The exact cleansing process used will depend on the source of the gas to be treated, whether the gas is to be used or released to the atmosphere and any restrictions associated therewith. The cleansing is preferably performed in the same manner as cooling. Thus the cleansing fluid is sprayed onto the gas flow and allowed to fall through the horizontal gas stream. Preferably the acidic gas-depleted gas is then passed through a heat exchanger.

In the cooling, absorbing and cleaning sections, the liquid is preferably sprayed using spray nozzles that are arranged on any side of the tunnel wall, or within the tunnel, and the nozzles may direct droplets in any direction. The droplets may have a counter-current, co-current or orthogonal direction compared to the horizontal gas flow. The nozzles are preferably selected to provide droplets of a size adapted to the velocity of the gas flow, e.g. to allow the droplets to follow the gas stream for a while before settling at the bottom of the tunnel.

In another preferred method of the invention the contacting is carried out in a part of the transport channel used for transporting gas to be treated to the acidic gas capture plant. Suitable systems for use in the method of the invention are described in WO2011/005116, the entire contents of which are hereby incorporated by reference.

The transport channel preferably comprises an absorption zone wherein contact is achieved by spraying liquid droplets of brine into the transport channel itself. The channel also comprises an outlet for acidic gas-depleted gas and at least one outlet for acidic gas-rich brine. The transport channel may have an angle of between 0 and 60° but is preferably horizontal. The brine is preferably sprayed with nozzles that direct the spray mainly in the flow direction of the gas being transported thus pushing it along the transport channel.

Optionally the transport channel further comprises a cooling zone upstream of the capture zone. Thus gas to be treated preferably passes through the cooling zone prior to entry to the capture zone. Optionally the transport tunnel further comprises a cleaning zone. Preferably this is downstream of the capture zone.

In the method of the invention utilising a transport channel, the gas to be treated enters the transport channel that would normally be void of processing equipment but which would lead to the acidic gas capture plant. Preferably shortly after entry into the transport channel, the gas is sprayed with cooling water in a cooling zone. Preferably the pressure of the cooling water is in the range 5-100 bars, e.g. 5-10 bars. This may be achieved using a pump before it is sprayed through nozzles. The cooling water preferably serves to push the gas through the transport channel. The cooling water is collected. Optionally brine may be used as the cooling water and in this case the collected brine is fed to a storage tank for subsequent pumping to a subterranean formation or is pumped directed to a subterranean formation.

The cooled gas preferably enters the absorption zone of the transport channel where it is sprayed with brine via nozzles. The brine is sprayed mainly in the flow direction of the gas and with a speed high enough to compensate for any pressure loss experienced in the first zone of the channel. The brine droplets move through the gas stream and absorb acidic gas therefrom. The acidic gas-rich brine is collected upstream, preferably by the use of a demister, and fed to a storage tank for subsequent pumping to a subterranean formation or is pumped directed to a subterranean formation.

The gas continues downstream in the channel and may optionally enter a second absorption zone wherein it is sprayed with further brine. Again the brine is preferably sprayed from nozzles and with a speed that pushes the gas through the channel. The brine droplets are collected upstream and pumped to a subterranean formation for storage. The number of stages needed for absorption is a trade-off against the brine flow. Typically 2 or 3 zones will be present.

The acidic gas-depleted gas preferably enters a cleaning zone wherein the gas may be washed with water and/or other cleaning fluid. The cleaning fluid is sprayed via nozzles. The cleaned acidic gas-depleted gas may then be released, sent for further treatment or for storage prior to use.

In preferred methods of the invention the acidic gas-rich brine pumped into the subterranean formation in step (ii) is a solution. In further preferred methods of the invention the acidic gas-rich pumped into the subterranean formation in step (ii) does not comprise solids. In particularly preferred methods of the invention, the acidic gas-rich brine is untreated prior to pumping into a subterranean formation for storage. As used herein the term “untreated” means that no chemicals are added to the acidic gas-rich brine and no constituents of the acidic gas-rich brine are removed. Thus

preferably the acidic gas-rich brine produced in step (i) is directly pumped into a subterranean formation for storage.

The brine for use in the methods and systems of the invention derives from the subterranean formation in which the acidic gas-rich brine is to be stored. In preferred methods and systems, the brine is pre-pumped out of the formation and stored in tanks prior to use. Alternatively, however, the brine may be pumped out of the formation at the same time as acidic-gas rich brine is being pumped into it. In this case the brine being pumped out of the formation is pumped from a relatively higher position (i.e. lesser depth) in the reservoir to the depth at which acidic gas-rich brine is being pumped into the reservoir. This avoids and minimises any mixing of the brines.

Preferably the subterranean formation into which the acidic gas-rich brine is pumped is offshore. Still more preferably the subterranean formation into which the acidic gas-rich brine is pumped is a formation at a depth of at least 800 metres, more preferably at least 1000 metres. Deep subterranean formations are preferred as the solubility of acidic gases such as CO_2 in brine increases with increasing depth and pressure.

The acidic gas-rich brine pumped into the reservoir for storage preferably comprises 1-8 mol % acidic gas, still more preferably 2-7 mol % acidic gas, e.g. 4-6 mol% acidic gas. The acidic gas-rich brine pumped into the reservoir for storage preferably comprises 1-8 mol % CO_2, still more preferably 2-7 mol % CO_2, e.g. 4-6 mol% CO_2. As a result of the increased concentration of acidic gas, e.g. CO_2, in the brine it will generally be more dense than the brine present in the formation into which it is pumped. This is advantageous since it ensures that the acidic-gas rich brine is substantially stored at the bottom of said subterranean formation. The density of the acidic gas-rich brine is preferably at least 2%, still more preferably at least 4%, and yet more preferably at least 7% higher than the density of the original brine.

