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(54) **Title:** SEQUESTRATION OF CARBON DIOXIDE

(57) **Abstract:** A method for sequestering carbon dioxide is disclosed comprising the steps of: (a) forming a mixture of an aqueous phase which comprises an aqueous solution of one or more salts and a water-immiscible phase which includes one or more tertiary amines; (b) introducing carbon dioxide into the mixture so as to form a precipitate of one or more of a bicarbonate, a carbonate or mixtures thereof and one or more tertiary amine salts; (c) removing the precipitate from the mixture; (d) causing the aqueous phase and the water-immiscible phase to separate; (e) removing the water-immiscible phase from the aqueous phase; (f) contacting the water-immiscible phase with water and heating so as to form one or more tertiary amines from the salts thereof in the water-immiscible phase and an acidic aqueous phase; and (g) separating the water-immiscible phase from the acidic aqueous phase.



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Sequestration of Carbon Dioxide

Cross-Reference to Related Applications

5 The present application claims priority from Australian patent application no. 2011902897 filed on 20 July 2011, the content of which is incorporated herein by reference.

Technical Field

10 This invention relates to processes for the capture of carbon dioxide, especially to the sequestration of carbon dioxide and more particularly to a process that converts the carbon dioxide into useful compounds.

Background Art

15 Carbon dioxide emissions may be the single biggest threat to life on the planet should they lead to a 'runaway greenhouse effect'. The Intergovernmental Panel on Climate Change (IPCC) is more than 90% sure that CO₂ emissions (and other greenhouse gases) are responsible for the observed 1°C temperature rise and 0.2 m sea-level rise. Meanwhile, the International Energy Agency (IEA) has predicted CO₂ emissions will rise by a further 66% before 2030. Consequently, the IPCC has
20 projected further rises in temperature (1-4°C) and sea-levels (0.2-0.6 m), which are expected to herald enormous changes to the natural world. Given that there is no sign that the burning of fossil fuels will ease in the future, technologies for the capture and storage of CO₂ are of unparalleled importance and immediate need. All over the world, including Australia, a price on carbon emissions is being implemented or considered.
25 A price on carbon relies heavily on technologies for the capture and storage of CO₂ being available. If they don't exist, there are no incentives for business to invest and governments are unable to enforce their schemes.

30 While considerable research is aimed at capturing and recovering CO₂ as a pure high pressure stream for subsequent storage, little research has been focused on the formation of carbonates. Rather, the most promising solution proposed so far for the CO₂ problem is widely considered to be capturing and compressing it followed by storage in large underground reservoirs, such as depleted oil fields and saline aquifers.

35 The formation of carbonates offers the potential of long term stable storage and/or the use of the so-formed carbonates in other industrial processes.

One of the conventional CO₂ capture technologies involves absorbing CO₂ in a mixture of primary and tertiary amines, including monoethanolamine (MEA) and methyldiethanolamine (MDEA) respectively. The reason for this is that while the primary amine forms a strong carbamate bond and therefore enables a high CO₂ loading due to the strength of the bond, considerable energy is needed to break it and regenerate the MEA (approximately 3-5 MJ/kg CO₂). In order to reduce the energy load, tertiary amines are blended. Tertiary amines don't bond with CO₂ but rather strip the solution of H⁺ ions thus driving the formation of HCO₃²⁻ and CO₃²⁻ ions in solution. The loading of CO₂ in solution as these ions is much lower but the energy needed to regenerate the MDEA is much less, such that the total energy needed to regenerate the MEA/MDEA is around 1-3 MJ/kg CO₂. However, the introduction of MDEA means that taller towers are needed for a given separation efficiency and so a balance between capital and operating (energy) cost must be struck.

It has been realised by the present inventor that if using the aforementioned amine process it was possible to cause the formation of solid bicarbonates and/or carbonates, then the process ought to be more effective in the sense that the carbon dioxide would be sequestered in a easy to store or reuse form, namely sodium bicarbonate. However, using the existing amine process does not lead to the formation of sodium bicarbonate.

Therefore, the present inventor now proposes the use of particular tertiary amines in a process that would directly lead to the formation of bicarbonates and/or carbonates.

Disclosure of Invention

Accordingly the present invention consists in a first aspect in a method for sequestering carbon dioxide comprising the steps of:

- (a) forming a mixture of an aqueous phase which comprises an aqueous solution of one or more salts and a water-immiscible phase which includes one or more tertiary amines;
- (b) introducing carbon dioxide into the mixture so as to form a precipitate of one or more of a bicarbonate, a carbonate or mixtures thereof and one or more tertiary amine salts;
- (c) removing the precipitate from the mixture;
- (d) causing the aqueous phase and the water-immiscible phase to separate;

- (e) removing the water-immiscible phase from the aqueous phase;
- (f) contacting the water-immiscible phase with water and heating so as to form one or more tertiary amines from the salts thereof in the water-immiscible phase and an acidic aqueous phase; and
- 5 (g) separating the water-immiscible phase from the acidic aqueous phase.