Correspondingly the acidic gas-depleted gas preferably comprises 0-50%, still more preferably 0-20 % and yet more preferably 0-10 % of the acidic gas present in the original gas. The acidic gas-depleted gas preferably comprises 0-20 mol% acidic gas, still more preferably 0-15 mol% acidic gas, e.g. 0-10 mol % acidic gas. The acidic gas-depleted gas preferably comprises 0-20 mol % CO_2, still more preferably 0-15 mol % CO_2, e.g. 0-10 mol% CO_2. Generally this gas is sent for further processing, to storage for future use as fuel or released to the atmosphere. The amount of acidic gas present in the acidic gas-depleted gas partially depends on the gas treated in the method of the invention. The table below shows preferred levels of acidic gas present in acidic gas-depleted gas achieved in the methods of the invention.

Source	[CO_2] (mol%)	[H_2S] mol%	[CO_2] mol% After cleaning	[H_2S] mol% After cleaning
Flue gas from gas power plant	3-5	<1	0.3-1	<0.01
Flue gas from coal power plant	10-15	<1	1-2	<0.01
Gas from cement production	18-25	<1	1-5	<0.01
Gas from steam generator	6-10	<1	0.5-2	<0.01
Sour gas	5-40	1-40	0.05-3	< 4 ppm
Acid gas	3-80	<1	0.05-3	< 4 ppm
Syngas from coal gasification	20-50	<1	0.5-10	< 4 ppm
Syngas from natural gas reforming	20-30	<1	0.5-10	< 4 ppm

Some preferred methods of the invention further comprise purifying a portion of the captured CO_2, e.g. for use in enhanced oil recovery techniques. These methods preferably further comprise the steps of:

(ia) separating the acidic gas-rich brine into at least a first portion and a second portion;

(ib) reducing the pressure of the first portion of acidic gas-rich brine to produce CO_2 gas and brine and;

(ii) pumping the second portion of acidic gas-rich brine into a subterranean formation for storage.

Thus a further preferred method of the present invention comprises:(i) contacting the gas with brine to produce an acidic gas-rich brine and an acidic gas-depleted gas;

(ia) separating the acidic gas-rich brine into at least a first portion and a second portion;

(ib) reducing the pressure of the first portion of acidic gas-rich brine to produce CO_2 gas and brine and;

(ii) pumping the second portion of acidic gas-rich brine into a subterranean formation for storage,

wherein at least some of the brine used in step (i) derives from the subterranean formation into which said acidic-gas rich brine is pumped in step (ii).

In preferred methods of the invention the CO_2 gas obtained in step (ib) has a purity of at least 99 %, more preferably at least 99.5 % and still more preferably at least

99.9 %. Preferably the CO_2 gas is used in enhanced oil recovery. More preferably the CO_2 gas is mixed with acidic gas-rich brine to produce brine that is super saturated with CO_2. Particularly preferably the acidic gas-rich brine mixed with the CO_2 is obtained in step (ia). Thus in some methods of the present invention in step (ia) the acidic gas-rich brine is preferably separated into first, second and third portions. The first portion is used to obtain CO_2, The second portion is pumped to storage. The third portion is mixed with the CO_2 to produce CO_2 super saturated brine. The CO_2 super saturated brine is preferably used in enhanced oil recovery.

In further preferred methods of the invention the brine produced in step (ib) is recycled for contacting with further gas.

The methods of the present invention may be operated continuously or batchwise. Preferably the methods of the invention are operated continuously.

The methods of the present invention may be carried out using a system as hereinbefore described. In preferred systems the contact vessel is an absorption column. In further preferred methods, the means for supplying said gas supplies said gas to the bottom of said contact vessel. In yet further preferred methods the means for supplying said brine supplies said brine to the top of said contact vessel.

In other preferred systems of the invention, the contact vessel is a horizontal tunnel comprising treatment sections or a transport channel for transporting gas to be treated to an acidic gas capture plant.

Preferred systems comprise a means for cooling said brine prior to its introduction into the contact vessel. Further preferred systems comprise a means for compressing said brine prior to its introduction into the contact vessel.

Preferred systems further comprise a means for heating and/or expanding the acidic gas-depleted gas after it has been treated by the method of the present invention.

Preferred systems of the invention further comprise a means to monitor the acidic gas content of said acidic-gas depleted gas. This is advantageous as it can be used to ensure that only gas having a sufficiently low level of acidic gas, e.g. CO_2, is released to the atmosphere or sent for storage prior to use as a fuel. If an acidic gas-depleted gas comprises a higher than desirable level of acidic gas, the gas can be routed back to the contact vessel or to a different contact vessel. Preferred systems of the invention therefore comprise a plurality of contact vessels connected in series.

Another preferred system of the present invention further comprises:

(g) a means for dividing the acidic gas-rich brine into at least a first portion and a second portion;

(h) a means for transporting the first portion to a depressuriser for reducing the pressure of the first portion of acidic gas-rich brine, wherein said depressuriser has an outlet for CO_2 gas and an outlet for brine;

(i) a means for transporting the second portion of acidic gas-rich brine to the pump.

Thus a preferred system of the present invention comprises:

(a) a means for supplying said gas to a contact vessel;

(b) a means for supplying brine to said contact vessel;

(c) a contact vessel for contacting said gas with said brine to produce an acidic gas-rich brine and an acidic gas-depleted gas;

(d) an outlet for said acidic gas-depleted gas;

(e) an outlet for said acidic-gas rich brine;

(g) a means for dividing the acidic gas-rich brine into at least a first portion and a second portion;

(h) a means for transporting the first portion to a depressuriser;

(i) a depressuriser for reducing the pressure of the first portion of acidic gas-rich brine having an outlet for CO_2 gas and an outlet for brine;

(j) a means for transporting the second portion of acidic gas-rich brine to a pump; and

(f) a pump for transporting said acidic gas-rich brine into a subterranean formation.

In preferred systems of the invention, the depressuriser is a flash tank.

In some preferred systems the outlet for CO_2 gas in the depressuriser is connected to a storage tank.

In particularly preferred systems of the invention, the means for dividing the acidic gas-rich brine divides the brine into first, second and third portions and the system further comprises a means for transporting the third portion to a mixing tank. In particularly preferred systems the outlet for CO_2 gas in the depressuriser is connected to the mixing tank. Preferably the mixing tank has an outlet for CO_2 super saturated brine.

In a further preferred system of the present invention, the outlet for brine of the depressuriser is connected to the means for supplying brine to the contact vessel.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS OF THE INVENTION

The invention will now be described with reference to the following non-limiting examples.

Figure 1 shows the relationship between CO_2 storage mechanism, the time necessary to achieve it and the associated safety level of such state-of-the-art CCS methods;

Figure 2 shows a typical prior art method for CO_2 capture and storage;

Figure 3 shows a schematic diagram of a method of the invention;

Figure 4 shows a schematic diagram of a preferred system of the invention;

Figure 5 shows a schematic diagram of a further method of the invention; and

Figure 6 shows a schematic diagram of a further preferred method of the invention wherein CO_2 is captured, purified and stored.

Referring to Figure 1, it can be seen that 1 year after CO_2 in the form of gas is introduced into a formation, the vast majority of it is trapped on the basis of structural and stratigraphic trapping. This means that the gaseous CO_2 present in the formation is trapped merely by the fact that it cannot find a route out of the formation. The CO_2 will, however, migrate within the formation. It is impossible to control and very difficult to monitor the precise location of the CO_2 whilst it is in gas form.

It can also be seen from Figure 1 that the trapping of CO_2 by solubility trapping, i.e. dissolution in formation water, is not achieved until at least 50 years after the CO_2 is injected into the formation. Moreover it is 1000 years following injection until a significant proportion (e.g. about 30% of the CO_2 present) is trapped in this form. After 1000 years, about 15 % CO_2 is stored on the basis of structural and stratigraphic trapping, about 30% is stored on the basis of residual CO_2 trapping, about 30 % as solubility trapping and the remainder by mineral trapping. This is not ideal since as long as CO_2 exists in gas form it is free to migrate within the formation and it is impossible to control and difficult to monitor.

The methods and systems of the present invention overcome this problem by pumping the CO_2 into a subterranean formation in a brine. This means that the CO_2 is put in place with solubility trapping as the trapping mechanism.

Referring to Figure 2, it shows a typical prior art technique for the capture and storage of CO_2. Gas to be treated, generally cooled, is introduced in an inlet chamber 1 at the bottom of the absorption column 2. From the inlet chamber 1, the gas flows upwards in the absorption column and countercurrent to liquid absorbent, e.g. amine solution. Typically 80-99 % of the original CO_2 present in the gas is removed by absorption. The gas exits via line 3 and is released to the atmosphere, sent for further treatment or sent to storage prior to use as a fuel.

Absorbent is introduced into the column via line 4 and is sprayed on top of the gas by means of liquid distribution means. The absorbent is collected from the bottom of the column and withdrawn via line 5.

In the regeneration column 6 the CO_2 rich absorbent flows downwards, countercurrent to a flow of released CO_2 and water vapour. Lean absorbent leaves the regeneration column through an outlet 7. The lean absorbent is recycled back to the

absorption column 2 through line 8 and optionally cooled in a heat exchanger (not shown) against rich absorbent. In the heat exchanger the relatively cold CO_2 rich absorbent is heated against the relatively hot lean absorbent.

CO_2 released from the absorbent and water vapour is withdrawn from the regenerator column through line 9. The gas in the line is cooled in a reflux condenser 10 to condense water that is separated from the remaining gas, mainly comprising CO_2. The CO_2, withdrawn in line 11, may be further treated, e.g. drying, compression and/or deposition. The condensed water is withdrawn through line 12 and pumped back to the bottom of the regeneration column.

A major disadvantage of this process is the generation of water vapour is energy intensive.

Referring to Figure 3 it shows a preferred method of the invention. Flue gas 100, generally cooled and compressed, is introduced at the bottom of the absorption column 101. From the inlet 102, the gas flows upwards in the absorption column and countercurrent to brine, in one or more contact sections, 103, 104. The brine is from the subterranean formation 115 in which the CO_2 rich brine that results from the method will be stored.

The illustrated absorption column is provided with two serially connected contact sections 103, 104 but any number of such sections may be included. After leaving the contact sections 103, 104 the gas is washed by a countercurrent flow of water in a washing section 105 to remove any impurities in the gas flow. Washing water is introduced via line 106 and sprayed at the top of the washing section 105. The water is collected at plate 107 below the washing section and removed via line 108. CO_2 depleted gas is withdrawn through line 109. The column 101 may comprise several water sections or other types of polishing/washing sections in the upper part. Typically 80-99 % of the original CO_2 present in the gas is removed by absorption.

Brine is introduced into the column via line 110 and is sprayed on top of the upper contact section 104 by means of liquid distribution means. The brine flows through the upper contact section 104 and is collected at a plate 111. The brine is withdrawn via line 112 and sprayed at the top of the lower contact section 103. After flowing through the lower contact section 103 the brine and the CO_2 absorbed thereto is collected from the bottom of the column and withdrawn via line 113.

The temperature of the brine in the absorption step is generally from about 5 to 40 ^{o}C, for example from 10 to 15 ^{o}C. The overall pressure in the absorption step is generally from about 50 to 200 barg, preferably from about 80 to 150 barg.

The CO_2 rich brine collected at the bottom of the column is then withdrawn to a storage tank 114. Once the level of CO_2 rich brine in the storage tank reaches a certain level, it is pumped to the subterranean formation 115 for storage. The CO_2 rich brine is more dense that the formation water present and therefore sinks to the bottom of the reservoir where the CO_2 is safely stored.