The invention further consists in a second aspect in a method for sequestering carbon dioxide comprising the steps of:

- 10 (a) forming a mixture of an aqueous phase which comprises an aqueous solution of one or more salts and an ion exchange resin having tertiary amine functionality;
- (b) introducing carbon dioxide into the mixture so as to form a precipitate of one or more of a bicarbonate, a carbonate or mixtures thereof and one or more tertiary amine salts on the ion exchange resin;
- (c) removing the precipitate from the mixture;
- 15 (d) removing the ion exchange resin from the aqueous phase;
- (e) regenerating the tertiary amine functionality of the ion exchange resin by contacting the same with hot water.

The invention still further consists in a third aspect in a method for sequestering carbon dioxide comprising the steps of:

- 20 (a) forming a mixture of an aqueous phase which comprises an aqueous solution of one or more salts and a solid matrix impregnated with one or more tertiary amines;
- (b) introducing carbon dioxide into the mixture so as to form a precipitate of one or more of a bicarbonate, a carbonate or mixtures thereof and one or more tertiary amine salts on the ion exchange resin;
- 25 (c) removing the precipitate from the mixture;
- (d) removing the ion solid matrix from the aqueous phase;
- (e) regenerating the tertiary amine functionality of the solid matrix by contacting the same with hot water.
- 30 (f) contacting the solid matrix with hot water so as to form one or more tertiary amines from the salts thereof impregnated in the solid matrix and an acidic aqueous phase; and
- (g) separating the solid matrix from the acidic aqueous phase.

The invention still further consists in a fourth aspect in a method for
35 sequestering carbon dioxide comprising the steps of:

- (a) forming a mixture which comprises an aqueous solution of one or more salts and one or more tertiary amines;
- (b) lowering the temperature and introducing carbon dioxide into the mixture so as to form a precipitate of one or more of a bicarbonate, a carbonate or mixtures thereof and one or more tertiary amine salts;
- (c) removing the precipitate from the mixture;
- (d) heating the mixture so as to regenerate the tertiary amine functionality and produce an acid.
- (e) contacting the heated mixture with a silicate mineral containing alkali and/or alkaline earth metals so as to produce an aqueous solution of alkali and/or alkaline earth metal salts;
- (f) removing undissolved silicates from the mixture of step (e); and optionally
- (g) returning the aqueous solution of alkali and/or alkaline earth metal salts from step (f) for use in step (a).

Throughout this specification the word "comprise", or variations such as "comprises" or "comprising", will be understood to imply the inclusion of a stated element, integer or step, or group of elements, integers or steps, but not the exclusion of any other element, integer or step, or group of elements, integers or steps.

Any discussion of documents, acts, materials, devices, articles or the like which has been included in the present specification is not to be taken as an admission that any or all of these matters form part of the prior art base or were common general knowledge in the field relevant to the present disclosure as it existed before the priority date of each claim of this application.

Description of the Invention

The aqueous salt solution may comprise an aqueous solution of one or more of the salts of alkali and alkaline earth metals. In particular, the alkali and alkaline earth metals may be selected from sodium, potassium, calcium and magnesium or mixtures thereof.

The salts of the alkali and alkaline earth metals may be selected from halide, sulphate, hydroxide, phosphate and oxide or mixtures thereof.

Preferably the salts and/or the aqueous salt solutions will be naturally occurring. In such cases, typically the salt component will constitute a mixture of a variety of salts such as sodium, potassium, magnesium and calcium halides. The advantage of using such naturally occurring salts is primarily one of cost.

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In some cases, the aqueous salt solution may be a by-product of a mining process. Such an example is encountered in solution mining, particularly the solution mining of potash.

10 It will of course be appreciated that naturally occurring salts may be readily dissolved in an available water source to provide the requisite solutions for use in the invention.

Finally, in one embodiment of the invention, acid is generated by the process.
15 Such acid may be reacted with minerals such as serpentine, olivine and peridotite to form the requisite salt solutions.

The concentration of salts in aqueous solution may vary widely. For example, a typically broad range might be 0.05 to 30% w/v, preferably 1 to 15% w/v, most
20 preferably 5 to 10% w/v.

The one or more tertiary amines may be selected from the group consisting of compounds of the formula $NR_1R_2R_3$ where each of R_1 , R_2 and R_3 may each independently consist of a C_1 - C_{10} linear or branched alkyl, cyclic, alicyclic, alkenyl,
25 aryl, aralkyl, and alkaryl groups and mixtures thereof.

Preferably, the one or more tertiary amines are selected from the group consisting of straight chain trialkylamines of various chain lengths, including trimethylamine, triethylamine, tripropylamine, tributylamine, tripentylamine,
30 trihexylamine, triheptylamine and trioctylamine and branched chains including tris(2-ethylhexyl)amine and mixtures thereof.

Particularly preferred is tripentylamine.

35 In one embodiment it is preferred that the boiling point of the one or more tertiary amines at atmospheric pressure is $> 100^\circ\text{C}$.

In one embodiment, the concentration of the one or more amines may be at least 0.5% w/v. Preferably the concentration of the one or more amines is at least 1% w/v. Most preferably the concentration of the one or more amines is at least 5 % w/v. It will
5 of course be appreciated that the concentration of the one or more amines will be largely determined by the amount of bicarbonate and/or carbonate to be produced using a particular salt solution. This assumes that the concentration of the metal ions in the salt solution is adequate and sufficient carbon dioxide is available. It therefore follows that whilst it is desirable for a small excess of the one or amines to be present, the
10 process is generally not assisted by the presence of excess amines. It is therefore preferable that the concentration of the one or more amines be no more than 40% w/v, preferably no more than 30% w/v.

In the first aspect of the invention, the one or more tertiary amines may be
15 dissolved in a water-immiscible solvent. The water-immiscible solvent may be selected from the group consisting of alcohols, ethers, aliphatic hydrocarbons, aromatic hydrocarbons, halogenated hydrocarbons, and combinations thereof.

Preferably, the water-immiscible solvent is selected from alcohols including
20 butanol, pentanol, hexanol, heptanol, octanol, nonanol, decanol, and isomers thereof, and combinations thereof; ethers including diethylether, 1,4-dioxane, and 1,3-dioxane, and combinations thereof; aliphatic hydrocarbons including pentane, hexane, heptane, octane, nonane, decane, and isomers thereof, and combinations thereof; aromatic hydrocarbons including benzene, toluene, xylene, and isomers thereof, and
25 combinations thereof; and halogenated hydrocarbons including dichloromethane, chloroform, dichloroethane, trichloroethane, and isomers thereof, and combinations thereof.

In one embodiment, it is preferred that the boiling point of the water-immiscible
30 solvent at atmospheric pressure is $> 100^{\circ}\text{C}$.

Carbon dioxide is introduced into the mixture of the aqueous salt solution and the water-immiscible phase. Since the carbon dioxide is in gaseous form, it may be introduced at a pressure of from about 0.5 to 30 atmospheres. Preferably, the carbon
35 dioxide is introduced at from 0.5 to 10 atmospheres, most preferably from 0.5 to 5

atmospheres. It should be noted that these pressures are relative to (above) atmospheric pressure.

Although a variety of means may be used for the introduction of the carbon dioxide, a preferred means is by sparging.

Similarly, whilst there are various sources of carbon dioxide available, one source that is particularly suitable for use with the present invention are flue gases. In particular, flue gases emanating from power stations. These sources of carbon dioxide are particularly suitable as power stations also generate low-grade waste heat which may be used in the regeneration of the amine after the reaction has been completed.

Whilst the carbon dioxide is introduced into the mixture of aqueous salt solution and water-immiscible phase, temperature of the mixture may be maintained in the range of from 5-25°C. Preferably the temperature may be in the range of from 10-20°C during the introduction of the carbon dioxide.

In order to maximise the rate of reaction to form bicarbonate and/or carbonates, it is desirable to ensure that the mixture of aqueous salt solution and water-immiscible phase is agitated. In particular, it is preferred that the mixture is agitated to an extent sufficient so as to form an emulsion between the aqueous salt solution and the water-immiscible phase.

Following the formation of the precipitate of bicarbonate and/or carbonate, the precipitate may be removed from the aqueous salt solution by filtration or density separation.

Similarly, the water-immiscible phase may be removed from the aqueous salt solution by density separation.

Once the water-immiscible phase is removed from the aqueous phase, it is heated with water to a temperature, preferably in the range of from 80-95°C at about 1 atmosphere. Higher temperatures can enable a greater degree of acid regeneration and can be carried out with correspondingly higher pressures. Temperatures >100°C and pressures >1 atmosphere may be preferred. In this way, the one or more tertiary amines are regenerated and the corresponding acid is formed in the hot water.

Alternatively, the aforementioned regeneration step may be performed with water to a temperature $>95^{\circ}\text{C}$. If performed in this way, it is desirable that the pressure is increased sufficiently so as to prevent the water and or the water-immiscible phase from boiling.

One advantageous way of performing the regeneration step is to use a counter-current multi-stage device in which hot water enters at one end thereof and water-immiscible phase enters at the other end thereof.