The method and system of the present invention has a number of advantages over the above-described prior art carbon capture and storage technique as follows:

- It eliminates the need for a regenerator and the associated use of steam to separate CO_2 from the absorbent, which provides both cost and energy savings
- By extracting brine from a formation, the volume/space available for storage of CO_2-rich brine is increased, thus increasing storage capacity and reducing pressure build-up significantly
- By injecting CO_2-rich brine into a formation, which will have a higher density than formation water, the solution will migrate to the bottom of the reservoir and the CO_2 will be significantly safer compared to state-of-the-art methods wherein significant amounts of CO_2 migrate to the top of the formation
- No high concentrations of CO_2 will exist in the methods or systems of the invention.

Referring to Figure 4, it illustrates a system of the present invention. The system comprises a line 201 for supplying gas, a line 202 for supplying brine and an absorption column 200. The line 202 supplies brine from the subterranean formation in which the CO_2 rich brine will be stored.

Preferably the line 201 supplies the gas, e.g. natural gas, to the bottom of the column 200. Preferably the line 202 supplies the brine to the top of the column 200. The column also comprises an outlet 203 for the acidic gas-depleted gas and an outlet 204 for the acidic-gas rich brine. Preferably the system comprises a means 205 for monitoring the acidic gas content of said acidic gas-depleted gas. The system also comprises pumps 206 for transporting the acidic gas-rich brine into a subterranean formation 211.

Some preferred systems of the present invention comprise one absorption column. Other preferred systems, such as the one shown in Figure 4, comprise a plurality of absorption columns 200 and 210 connected in series. In this case the outlet 203 for the acidic gas-depleted gas is connected to a line 207 for supplying gas to the second column 210. The acidic gas-rich brines from both columns 200 and 210 are collected, combined and pumped to storage tank 208 from where they are transported into the subterranean formation. The acidic gas-depleted gas from the second column

210 is collected via line 209 and sent for further processing before being used as a fuel.

Referring to Figure 5, it shows a further preferred system of the invention. Syngas 308 comprising CO_2 and H_2S is recovered from UCG process 301. The temperature and pressure of the syngas may vary depending on the UCG process. Typically, however, the syngas will have a temperature in the range 10-100 ^oC and a pressure of 15-200 barg. The syngas 308 is introduced into a first section 302 of the horizontal tunnel. In this section 302, the syngas can optionally be compressed. The section 302 also preferably comprises a damper that can be opened to direct syngas directly to storage 307. This option can, for example, be utilised during maintenance of a section.

After passing through section 302, the syngas 309 enters the cooling section 304. Within this section the syngas is cooled to the necessary extent. Whilst the syngas flows horizontally through the section 304, water with a temperature below the desired gas temperature is sprayed as droplets into the stream. The water droplets absorb heat from the gas as they fall through the stream. The water is collected and drained from the bottom of the channel. Optionally brine may be used as the cooling water and in this case the brine is collected and pumped to the subterranean formation for storage.

The cooled syngas 310 flows horizontally from the cooling section into the absorption section 305 where droplets of brine are introduced into the syngas stream and allowed to fall through the gas. The brine therefore contacts the acidic gas, in this case CO_2 and H_2S, and absorbs it. Optionally a filler material may be used in the absorption section.

The acidic gas-rich brine leaves the tunnel as stream 311 and is collected. It is then pumped to a subterranean formation for storage.

The acidic gas-depleted gas 312 flows horizontally into the next section 306 of the tunnel via a demister (not shown) where the syngas is washed with water or cleansed with other fluid. The cleansing is performed in the same manner as the cooling and absorption, namely by spraying the cleansing fluid through nozzles into the horizontal stream, letting the droplets fall through the gas and collecting the medium at the bottom of the tunnel. Optionally further cleansing sections may be provided for the removal of other impurities, e.g. NO_x and/or SO_2. The cleansed syngas 313 passes to a heat exchanger 303 which heats the syngas stream. Preferably the syngas 313 undergoes an expansion in an expansion unit 314 prior to entry into the heat

exchanger 303. The product of the process is an acidic gas-depleted syngas 315 that is sent to storage 307 prior to use in energy generation.

Referring to Figure 6, it shows a further preferred method of the invention wherein a portion of captured CO_2 is purified. The method shown in Figure 6 is the same as that in Figure 3 except that CO_2 rich brine 113 is divided into three portions. A first portion is transported to a depressuriser 120 wherein the pressure of the CO_2 rich brine is reduced to produce CO_2 gas and brine. The CO_2 gas has a purity of >99 %. The brine is recycled via line 121 to line 110 supplying brine to the contact vessel. The CO_2 gas is transported via line 122 to a mixing tank 123.

A second portion of the CO_2 rich brine is transported to storage tank 114 prior to pumping into a subterranean formation 115 for storage.

A third portion of the CO_2 rich brine is transported via line 124 to mixing tank 123. Thus in mixing tank 123 CO_2 brine and CO_2 are mixed to produce CO_2 super saturated brine. This is removed from the tank via line 125 and used in enhanced oil recovery.

CLAIMS:

1. A method for capturing and storing an acidic gas from a gas comprising:
(i) contacting said gas with brine to produce an acidic gas-rich brine and an acidic gas-depleted gas; and
(ii) pumping said acidic gas-rich brine into a subterranean formation for storage, wherein at least some of said brine used in step (i) derives from the subterranean formation into which said acidic-gas rich brine is pumped in step (ii).

2. A method as claimed in claim 1 , wherein all of said brine used in step (i) derives from the subterranean formation into which said acidic-gas rich brine is pumped in step (ii).

3. A method as claimed in claim 1 or 2, wherein said acidic gas-rich brine produced in step (i) and/or pumped into said subterranean formation in step (ii) is a solution.

4. A method as claimed in any one of claims 1 to 3, wherein said acidic gas-rich brine produced in step (i) and/or pumped into said subterranean formation in step (ii) does not comprise solids.

5. A method as claimed in any one of claims 1 to 4, wherein said brine is untreated prior to contact with said gas.

6. A method as claimed in any one of claims 1 to 5, wherein no chemicals are added during the contacting step.

7. A method as claimed in any one of claims 1 to 6, wherein said acidic gas-rich brine is untreated prior to pumping into a subterranean formation for storage.