Following regeneration of the one or more tertiary amines, an aqueous acidic solution is formed. For example, if the aqueous salt solution used is potassium chloride, the acidic aqueous solution formed on regeneration of the one or more tertiary amines will be hydrochloric acid. Such a solution has some commercial value and may be used in another unrelated chemical process.

Alternatively, it may be used to form a further aqueous solution of one or more salts by contacting the acidic aqueous phase with a mineral such as serpentine, olivine and peridotite. These minerals are readily available at relatively low cost.

As mentioned above, this invention has particular applicability in the treatment of flue gases which emanate from power stations. It is expected that in the flue gas emissions of a typical coal-fired power station, at least 70 % w/w of carbon dioxide will captured, preferably at least 85 % w/w, most preferably at least 98 % w/w. Note that power stations generally emanate carbon dioxide in a concentration of about 5 to 18 % by volume, although higher concentrations occur when oxy-firing is used.

Best Mode for Carrying Out the Invention

Examples

In order to better understand the nature of the invention, a number of examples will now be described.

Example 1:

When 1 g of CaCl_2 dissolved in 100 ml of distilled water is sparged with a low flow rate of CO_2 (2.5 L/min and 1.5 atm) the pH of the aqueous salt solution reaches 4.5. When this aqueous solution is mixed with 100 ml of kerosene containing 0.36 M tripropylamine, the pH of the aqueous phase increases from 4.5 to approximately 7.5 within 30 seconds. Within a few minutes a white grainy precipitate forms which has been confirmed by X-ray Diffraction analysis to be CaCO_3 . The yield of CaCO_3 was found to be 0.57 g after 30 minutes increasing to 0.77 g after 90 minutes.

Example 2:

When the tripropylamine in Example 1 is replaced with tributylamine and all other experimental conditions described in Example 1 remain the same, the yield of CaCO_3 is found to be 0.5 g after 90 minutes.

Example 3:

The reason for the drop in yield from 0.77 g to 0.5 g between Example 1 and Example 2 is thought to be due to the shorter chain length of the tripropylamine enabling a higher pH. It was found that maximum pH values achieved in the aqueous phase for tripropylamine, tributylamine, triethylamine, trihexylamine and trioctylamine (all dissolved in 100 ml of kerosene and having a concentration of 0.36 M) were 7.9, 6.4, 5.7, 5.1 and 4.6, respectively. The corresponding yields of CaCO_3 were found to be 0.77 g, 0.50 g, and below 0.05 g for triethylamine, trihexylamine and trioctylamine. This indicates that the shorter chain lengths are more effective for complexing protons, raising pH, and enabling carbonate to precipitate.

Example 4:

When the kerosene solvent used in Example 1 is replaced with 1-octanol, higher pH values and higher carbonate yields were also obtained for the shorter chain length trialkylamines. Both tripropylamine and tributylamine reached a maximum pH of 6.9 and gave yields of 0.6 g while trihexylamine and trioctylamine gave maximum pH values of 6.4 and 6.2 and CaCO_3 yields of approximately 0.1 g.

Example 5:

When the CaCl_2 used in Example 1 is replaced by 17.4 g NaCl, 4.1 g of NaHCO_3 was found to precipitate with the use of 1.44 M tripropylamine in 100 ml of kerosene. Precipitation was not found to occur for tributylamine or the higher chain length trialkylamines. This is not wholly surprising given that NaHCO_3 has a higher

solubility than CaCO_3 and is therefore more difficult to precipitate. When the kerosene solvent is replaced by 1-octanol, the yield of NaHCO_3 was found to be 7.5 g and 4.0 g for 1.44 M tripropylamine and tributylamine, respectively, indicating that 1-octanol is a better solvent than kerosene for the precipitation of NaHCO_3 . This is on account of the higher pH generated. The maximum pH of 1.44 M tripropylamine in 1-octanol was found to be 9 compared to 8.2 when kerosene is used as the solvent.

Example 6:

The regeneration of amines was investigated by mixing the acid loaded amines from the above examples with 100 ml of distilled water and increasing the temperature up to 100°C. For the acid loaded amine from Example 1, the pH decreased from 7.5 at 20°C to 5.75 at 100°C, showing that acid is being stripped off from the amine. This is expected given that the acid association constants for the amines decreases with increasing temperature. For the acid loaded amine from Example 5 with the use of 17.4 g NaCl, 1.44 M tripropylamine and 1-octanol as the solvent, the pH decreased from 7.8 at 20°C to 5.6 at 100°C. For the acid loaded amine from Example 5 with the use of 17.4 g NaCl, 1.44 M tributylamine and 1-octanol as the solvent, the pH decreased from 6.7 to 4.9. It is important to note that this level of acid regeneration is from a single stage and greater removal efficiencies are expected when using higher temperatures (combined with higher pressures) and using a multiple-stage counter-current contacting device.

Example 7

In order to further understand the regeneration capability of the tertiary amines, they were titrated against 0.1 M HCl at 5°C, 18°C, 55°C and 85°C. Tripropylamine reached a pH of 9.5 at 18°C, 8.1 at 55°C and 7.1 at 85°C. Tributylamine reached a pH of 8.7 at 5°C, 7.6 at 18°C, 6.5 at 55°C and 5.8 at 85°C. Tripentylamine reached a pH of 6.5 at 5°C, 5.7 at 18°C, 4.2 at 55°C and 4.0 at 85°C. It follows that if a pH of 6.5 is high enough to precipitate carbonates, tripentylamine is a preferred tertiary amine as it reaches a lower pH upon regeneration and consequently releases more H^+ ions. It also follows that regenerating the tertiary amine at still higher temperatures and correspondingly higher pressures may be preferred to maximise acid production.

It will be appreciated by persons skilled in the art that numerous variations and/or modifications may be made to the invention as shown in the specific embodiments without departing from the scope of the invention as broadly described.

The present embodiments are, therefore, to be considered in all respects as illustrative and not restrictive.

ITEMS:

- 5 A. A method for sequestering carbon dioxide comprising the steps of:
- (a) forming a mixture of an aqueous phase which comprises an aqueous solution of one or more salts and a water-immiscible phase which includes one or more tertiary amines;
 - (b) introducing carbon dioxide into the mixture so as to form a precipitate of one or more of a bicarbonate, a carbonate or mixtures thereof and one or more tertiary amine salts;
 - (c) removing the precipitate from the mixture;
 - (d) causing the aqueous phase and the water-immiscible phase to separate;
 - (e) removing the water-immiscible phase from the aqueous phase;
 - 15 (f) contacting the water-immiscible phase with water and heating so as to form one or more tertiary amines from the salts thereof in the water-immiscible phase and an acidic aqueous phase; and
 - (g) separating the water-immiscible phase from the acidic aqueous phase.
- 20 B. A method for sequestering carbon dioxide comprising the steps of:
- (a) forming a mixture of an aqueous phase which comprises an aqueous solution of one or more salts and an ion exchange resin having tertiary amine functionality;
 - (b) introducing carbon dioxide into the mixture so as to form a precipitate of one or more of a bicarbonate, a carbonate or mixtures thereof and one or more tertiary amine salts on the ion exchange resin;
 - 25 (c) removing the precipitate from the mixture;
 - (d) removing the ion exchange resin from the aqueous phase;
 - (e) regenerating the tertiary amine functionality of the ion exchange resin by contacting the same with hot water.
- 30 C. A method for sequestering carbon dioxide comprising the steps of:
- (a) forming a mixture of an aqueous phase which comprises an aqueous solution of one or more salts and a solid matrix impregnated with one or more tertiary amines;
 - (b) introducing carbon dioxide into the mixture so as to form a precipitate of one or more of a bicarbonate, a carbonate or mixtures thereof and one or more tertiary amine salts on the ion exchange resin;
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- (c) removing the precipitate from the mixture;
 - (d) removing the ion solid matrix from the aqueous phase;
 - (e) regenerating the tertiary amine functionality of the solid matrix by contacting the same with hot water.
- 5 (f) contacting the solid matrix with hot water so as to form one or more tertiary amines from the salts thereof impregnated in the solid matrix and an acidic aqueous phase; and
- (g) separating the solid matrix from the acidic aqueous phase.
- 10 D. A method for sequestering carbon dioxide comprising the steps of:
- (a) forming a mixture which comprises an aqueous solution of one or more salts and one or more tertiary amines;
 - (b) lowering the temperature and introducing carbon dioxide into the mixture so as to form a precipitate of one or more of a bicarbonate, a carbonate or mixtures thereof and
- 15 one or more tertiary amine salts;
- (c) removing the precipitate from the mixture;
 - (d) heating the mixture so as to regenerate the tertiary amine functionality and produce an acid.
 - (e) contacting the heated mixture with a silicate mineral containing alkali and/or
- 20 alkaline earth metals so as to produce an aqueous solution of alkali and/or alkaline earth metal salts;
- (f) removing undissolved silicates from the mixture of step (e); and optionally
 - (g) returning the aqueous solution of alkali and/or alkaline earth metal salts from step (f) for use in step (a).
- 25 E. The method of item A wherein the one or more tertiary amines are in a water-immiscible solvent.
- F. The method of any one of items A to E wherein the one or more tertiary amines
- 30 are selected from the group consisting of compounds of the formula $NR_1R_2R_3$ where each of R_1 , R_2 and R_3 may each independently consist of a C_1 - C_{10} linear or branched alkyl, cyclic, alicyclic, alkenyl, aryl, aralkyl, and alkaryl groups and mixtures thereof.
- G. The method of item F wherein the one or more tertiary amines are selected from
- 35 the group consisting of straight chain trialkylamines of various chain lengths, including trimethylamine, triethylamine, tripropylamine, tributylamine, tripentylamine,

trihexylamine, triheptylamine and trioctylamine and branched chains including tris(2-ethylhexyl)amine and mixtures thereof.