8. A method as claimed in any one of claims 1 to 7, further comprising:
(ia) dividing said acidic gas-rich brine into at least a first portion and a second portion;
(ib) reducing the pressure of said first portion of acidic gas-rich brine to produce CO_2 gas and brine and;

(ii) pumping said second portion of acidic gas-rich brine into a subterranean formation for storage.

9. A method as claimed in claim 8, wherein said CO_2 gas has a purity of at least 99 %.

10. A method as claimed in claim 8 or 9, wherein said CO_2 gas is used in enhanced oil recovery.

11. A method as claimed in claim 8 or 9, wherein said CO_2 gas is mixed with acidic gas-rich brine to produce brine that is super saturated with CO_2.

12. A method as claimed in claim 11, wherein said CO_2 super saturated brine is used in enhanced oil recovery.

13. A method as claimed in any one of claims 8 to 12, wherein said brine produced in step (ib) is recycled for contacting with further gas.

14. A method as claimed in any one of claims 1 to 13, wherein said gas is an exhaust gas or a fuel gas.

15. A method as claimed in claim 14, wherein said gas is an exhaust gas, gas from industrial manufacturing processes or gas produced during hydrocarbon recovery.

16. A method as claimed in claim 14, wherein said gas is a fuel gas.

17. A method as claimed in any one of claims 1 to 16, wherein said acidic gas is CO_2.

18. A method as claimed in any one of claims 1 to 17, wherein said contacting is in at least one absorption column.

19. A method as claimed in claim 18, wherein said contacting is in one absorption column.

20. A method as claimed in claim 18, wherein said contacting is in a plurality of absorption columns connected in series.

21. A method as claimed in any one of claims 1 to 17, wherein said contacting is in a horizontal tunnel comprising treatment sections.

22. A method as claimed in any one of claims 1 to 17, wherein said contacting is in a part of a transport channel for transporting gas to be treated to an acidic gas capture plant.

23. A method as claimed in any one of claims 1 to 22, wherein said acidic-gas rich brine is denser than the brine present in the formation into which it is pumped.

24. A method as claimed in any preceding claim which operates continuously.

25. A system for capturing and storing an acidic gas from a gas comprising:
(a) a means for supplying said gas to a contact vessel;
(b) a means for supplying brine to said contact vessel;
(c) a contact vessel for contacting said gas with said brine to produce an acidic gas-rich brine and an acidic gas-depleted gas;
(d) an outlet for said acidic gas-depleted gas;
(e) an outlet for said acidic-gas rich brine; and
(f) a pump for transporting said acidic gas-rich brine into a subterranean formation.

26. A system as claimed in claim 25, wherein said contact vessel is an absorption column.

27. A system as claimed in claim 25, wherein said contact vessel is a horizontal tunnel comprising treatment sections.

28. A system as claimed in claim 25, wherein said contact vessel is a part of a transport channel for transporting gas to be treated to an acidic gas capture plant.

29. A system as claimed in any one of claims 25 to 28, further comprising a means to monitor the acidic gas content of said acidic-gas depleted gas.

30. A system as claimed in any one of claims 25 to 29, further comprising:

(g) a means for dividing said acidic gas-rich brine into at least a first portion and a second portion;

(h) a means for transporting said first portion to a depressuriser;

(i) a depressuriser for reducing the pressure of said first portion of acidic gas-rich brine having an outlet for CO_2 gas and an outlet for brine;

(j) a means for transporting said second portion of acidic gas-rich brine to said pump.

31. A system as claimed in claimed in claim 30, wherein said means for dividing said acidic gas-rich brine divides said brine into first, second and third portions and said system further comprises a means for transporting said third portion to a mixing tank.

32. A system as claimed in claim 31, wherein said outlet for CO_2 gas of said depressuriser is connected to said mixing tank.

33. A system as claimed in any one of claims 30 to 32, wherein said outlet for brine of said depressuriser is connected to said means for supplying brine to said contact vessel.