5 H. The method of item G wherein the branched chain tertiary amine is tripentylamine.

I. The method of any one of items A to H wherein the aqueous solution of one or more of the salts comprises alkali and alkaline earth metals salts.

10 J. The method of item I wherein the alkali and alkaline earth metals are selected from sodium, potassium, calcium and magnesium.

K. The method of any one of items A to J wherein the salts are selected from halide, sulphate, hydroxide, phosphate and oxide or mixtures thereof.

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L. The method of any one of items A to K wherein the salts are naturally occurring.

M. The method of any one of items A to L wherein the aqueous salt solution is naturally occurring.

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N. The method of any one of items A to M wherein the aqueous salt solution is a by-product of a mining process.

O. The method of item N wherein the mining process is solution mining.

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P. The method of item O wherein the solution mining is in relation to potash.

Q. The method of item A wherein the water-immiscible solvent is selected from the group consisting of alcohols, ethers, aliphatic hydrocarbons, aromatic hydrocarbons, halogenated hydrocarbons, and combinations thereof.

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R. The method of item Q wherein the solvent is selected from alcohols including butanol, pentanol, hexanol, heptanol, octanol, nonanol, decanol, and isomers thereof, and combinations thereof; ethers including diethylether, 1,4-dioxane, and 1,3-dioxane, and combinations thereof; aliphatic hydrocarbons including pentane, hexane, heptane, octane, nonane, decane, and isomers thereof, and combinations thereof; aromatic

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hydrocarbons including benzene, toluene, xylene, and isomers thereof, and combinations thereof; and halogenated hydrocarbons including dichloromethane, chloroform, dichloroethane, trichloroethane, and isomers thereof, and combinations thereof.

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S. The method of any one of items A to R wherein the boiling point of the one or more tertiary amines at atmospheric pressure is $> 100^{\circ}\text{C}$.

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T. The method of item A wherein the boiling point of the water-immiscible solvent at atmospheric pressure is $> 100^{\circ}\text{C}$.

U. The method of any one of items A to T wherein the carbon dioxide is introduced at a pressure of from 1 to 30 atmospheres.

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V. The method of any one of items A to U wherein the carbon dioxide is introduced by sparging.

W. The method of any one of items A to V wherein the source of carbon dioxide is a flue gas.

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X. The method of one any of items A to W wherein the temperature of the mixture is maintained in the range of from $5\text{-}25^{\circ}\text{C}$ during the introduction of the carbon dioxide.

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Y. The method item A wherein the mixture is agitated so as to form an emulsion between the phases.

Z. The method of one of items A to Y wherein the precipitate is removed by filtration or density separation.

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AA. The method of item A wherein the water-immiscible phase is removed from the aqueous phase by density separation.

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BB. The method of item A wherein the water-immiscible phase after removal from the aqueous phase is heated with water to a temperature in the range of from $80\text{-}95^{\circ}\text{C}$ at about 1 atmosphere.

CC. The method of item A wherein the water-immiscible phase after removal from the aqueous phase is heated with water to a temperature $>95^{\circ}\text{C}$ and at a pressure so as to prevent the water and or the water-immiscible phase from boiling.

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DD. The method of item A wherein the water-immiscible phase after removal from the aqueous phase is heated with water in a counter-current multi-stage device in which hot water enters at one end thereof and water-immiscible phase enters at the other end thereof.

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EE. The method of item A further comprising the step:

(h) forming a further aqueous solution of one or more salts by contacting the acidic aqueous phase with a mineral.

15 FF. The method of item B or item C wherein the hot water following regeneration is acidic and is used to form a further aqueous solution of one or more salts by contacting the acidic hot water with a mineral.

20 GG. The method of item EE or item FF wherein the mineral is selected from the group consisting of serpentine, olivine and peridotite.

CLAIMS:

1. A method for sequestering carbon dioxide comprising the steps of:
 - (a) forming a mixture of an aqueous phase which comprises an aqueous solution of
5 one or more salts and a water-immiscible phase which includes one or more tertiary amines;
 - (b) introducing carbon dioxide into the mixture so as to form a precipitate of one or more of a bicarbonate, a carbonate or mixtures thereof and one or more tertiary amine salts;
 - 10 (c) removing the precipitate from the mixture;
 - (d) causing the aqueous phase and the water-immiscible phase to separate;
 - (e) removing the water-immiscible phase from the aqueous phase;
 - (f) contacting the water-immiscible phase with water and heating so as to form one or more tertiary amines from the salts thereof in the water-immiscible phase and an
15 acidic aqueous phase; and
 - (g) separating the water-immiscible phase from the acidic aqueous phase.
2. A method for sequestering carbon dioxide comprising the steps of:
 - (a) forming a mixture of an aqueous phase which comprises an aqueous solution of
20 one or more salts and an ion exchange resin having tertiary amine functionality;
 - (b) introducing carbon dioxide into the mixture so as to form a precipitate of one or more of a bicarbonate, a carbonate or mixtures thereof and one or more tertiary amine salts on the ion exchange resin;
 - (c) removing the precipitate from the mixture;
 - 25 (d) removing the ion exchange resin from the aqueous phase;
 - (e) regenerating the tertiary amine functionality of the ion exchange resin by contacting the same with hot water.
3. A method for sequestering carbon dioxide comprising the steps of:
 - 30 (a) forming a mixture of an aqueous phase which comprises an aqueous solution of one or more salts and a solid matrix impregnated with one or more tertiary amines;
 - (b) introducing carbon dioxide into the mixture so as to form a precipitate of one or more of a bicarbonate, a carbonate or mixtures thereof and one or more tertiary amine salts on the ion exchange resin;
 - 35 (c) removing the precipitate from the mixture;
 - (d) removing the ion solid matrix from the aqueous phase;

- (e) regenerating the tertiary amine functionality of the solid matrix by contacting the same with hot water.
 - (f) contacting the solid matrix with hot water so as to form one or more tertiary amines from the salts thereof impregnated in the solid matrix and an acidic aqueous phase; and
 - (g) separating the solid matrix from the acidic aqueous phase.
4. A method for sequestering carbon dioxide comprising the steps of:
- (a) forming a mixture which comprises an aqueous solution of one or more salts and one or more tertiary amines;
 - (b) lowering the temperature and introducing carbon dioxide into the mixture so as to form a precipitate of one or more of a bicarbonate, a carbonate or mixtures thereof and one or more tertiary amine salts;
 - (c) removing the precipitate from the mixture;
 - (d) heating the mixture so as to regenerate the tertiary amine functionality and produce an acid.
 - (e) contacting the heated mixture with a silicate mineral containing alkali and/or alkaline earth metals so as to produce an aqueous solution of alkali and/or alkaline earth metal salts;
 - (f) removing undissolved silicates from the mixture of step (e); and optionally
 - (g) returning the aqueous solution of alkali and/or alkaline earth metal salts from step (f) for use in step (a).
5. The method of claim 1 wherein the one or more tertiary amines are in a water-immiscible solvent.
6. The method of any one of claims 1 to 5 wherein the one or more tertiary amines are selected from the group consisting of compounds of the formula $NR_1R_2R_3$ where each of R_1 , R_2 and R_3 may each independently consist of a C_1 - C_{10} linear or branched alkyl, cyclic, alicyclic, alkenyl, aryl, aralkyl, and alkaryl groups and mixtures thereof.
7. The method of claim 6 wherein the one or more tertiary amines are selected from the group consisting of straight chain trialkylamines of various chain lengths, including trimethylamine, triethylamine, tripropylamine, tributylamine, tripentylamine, trihexylamine, triheptylamine and trioctylamine and branched chains including tris(2-ethylhexyl)amine and mixtures thereof.

8. The method of claim 7 wherein the branched chain tertiary amine is tripropylamine.
- 5 9. The method of any one of claims 1 to 8 wherein the aqueous solution of one or more of the salts comprises alkali and alkaline earth metals salts.
10. The method of claim 9 wherein the alkali and alkaline earth metals are selected from sodium, potassium, calcium and magnesium.
- 10 11. The method of any one of claims 1 to 10 wherein the salts are selected from halide, sulphate, hydroxide, phosphate and oxide or mixtures thereof.
12. The method of any one of claims 1 to 11 wherein the salts are naturally
15 occurring.
13. The method of any one of claims 1 to 12 wherein the aqueous salt solution is naturally occurring.
- 20 14. The method of any one of claims 1 to 13 wherein the aqueous salt solution is a by-product of a mining process.
15. The method of claim 14 wherein the mining process is solution mining.
- 25 16. The method of claim 15 wherein the solution mining is in relation to potash.
17. The method of claim 1 wherein the water-immiscible solvent is selected from the group consisting of alcohols, ethers, aliphatic hydrocarbons, aromatic hydrocarbons, halogenated hydrocarbons, and combinations thereof.
- 30 18. The method of claim 17 wherein the solvent is selected from alcohols including butanol, pentanol, hexanol, heptanol, octanol, nonanol, decanol, and isomers thereof, and combinations thereof; ethers including diethylether, 1,4-dioxane, and 1,3-dioxane, and combinations thereof; aliphatic hydrocarbons including pentane, hexane, heptane,
35 octane, nonane, decane, and isomers thereof, and combinations thereof; aromatic hydrocarbons including benzene, toluene, xylene, and isomers thereof, and

combinations thereof; and halogenated hydrocarbons including dichloromethane, chloroform, dichloroethane, trichloroethane, and isomers thereof, and combinations thereof.