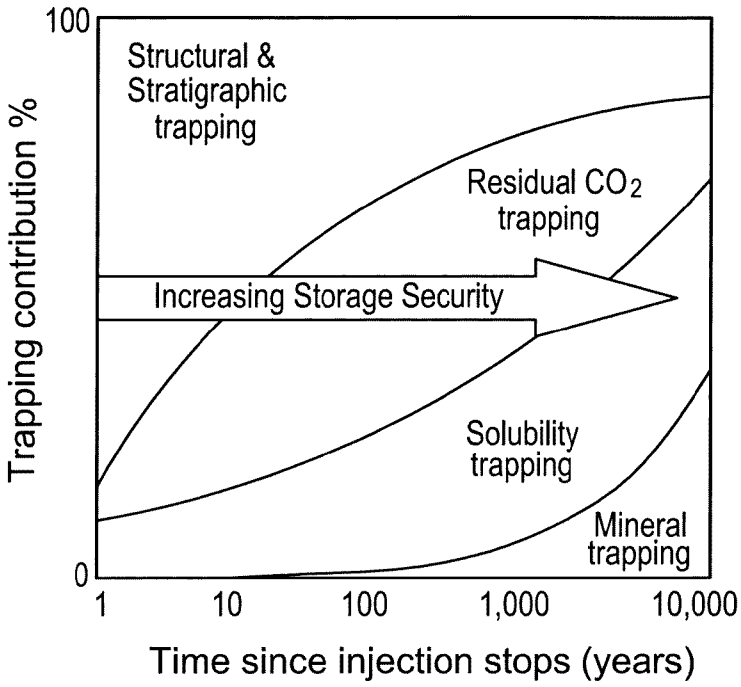

Figure 1

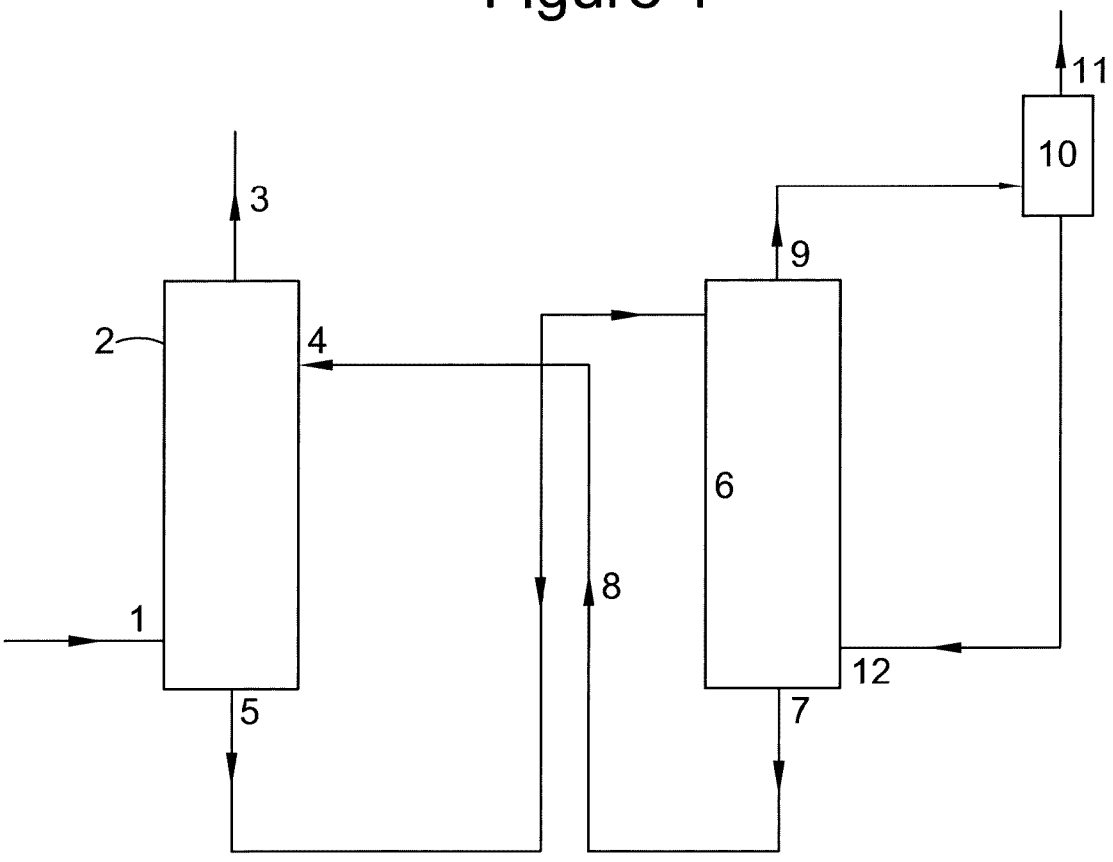

Figure 2

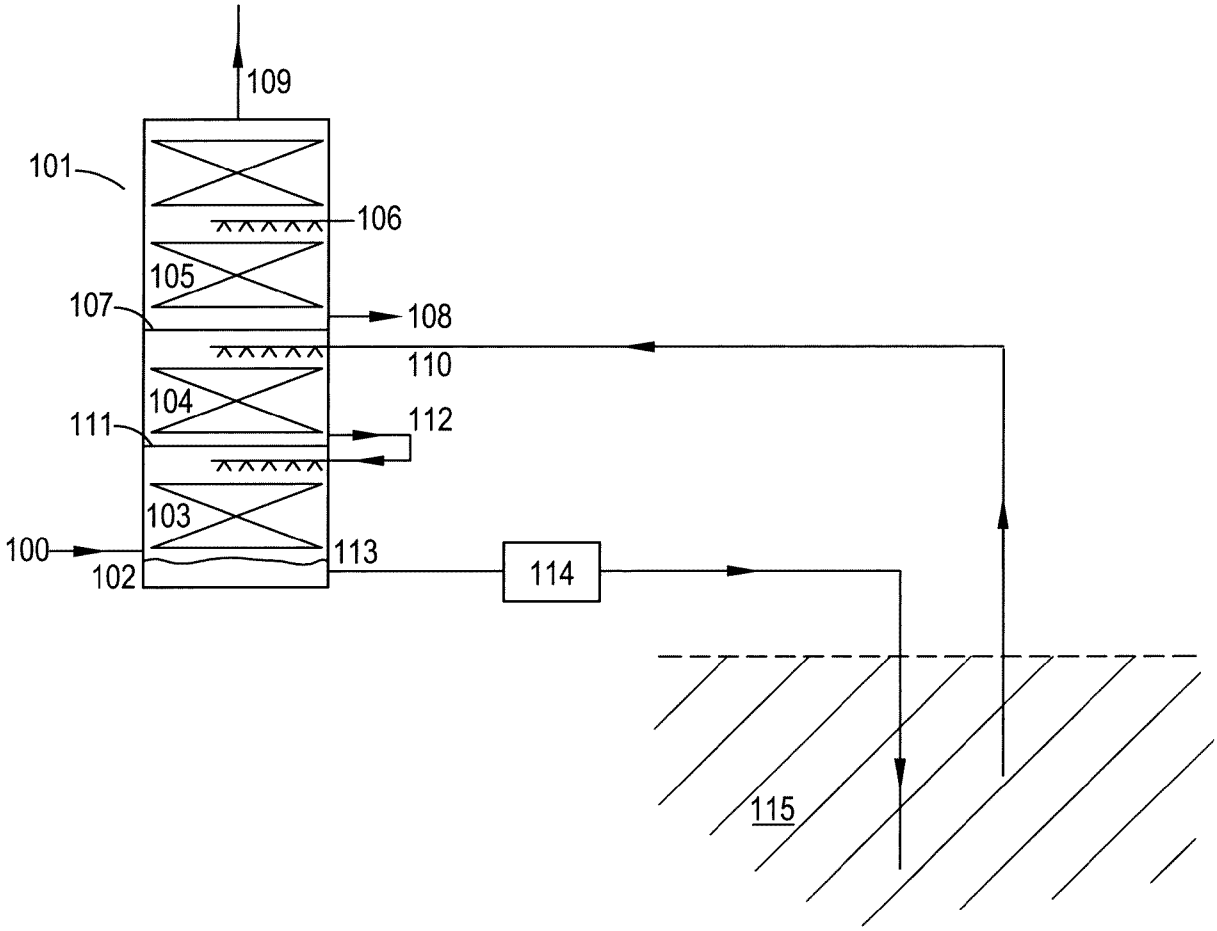

Figure 3