- 5 19. The method of any one of claims 1 to 18 wherein the boiling point of the one or more tertiary amines at atmospheric pressure is $> 100^{\circ}\text{C}$.
20. The method of claim 1 wherein the boiling point of the water-immiscible solvent atmospheric pressure is $> 100^{\circ}\text{C}$.
- 10 21. The method of any one of claims 1 to 20 wherein the carbon dioxide is introduced at a pressure of from 1 to 30 atmospheres.
22. The method of any one of claims 1 to 21 wherein the carbon dioxide is
15 introduced by sparging.
23. The method of any one of claims 1 to 22 wherein the source of carbon dioxide is a flue gas.
- 20 24. The method of one any of claims 1 to 23 wherein the temperature of the mixture is maintained in the range of from $5\text{-}25^{\circ}\text{C}$ during the introduction of the carbon dioxide.
- 25 25. The method claim 1 wherein the mixture is agitated so as to form an emulsion between the phases.
26. The method of one of claims 1 to 25 wherein the precipitate is removed by filtration or density separation.
- 30 27. The method of claim 1 wherein the water-immiscible phase is removed from the aqueous phase by density separation.
28. The method of claim 1 wherein the water-immiscible phase after removal from the aqueous phase is heated with water to a temperature in the range of from $80\text{-}95^{\circ}\text{C}$ at
35 about 1 atmosphere.

29. The method of claim 1 wherein the water-immiscible phase after removal from the aqueous phase is heated with water to a temperature $>95^{\circ}\text{C}$ and at a pressure so as to prevent the water and or the water-immiscible phase from boiling.
- 5 30. The method of claim 1 wherein the water-immiscible phase after removal from the aqueous phase is heated with water in a counter-current multi-stage device in which hot water enters at one end thereof and water-immiscible phase enters at the other end thereof.
- 10 31. The method of claim 1 further comprising the step:
(h) forming a further aqueous solution of one or more salts by contacting the acidic aqueous phase with a mineral.
- 15 32. The method of claim 2 or claim 3 wherein the hot water following regeneration is acidic and is used to form a further aqueous solution of one or more salts by contacting the acidic hot water with a mineral.
33. The method of claim 31 or claim 32 wherein the mineral is selected from the group consisting of serpentine, olivine and peridotite.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU2012/000870

A. CLASSIFICATION OF SUBJECT MATTER

B01D 53/62 (2006.01) B01J 41/04 (2006.01)

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)

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 & WPI: IPC B01D 53/00/low, B01D 15/00/low, B01D 11/00/low, B01J 41/00/low, B01J 20/00/low, B01J 14/00/low, B01J 39/00/low, B01J 43/00/low, B01J 45/00/low, B01J 47/00/low, B01J 49/00/low, Keywords (carbon dioxide, sequestration & like terms); and Keywords (carbon dioxide, sequestration, carbonate, amine, resin, alkali & like terms)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	Documents are listed in the continuation of Box C	



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	"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
"E" earlier application or patent but published on or after the international filing date	"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
"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)	"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
"O" document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family
"P" document published prior to the international filing date but later than the priority date claimed	

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INTERNATIONAL SEARCH REPORT		International application No.
C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		PCT/AU2012/000870
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 7842126 B1 (DILMORE et al.) 30 November 2010 Abstract; figure 1; column 6, line 40 - column 7, line 3; column 7, lines 25-30; column 8, lines 1-10, 10-38; column 13, lines 1-2	1-33
A	US 2010/0150804 A1 (DAVIS, Jr.) 17 June 2010 Abstract; claim 81; para.6, 10	1-33
A	US 2011/0088550 A1 (TIRIO) 21 April 2011 Abstract; para 5-6	1-33

INTERNATIONAL SEARCH REPORT		International application No.	
Information on patent family members		PCT/AU2012/000870	
This Annex lists known patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.			
Patent Document/s Cited in Search Report		Patent Family Member/s	
Publication Number	Publication Date	Publication Number	Publication Date
US 7842126 B1	30 Nov 2010	US 7842126 B1	30 Nov 2010
US 2010/0150804 A1	17 Jun 2010	US 2010150804 A1	17 Jun 2010
		WO 2008122030 A2	09 Oct 2008
US 2011/0088550 A1	21 Apr 2011	EP 2490789 A1	29 Aug 2012
		US 2011088550 A1	21 Apr 2011
		US 2012228553 A1	13 Sep 2012
		WO 2011049759 A1	28 Apr 2011
End of Annex			