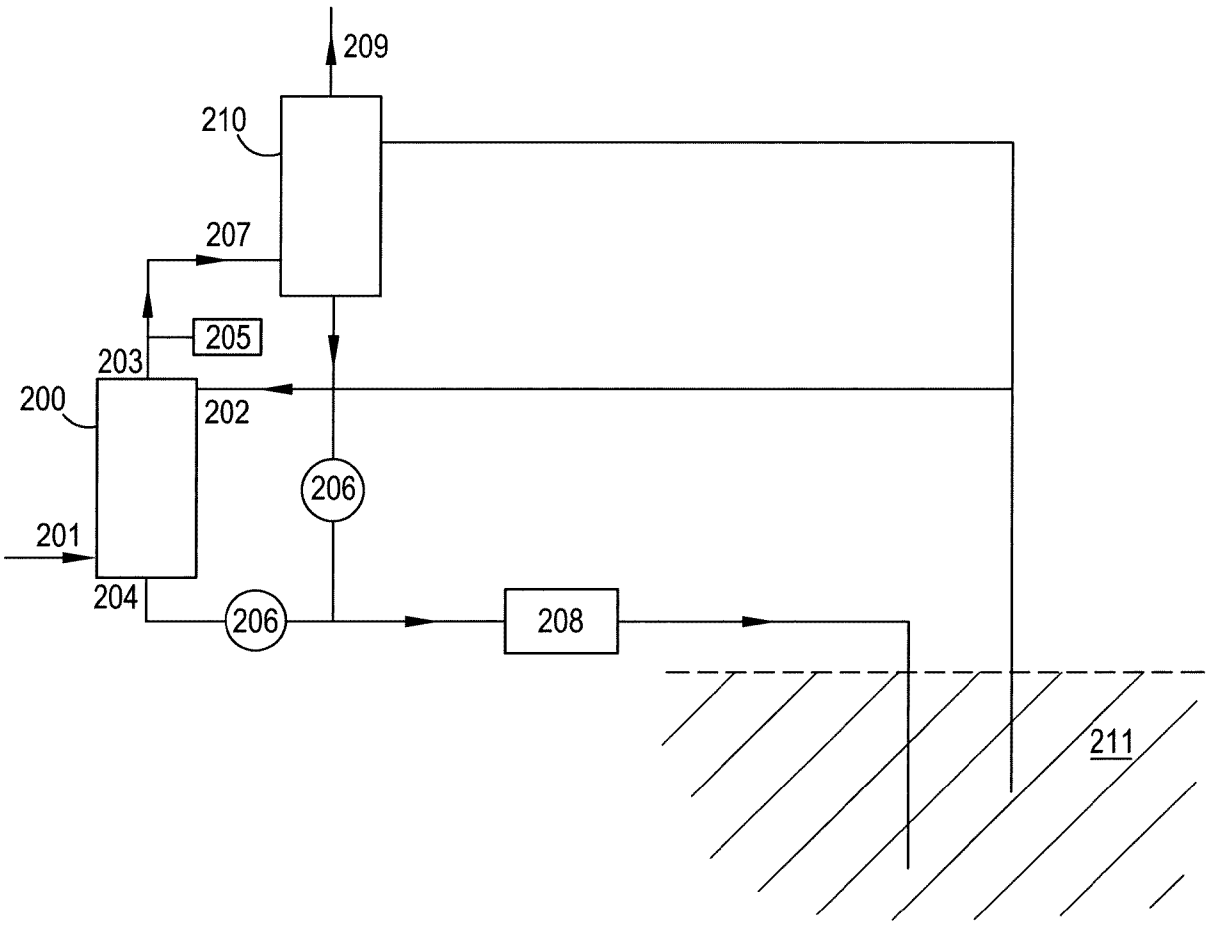

Figure 4

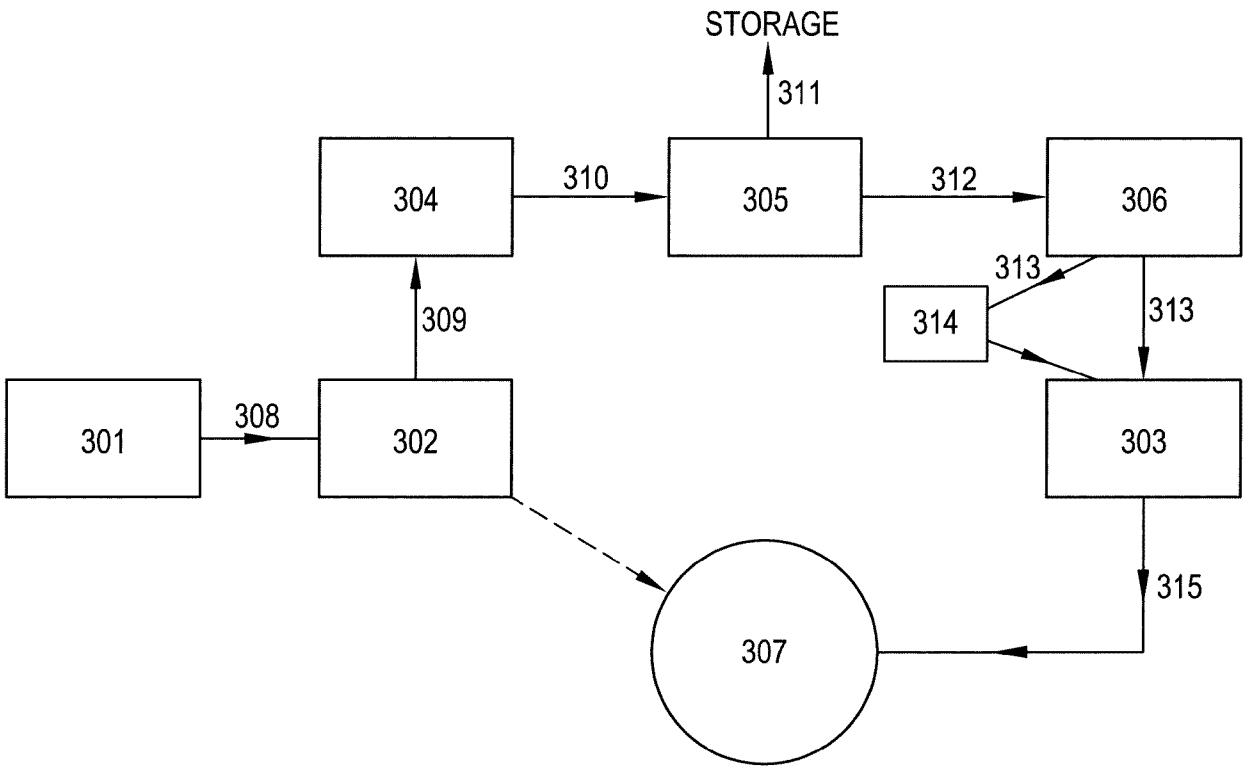
STORAGE
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Figure 5

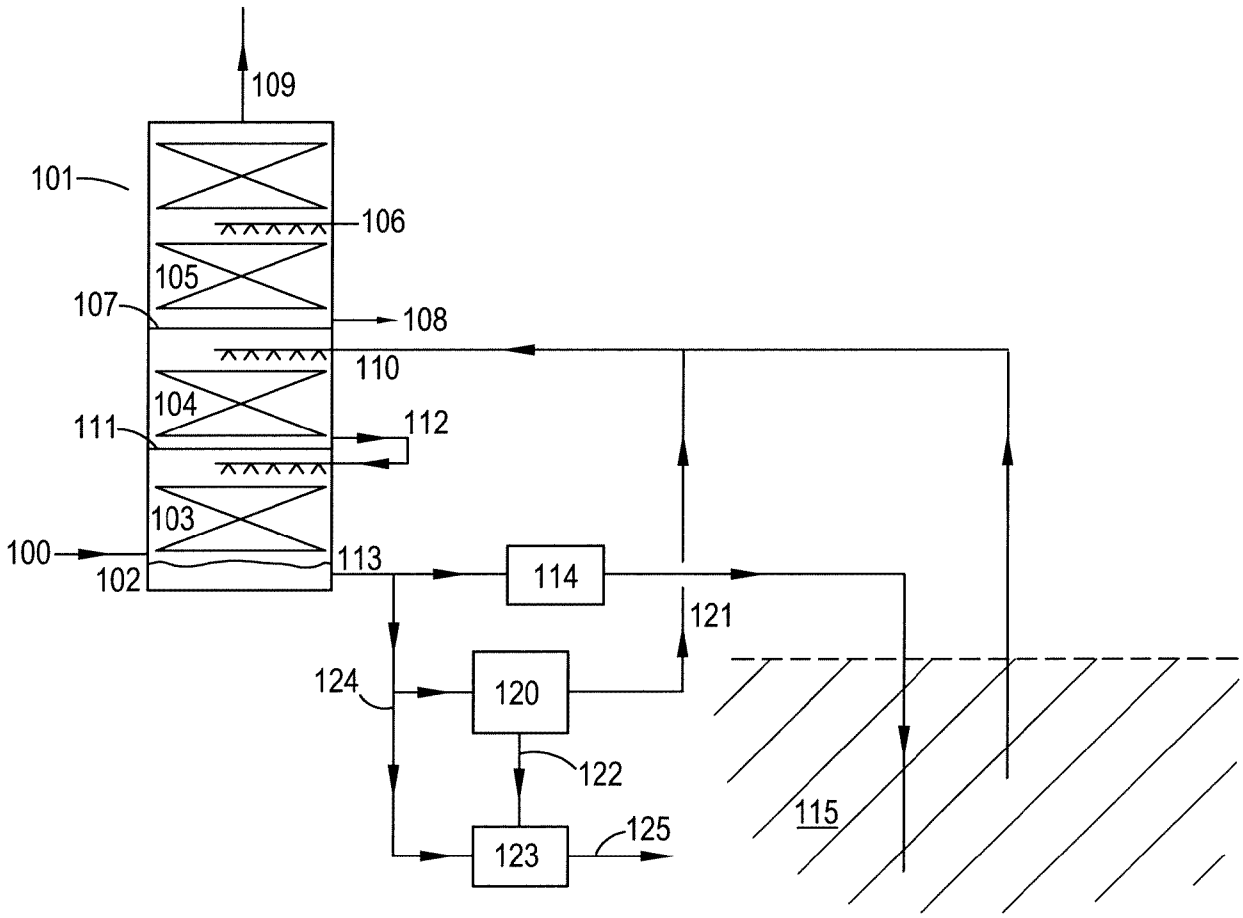
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Figure 6

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2013/056462

A. CLASSIFICATION OF SUBJECT MATTER
INV. B01D53/14
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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2011/017609 A1 (CALERA CORP [US]; CONSTANTZ BRENT R [US]; SELF KYLE [US]; SEEKER WILLI) 10 February 2011 (2011-02-10) paragraph [0062] - paragraph [0066] paragraph [0179] paragraph [0183] - paragraph [0187] claims 62,75; figures 2-5 ----- -/--	1-33

[X] Further documents are listed in the continuation of Box C.

[X] 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	Date of mailing of the international search report
23 May 2013	06/06/2013

Name and mailing address of the ISA/	Authorized officer
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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2013/056462

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